

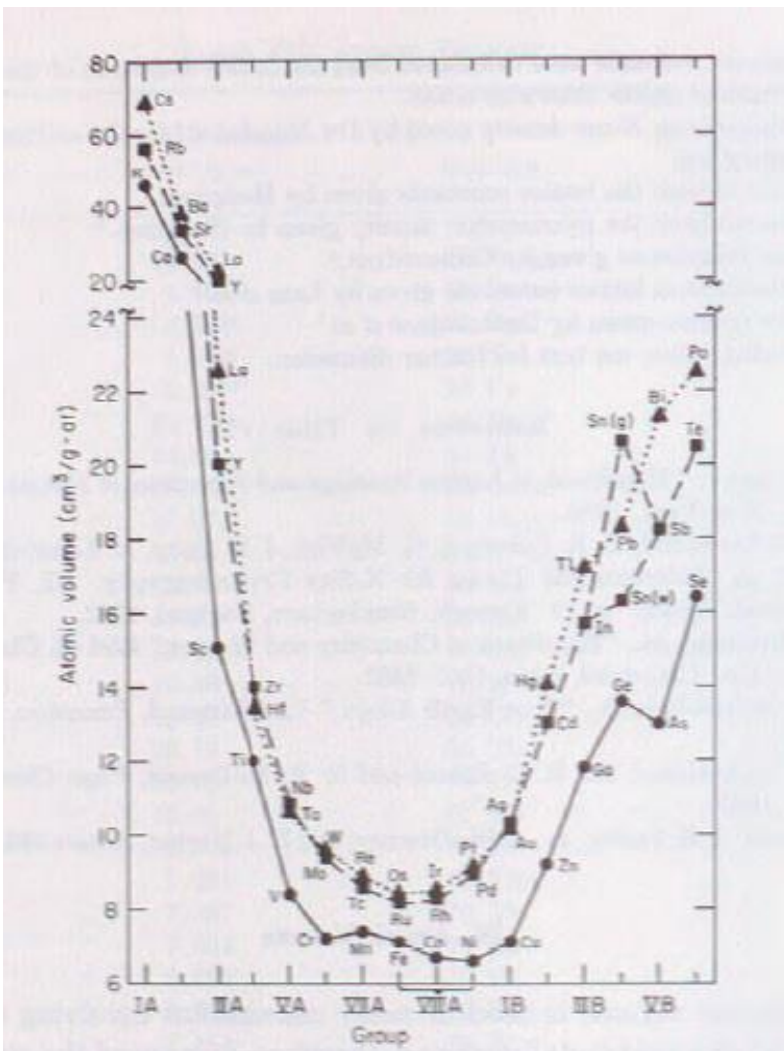
## **Relationship Between Elastic Modulus and Thermodynamic Properties of Elemental Metals**

Note: I apologize for the slightly skewed or blurred figures from the Gschneidner paper. They are like that in the scan but they look very poor transplanted.

## Abstract


The elastic modulus is a material property that is easy to measure macroscopically and very useful. It correlates well with various thermodynamic material properties such as melting point and heat of evaporation. The relationship between elastic modulus and location in the periodic table, along with several thermodynamic properties will be examined for elemental metals. It is shown that the stiffness and resistance to evaporation of these materials is largest in the center of a period, while the atomic volume is smallest near the center. Overall, cohesive energy and bond strength is shown to be the underlying cause in the correlation between elastic modulus and other material properties.

## Introduction



**Figure 1.** Atomic volume of the atoms of the fourth, fifth, and sixth periods of the Periodic Table [1].

- interatomic spring constant and atomic volume. In this paper we will examine the experimental and theoretical relationship between the elastic modulus of an elemental metal and thermodynamic properties such as melting temperature and heat of evaporation.

This paper will  focusing on the interrelationships between mechanical properties of metals such as elastic modulus and their relationship with thermodynamic properties such as heat of evaporation and melting point. Explanations for the correlations between mechanical and thermodynamic properties of metal elements will be examined, and figures from several classic papers on the matter will be highlighted.

