WHAT MAKES A METAL?*

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A LARGE number of elements on this planet (79 out of 103) are metallic under ambient conditions (figure 1) and several criteria to explain the metallic nature of elements have been explored in the literature. Metals such as copper, gold and silver possess high density, malleability and other well known features associated with metals. Such features are by no means universal as illustrated by sodium and potassium. Many complex inorganic solids (oxides, sulphides, etc), organic solids (*e.g.* TTF-TCNQ) and polymers are known to be metallic. Several solids also exhibit transitions from the non-metallic to the metallic state. The fundamental problem as to why certain substances are metallic has been of vital interest in condensed matter science for the past several years[1]. In this article we shall restrict ourselves to the metallic behaviour of elements.

One of the early criteria for metallicity is due to Hubbard[2] who proposed that the ratio of the band width, Δ, and the Coulomb repulsion energy, U, provides the basis for distinguishing the metallic state from the non-metallic (insulating) state (figure 2). The exact condition for metallization is given as,

$$\left(\frac{\Delta}{U}\right)_{\text{critical}} \gtrsim 1.2 \qquad (1)$$

* Based on a lecture delivered at the Golden Jubilee Meeting of the Indian Academy of Sciences, Bangalore, February 1985.

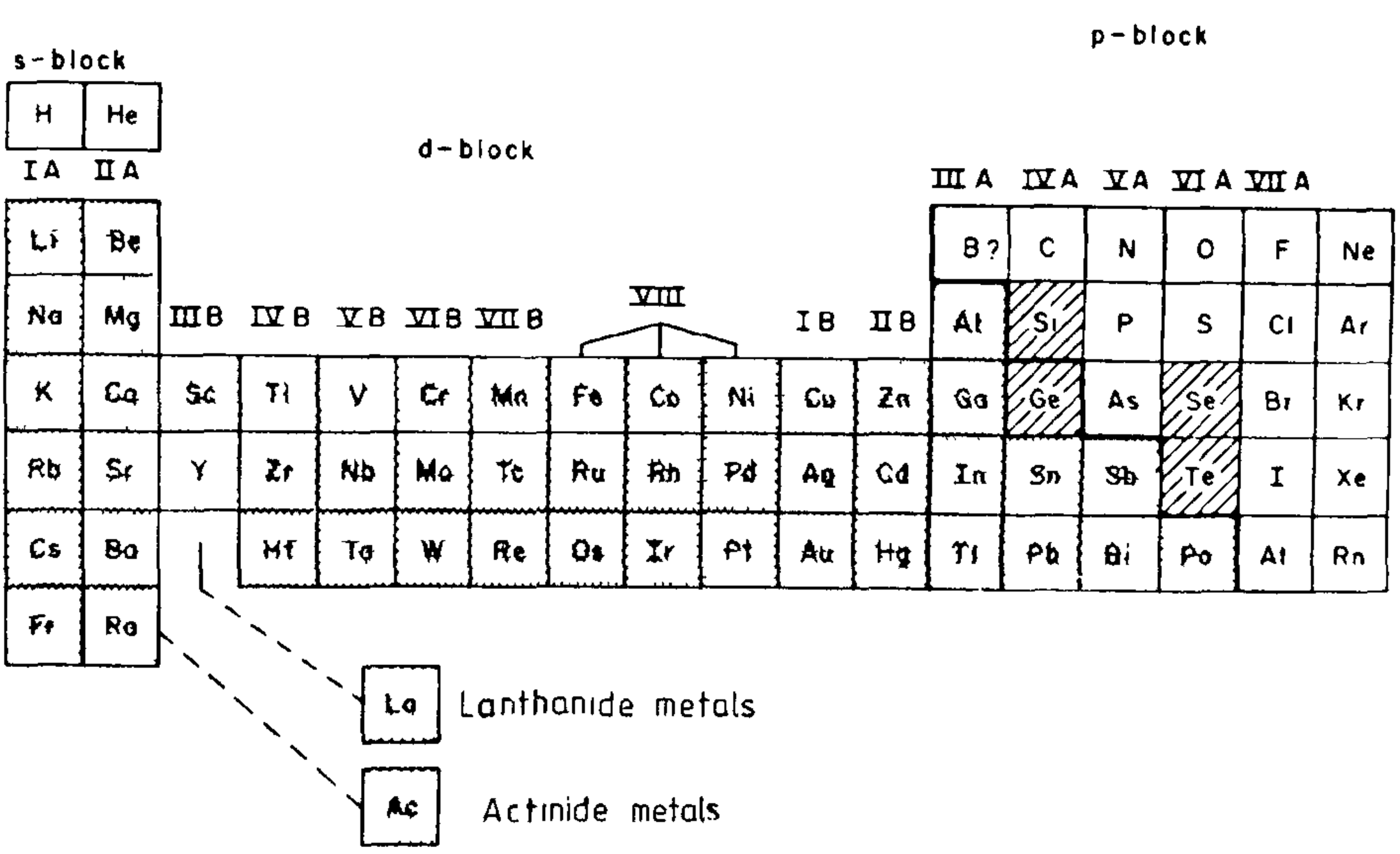

Figure 1. Periodic table showing metallic and non-metallic elements. Hatched squares represent metals. Elements Si, Ge, Se and Te become metallic in the molten state; boron may also exhibit this behaviour.

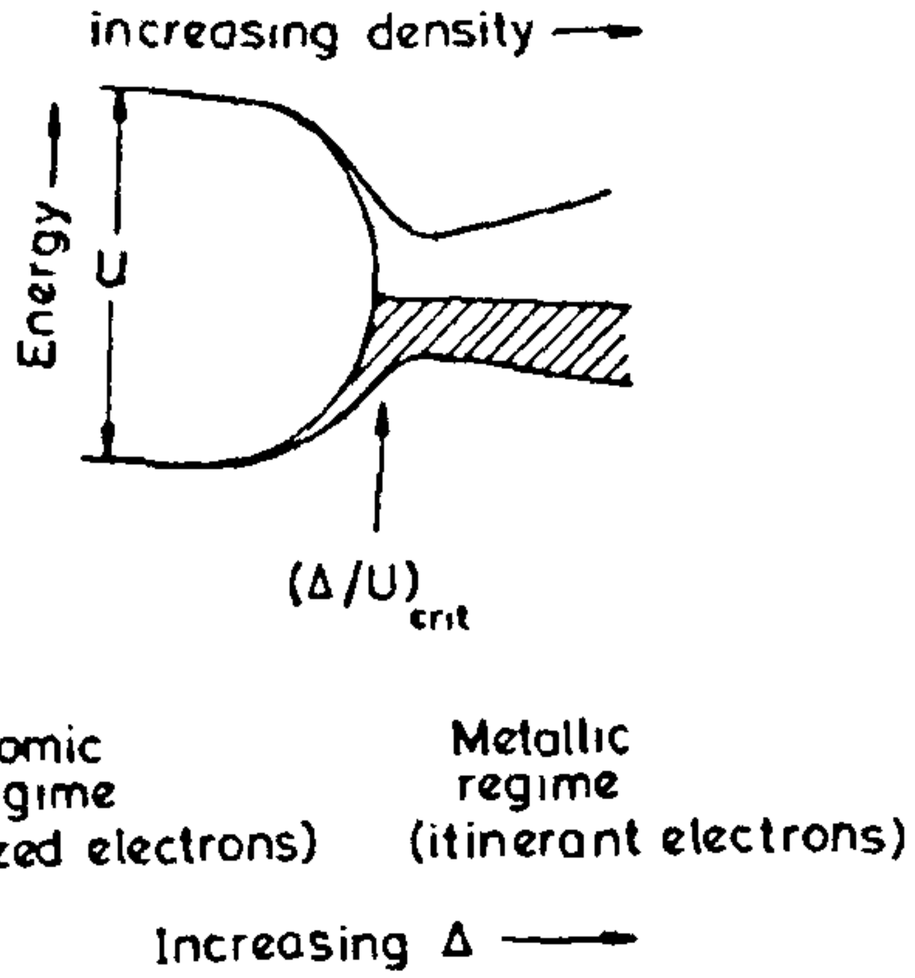

Figure 2. Metal to non-metal transition according to the Hubbard model. When Δ/U is small, elements show atomic behaviour of electrons (*e.g.* Cs atom); when Δ/U is greater than the critical value, elements show metallic behaviour (Cs metal). Δ/U increases in the same direction as the density.

