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THE DENSITIES OF LIQUID IRON AND NICKEL AND AN ESTIMATE OF THEIR CRITICAL TEMPERATURE

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FOR the last two years experimental density determinations were made at the Institute of a number of metals from the melting point to the normal boiling point (Sn, Pb, In, Mg, Bi, U, Cu, Sb, Ag(1)). We have also shown(2,3,4,5) that the critical temperatures of metals can be estimated by two essentially independent methods; (a) from the law of rectilinear diameter, determined by the experimental densities of the liquid metal and its saturated vapour and (b) from the theorem of corresponding states, using the experimental data on liquid mercury, which cover the whole liquid range from the melting to the critical point. The use of both methods is illustrated by the liquid range temperature diagrams of lead(6) and silver(6).

In the case of all metals investigated to date there is reasonable agreement between the two methods of calculating critical temperatures. We now wish to report *two exceptions*, namely liquid iron(7) and nickel(8) whose densities were also measured from the melting point to approximately the normal boiling point by both the Archimedean and maximum bubble methods with excellent agreement. The liquid densities are straight line functions of temperature and are expressed by the following equations:

$$D^{\mathrm{Fe}}_{(\mathrm{liq.})} = 8{\cdot}618 - 8{\cdot}83 \times 10^{-4}T$$

and

$$D^{\mathrm{Ni}}_{(\mathrm{liq.})} = 9{\cdot}908 - 11{\cdot}589 \times 10^{-4}T$$

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(1) See various contributions by A. D. KIRSHENBAUM, J. A. CAHILL, P. J. MCGONIGAL and A. V. GROSSE in *J. Inorg. Nucl. Chem.*, *J. Phys. Chem.*, *J. Amer. Chem. Soc.* and *Trans. Quarterly of* A.S.M.

(2) A. V. GROSSE, *J. Inorg. Nucl. Chem.* **22**, 23 (1961).

(3) A. V. GROSSE, The Liquid Range of Metals, and Some of their Physical Properties at High Temperatures, Paper No. 2159, A. R. S., *Space Flight Report to the Nation*, New York, October 9–15, 1961.

(4) A. V. GROSSE, The Liquid Range of Metals and Some of their Physical Properties at High Temperatures, Report of the Research Institute of Temple University, October 19, 1960.

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(7) A. D. KIRSHENBAUM and J. A. CAHILL, *Trans. of the Met. Soc. of AIME*, **244** (1962). Presented before the 91st Annual Meeting of the Metallurgical Society of AIME in New York City, February 20, 1962.

(8) A. D. KIRSHENBAUM and J. A. CAHILL. *Trans, Quarterly of A.S.M.* In Press.

where D is in g/cm³ and T in °K. The liquid densities at the melting and normal boiling points are as follows:

	Fe	Ni
$D_{\text{m.p.}}$, (g/cm³)	7·015	7·905
m.p., (°K)	1805°	1728°
$D_{\text{b.p.}}$, (g/cm³)	5·828	6·304
b.p., (°K)	3160°	3110°

The equation of the rectilinear diameter, in the same units, are as follows:

$$D_{\phi}^{\text{Fe}} = 4{\cdot}309 - 4{\cdot}42 \times 10^{-4}\, T$$

and

$$D_{\phi}^{\text{Ni}} = 4{\cdot}954 - 5{\cdot}795 \times 10^{-4} T$$

The liquid range diagrams of the two metals were constructed and that of iron is given in Fig. 1. The critical temperatures of Fe, estimated *at* 6750°K, and of Ni, estimated *at* 6000°K, were based on the ratio of $D_{\text{b.p.}}/D_{\text{crit.p.}} \simeq 4{\cdot}35$, since this ratio is based on the liquid range diagram of many other metals[9], i.e. Hg, Bi, Ag, Pb, Sn and Ga. However, if we base our estimates of critical temperatures on the law of corresponding states and the following reliable heats and entropies of vaporization[10] of iron and nickel:

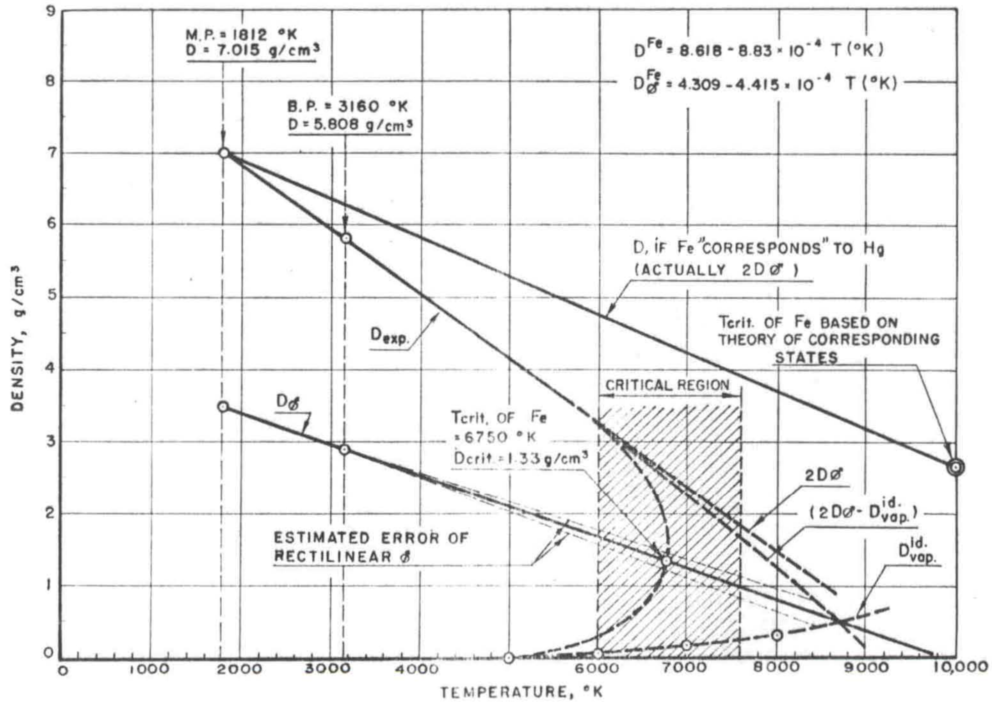

FIG. 1.

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[9] P. J. McGonigal, A. D. Kirshenbaum and A. V. Grosse, *J. Phys. Chem.*, **66**, 737 (1962).

	N.B.P. (°K)	$\Delta H_{\text{vap.}}$ (kcal/g atom)	ΔS (cal/g atom °K)	$T_{\text{red.}}$ based on Hg	$T_{\text{crit.}}$ (°K)
Fe	3160	83,900	26·7	0·31	10,000
Ni	3110	88,870	28·5	0·29	10,700

we obtain the values of 10,000 and 10,700°K for Fe and Ni respectively. If these values are correct it follows since the $D_{\text{b.p.}}/D_{\text{crit.p.}}$ given above would be the same for these two metals, that the slope of the D vs. T line and of the rectilinear diameter would be much more gradual than the experimental line. The D vs. T line for Fe, identified by D, if Fe corresponds to Hg, is the uppermost straight line in Fig. 1. It is apparent that the disagreement with the observed density line is outside of any