Elastic modulus is a bulk material property that measures the stiffness of a material exposed to a stress. It can be defined for both macroscopic and atomic level properties, which is part of its utility. Elastic modulus  $E$  as derived from Hooke's law is defined as:

$$E = \frac{\sigma}{\varepsilon} = \frac{k}{\Omega}$$

Thereby relating measurable quantities such as tensile stress and strain to the less visible properties

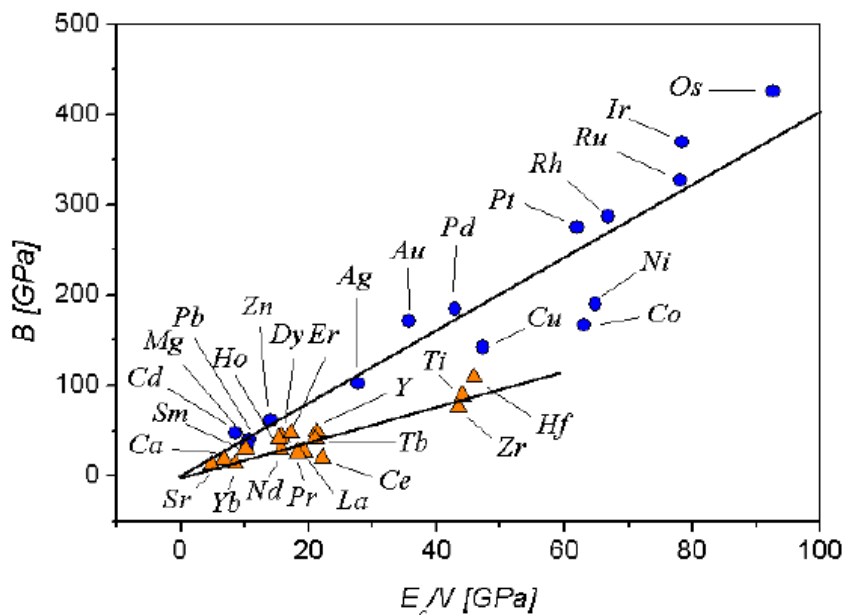
Another theme in this paper will be visually demonstrating the trends between positioning in the periodic table and quantities such as atomic volume and elastic modulus, as in figure 1. Plotting data in such a way elicits interesting observations about the relationship of the given property with atomic number, electronegativity, and bonding strength. Figure 1 plots the atomic volume of solid elements in the 4<sup>th</sup>, 5<sup>th</sup>, and 6<sup>th</sup> periods. One can see that both ends of the period exhibit high atomic volumes, while there is a very large dip and minima in the center of each period. For each row of the periodic table to show such similar behavior must be an insight into the underlying reason. This paper will examine several such plots and discuss the reasons and mechanisms for such behavior.

Overall this paper aims to examine several figures from the literature regarding the relationship between Young's modulus and thermodynamic properties, along with position on the periodic table influences in bulk material properties.

### Experiment and Theory

In this segment several figures from influential papers will be reviewed. Explanations from theory will be discussed, and simple models to demonstrate those relationships will be developed. As stated in the introduction, there have been papers that experimentally relate the Young's modulus to cohesive energy, or demonstrate it as a function of position in the periodic table for elemental metals. These visualizations can be very useful in understanding the underlying cause of variation in the modulus for neighboring elements.

Figure 2 demonstrates the linear relationship between the heat of evaporation and bulk modulus for various metals [3]. The paper details how the group plotted all the metals and got a very poor line of fit. However, they then realized that



**Figure 2.** Linear correlation between the experimental data on the bulk modulus  $B$  and cohesive energy density  $E_c/V$ . ● - structure A1 or A3, ▲ - structure A2, at the melting point.

structural differences at the melting point may be causing varying trends between A2 and A1 & A3 metals [3]. When they separated those groups and re-plotted the data, they observed that each group could be represented quite well by a linear trendline. The correlations they arrived at relate the bulk modulus B linearly to the cohesive energy density (the cohesive energy divided by the atomic volume) with correlation factors above 0.91 [3].