Mott[3] proposed a model to distinguish metals from non-metals based on the dielectric screening properties of a uniform electron gas. According to this model, there will be a first-order transition from the metallic to the non-metallic state when

$$n_c^{1/3} a_H \approx 0.25 \qquad (2)$$

Here n_c is the critical concentration of electrons required for metallization and a_H is the effective Bohr radius. Experimental data on doped semiconductors and other systems follow relation (2) quite closely[4].

Introduction of disorder in a solid can effectively transform it from the metallic to the insulating state[5,6]. The disorder-induced metal to non-metal transition (Anderson transition) has received wide attention in recent years[7]; doped semiconductors as well as many other systems including complex metal oxides exhibit such transitions[1,8]. This class of transitions would not however be relevant in discussing the metallicity of elements.

An intimate link between the metallic state, density and atomic properties was recognized by Herzfeld[9] quite some years ago. Herzfeld proposed that local field corrections, in an insulator drive it to become metallic when the insulator becomes sufficiently dense. The dielectric constant, ε, of such a system is expressed as,

$$\varepsilon = 1 + \frac{4\pi N\alpha}{1 - (4\pi N\alpha/3)} \qquad (3)$$

where α is the polarizability of atoms. When $(4\pi N\alpha/3) = 1$, ε diverges. The above equation in its simple form may not survive in dense systems since other processes contribute to α as atoms begin to overlap. According to Herzfeld, the characteristic frequency ν_0 of the bound electrons in atoms is diminished at finite densities to,

$$\nu = \nu_0 [1 - (R/V)]^{1/2} \qquad (4)$$

where R is the molar refractivity of the atom (equal to $4\pi N\alpha/3$) in the gaseous state and V is the molar volume in the condensed state. It becomes therefore obvious that the metal to non-metal transition should occur depending on whether (R/V) is less than or greater than unity.

$$\text{For a metal,} \quad (R/V) \geqslant 1$$
$$\text{For an insulator,} \quad (R/V) < 1 \qquad (5)$$

There has been considerable interest in detecting the polarization catastrophe at the metal-non-metal transition. What is pertinent to our discussion is that the (R/V) criterion can explain why most elements in the periodic table under ambient conditions are metallic in the solid state[4] (figure 3). The criterion predicts why hydrogen is metallic at high pressures; mercury is metallic because of its high density in the liquid state. This was the simplest operational criterion available hitherto to explain metallization of elements under ambient conditions.

The possibility of finding a simple thermodynamic criterion for metallization of elements has been recently explored in this laboratory[10]. The following features are noteworthy in this context. Many elemental metals such as Hg and Cs are liquids under ambient conditions. Solid metallic elements retain their metallic character in the molten state as well. Furthermore, some solid