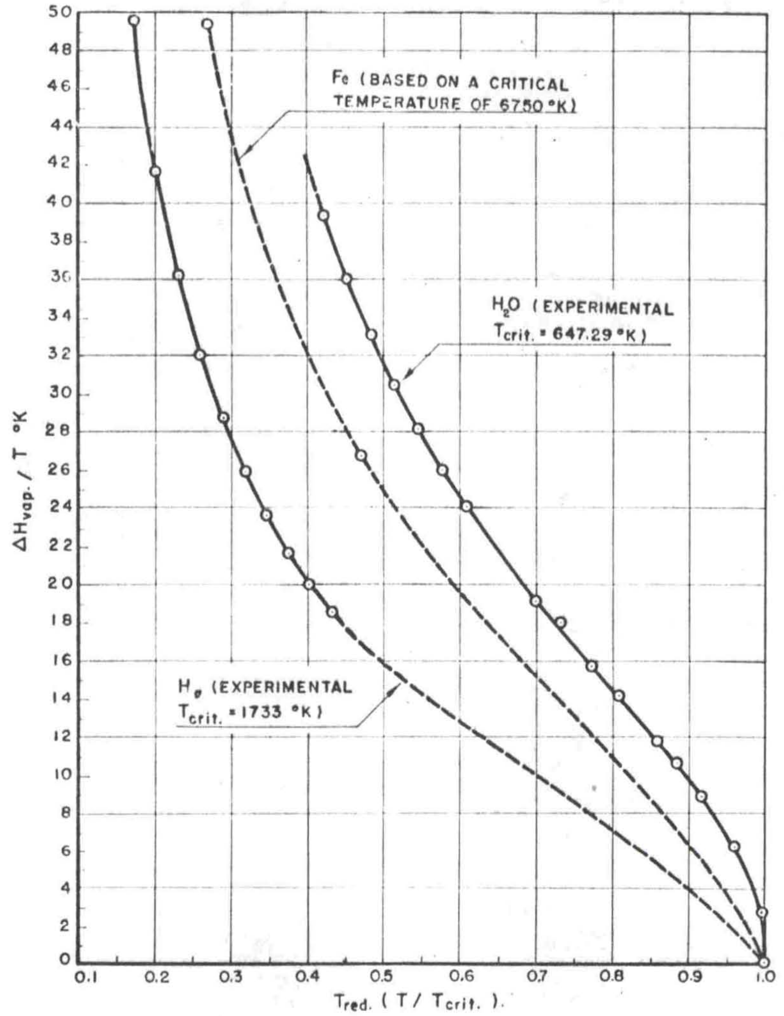

FIG. 2.

[10] D. R. STULL and G. C. SINKE, *Thermodynamic Properties of the Elements*, p. 112 and 135. Advances in Chemistry Series 18, American Chemical Society, Washington, D.C. (1956).

experimental error, indicated by the "error cone" of the rectilinear diameter, i. e., D_ϕ, in Fig. 1. The differences in the critical temperatures by the two methods are 3250°K (i.e. 10,000 − 6750°K) for Fe and 4700°K. (i.e. 10,700 − 6000°K) for Ni.

If one relies on the experimental liquid densites it follows that the reduced temperatures of Fe and Ni cannot follow the ΔS v. $T_{\text{red.}}$ curve of mercury. The true ΔS v. $T_{\text{red.}}$ curve of Fe and Ni estimated from our density measurements, is compared with Hg curve(*) in Fig. 2; a typical homopolar compound, namely H_2O is added as a reference. It is to be expected that some other metals, similar to Fe and Ni, will follow ΔS curves between those of Fe and Ni and the Hg curve.

The reason for this singular behavior of Fe and Ni, and presumably also of Co, can be expected to lie in the nature of the metallic bond. Fe, Co and Ni are transition metals with the highest metallic valence of six, in line with PAULING's concepts(12) and the smallest atomic radii (Fe = 1·170 Å; Co = 1·162 Å and Ni = 1·154 Å); these three metals also occupy the minima in the Lothar Meyer atomic volume vs. atomic number curve.

The critical temperature is in a way a measure of the strength of the metallic bond; thus the lower critical temperature than originally expected would imply that the strength of the metallic bond in the Fe-Ni tryad is less than in "simple" metals.

PAULING(13) stresses that "the metallic valence six for iron represents the maximum number of electrons that contribute to the formation of chemical bonds and *not the average* number". He illustrates this point by referring to the equation of state of metals, developed recently by MCMILLAN and LATTER(14). These authors showed that an isothermal equation of state can be derived from the coulomb virial theorem for "*simple*" *metals*, consisting of imperturbable metal kernels (ions) embedded in a uniform sea of valence or *S* electrons. Good agreement could be shown between the $\Delta H_{\text{form.}}$ of the normal gaseous metal ion kernel and the calculated metallic compressibility for the *alkali and alkaline earth metals, where valence shells are entirely constituted of S electrons* (1 and 2 respectively). In the case of transition metals, specifically in the case of Fe, Co and Ni, agreement is reached only if approximately *one half* of PAULING's maximum number of valence electrons was assumed to take part in the metallic bond formation. In the case of *metallic* iron with a valence six and two unpaired electrons occupying separate orbitals, PAULING assumes(13) the configuration $3d^5 4s 4p^2$, in contrast to the *free iron atom*, with a normal ^5D state, based on the configuration $3d^6 4s^2$.

Thus it is probable that in our case also the metallic bond of the typical transition metals, specifically Fe, Co and Ni, is relatively much weaker than in the case of the "simple" metals, i.e. alkali or alkaline earth metals and also Zn, Cd and Hg.

It is likely, therefore, that the other noble metals, i.e. of the VIII group of the periodic system, particularly Pd and Pt, will show lower critical temperatures than previously expected and therefore a much steeper slope in their D vs. T line.

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* It is based on BUSEY and GIAQUE's measurements(11) of ΔH_{vap} of Hg from its m.p. to 750°K.

(11) R. H. BUSEY and W. F. GIAQUE, *J. Amer. Chem. Soc.* **74**, 801–809 (1953).

(12) L. PAULING, *The Nature of the Chemical Bond* (3rd Ed.), Chap. 11, p. 393–448. Cornell Univ. Press (1960).

(13) L. PAULING, *The Nature of the Chemical Bond*, p. 416. Cornell Univ. Press (1960).

(14) W. G. MCMILLAN and A. L. LATTER, *J. Chem. Phys.* **20**, 15 (1958).