

experimental error, indicated by the "error cone" of the rectilinear diameter, i. e.,  $D_d$ , in Fig. 1. The differences in the critical temperatures by the two methods are  $3250^\circ\text{K}$  (i.e.  $10,000 - 6750^\circ\text{K}$ ) for Fe and  $4700^\circ\text{K}$ . (i.e.  $10,700 - 6000^\circ\text{K}$ ) for Ni.

If one relies on the experimental liquid densities it follows that the reduced temperatures of Fe and Ni cannot follow the  $\Delta S$  v.  $T_{\text{red}}$  curve of mercury. The true  $\Delta S$  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  $\text{H}_2\text{O}$  is added as a reference. It is to be expected that some other metals, similar to Fe and Ni, will follow  $\Delta S$  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<sup>(12)</sup> and the smallest atomic radii (Fe =  $1.170 \text{ \AA}$ ; Co =  $1.162 \text{ \AA}$  and Ni =  $1.154 \text{ \AA}$ ); 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 triad is less than in "simple" metals.

PAULING<sup>(13)</sup> 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<sup>(14)</sup>. 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<sup>(13)</sup> the configuration  $3d^6 4s 4p^2$ , 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.

\* It is based on BUSEY and GIAQUE's measurements<sup>(11)</sup> of  $\Delta H_{\text{vap}}$  of Hg from its m.p. to  $750^\circ\text{K}$ .

<sup>(11)</sup> R. H. BUSEY and W. F. GIAQUE, *J. Amer. Chem. Soc.* **74**, 801-809 (1953).

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

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

<sup>(14)</sup> W. G. McMILLAN and A. L. LATTER, *J. Chem. Phys.* **20**, 15 (1958).