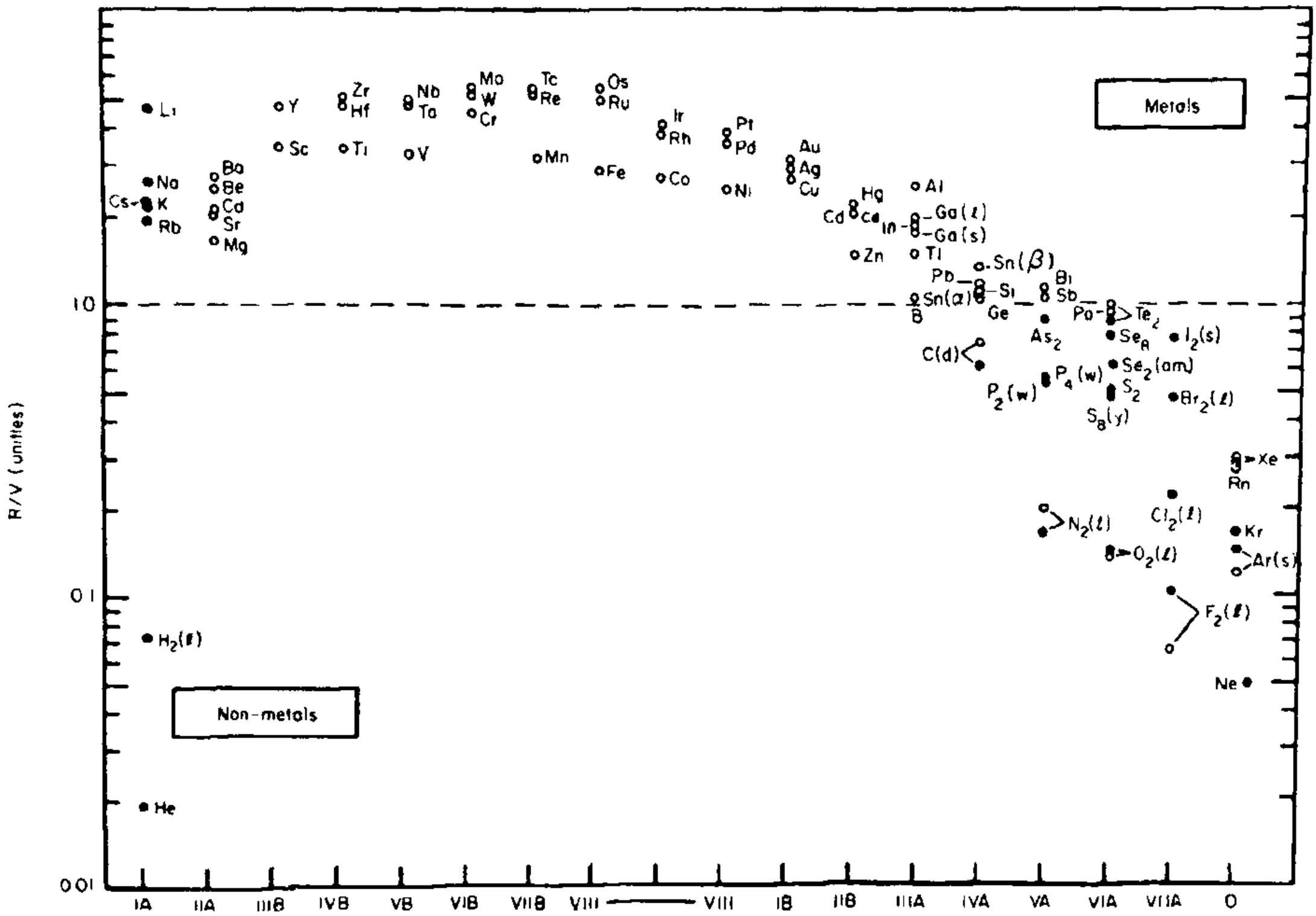

Figure 3. R/V ratios of Herzfeld for the *s*, *p* and *d* block elements of the periodic table delineating metals from non-metals (from Edwards and Sienko[4]).

elements (Si, Ge, Se and Te) become metallic in the molten state. The liquid state of metals is therefore more universal, with 83 elements out of 103 being metallic in the liquid state (figure 1). The thermodynamic property most relevant to distinguish metals and non-metals is found to be the latent heat of vapourization. This seems reasonable since the electrons would be localized in the vapour state.

In figure 4, the latent heats of vapourization, ΔH_v, of *s*, *p* and *d* block elements of the periodic table are plotted. The plot clearly distinguishes metals from non-metals. We see that metals generally have $\Delta H_v \gtrsim 42$ k Joule mol^{-1} or 0.44 eV; 0.44 eV then represents the minimum difference between the heat contents of the liquid and the vapour states necessary to render an element metallic. Figure 4 predicts *p* block elements such as Se, Te, Ge and Si to be metallic in the liquid state. The latent heat of vapourization appears to be as satisfactory as the R/V parameter of Herzfeld[9] (figure 3) and provides a much simpler operational criterion. The ΔH_v criterion predicts boron to be metallic in the liquid state and hydrogen to be metallic at high pressures.

In the literature, ΔH_v has been related to electronic and other properties of liquid metals, but this is the first time[10] that it is found to distinguish metals from non-metals. This is obviously because ΔH_v describes the transition between the limit of condensed state behaviour and the free (atomic or molecular) state. It turns out that ΔH_v is directly related to the Fermi energy. In most metals, ΔH_v is around 3.5 times E_F. Furthermore, ΔH_v can be shown to be proportional to $(R/V)^n$. A plot of $\log \Delta H_v$ against $\log (R/V)$ is indeed linear with a slope around 1.2. The ΔH_v criterion is thus linked to

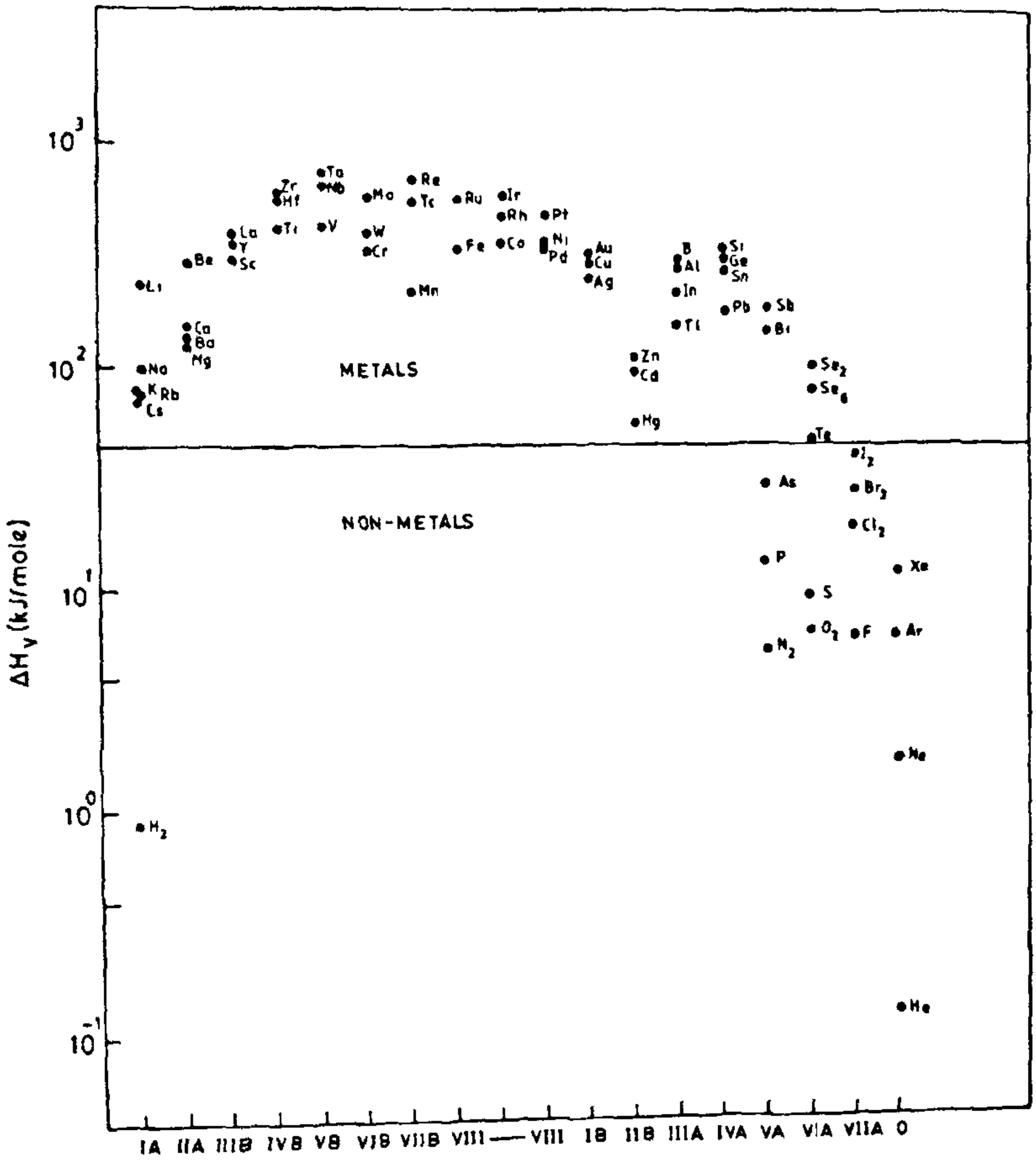

Figure 4. Latent heats of vapourization; ΔH_v, of the elements of the *s*, *p* and *d* blocks of the periodic table delineating metals from non-metals (from Rao and Ganguly[10]).

the Herzfeld criterion, indicating the importance of atomic polarizability in determining the metallic character of elements. The liquid state seems to represent the limit for the itinerant behaviour of electrons in metals.

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