We can attempt to model this behavior by deriving a mathematical relationship between the elastic modulus and the heat of evaporation. This calculation will require some approximations since a rigorous analysis of the potential well for interatomic forces would be mathematically rigorous. However, we can approximate the force-displacement curve of an atom being removed from a bulk material with a simple half sin curve described by the equation  $F = F_0 \sin\left(\frac{2\pi U}{\lambda}\right)$  [2]. The curve has a slope of the spring constant k as displacement goes to zero, and a maximum value of  $F_0 = \frac{\lambda k}{2\pi}$ . By definition, the work of breaking the bonds is given by:

$$W_B = \int_0^{\lambda/2} F(U) dU = \frac{\lambda F_0}{\pi} = \frac{k\lambda^2}{2\pi^2} \left(\frac{J}{atom}\right) \quad (1)$$

Now an approximation must be made about the displacement value reached at fracture,  $U_f$ . For this derivation we will take the displacement at fracture to be equal to  $1/8^{\text{th}}$  of the interatomic spacing. The microscopic version of the Young's modulus is defined as the spring constant k divided by the interatomic spacing of the crystal, as derived from first principles. Combining all of that information, a relationship between the work of bond breaking and the Young's modulus can be reached:

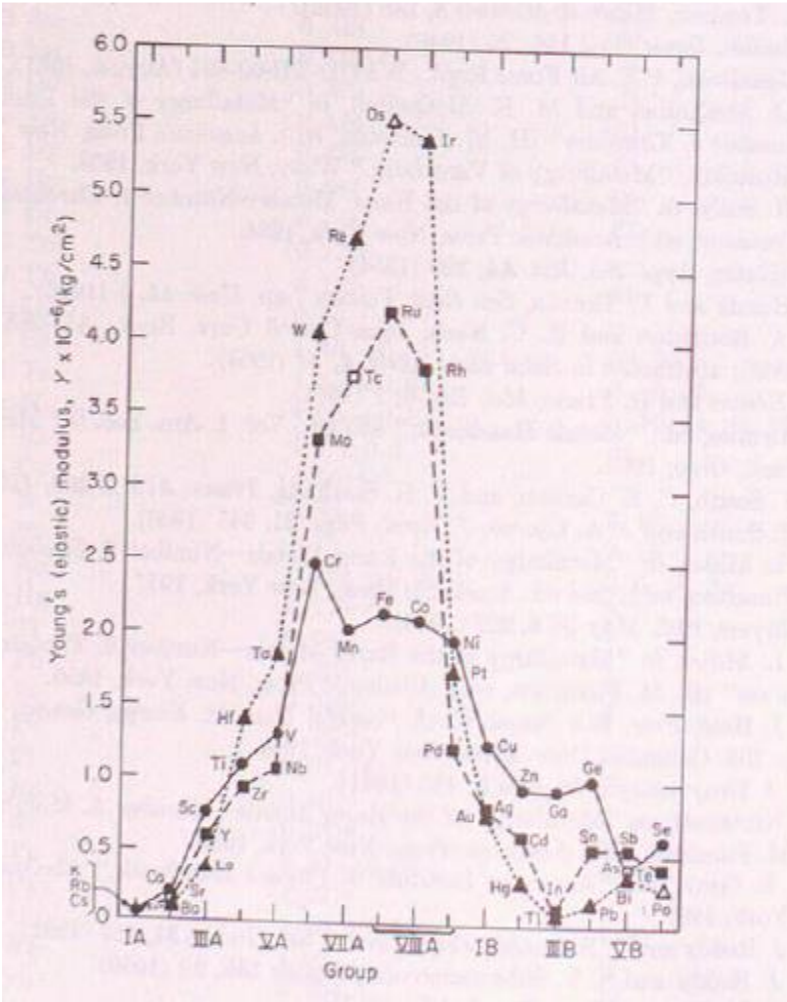
$$W_B = \frac{\lambda^2}{2\pi^2} \times E\Omega^{\frac{1}{3}} = \frac{E\Omega}{8\pi^2} \left(\frac{J}{atom}\right) \quad (2)$$

This relationship is exceedingly useful, as it relates measurable physical quantities to the thermodynamic work of bond breaking, which in turn can be related to the heat of evaporation with some geometric considerations. Since the total work of breaking bonds from an atom's nearest neighbors depends on packing factor, the number of bonds broken must be taken into account. With that in mind we define an  $E_z = E * \frac{Z}{6}$ , where Z represents the number of nearest neighbor atoms in the crystal structure. Defining the heat of evaporation of an atom:

$$\Delta H_v = \frac{Z}{2} W_B = \frac{Z}{2} \times \frac{6E_z}{Z} \times \frac{\Omega}{8\pi^2} = \frac{3\Omega E_z}{8\pi^2} \left(\frac{J}{atom}\right) \quad (3)$$

$$\frac{\Delta H_v}{\Omega} = \frac{3}{8\pi^2} E_z \left(\frac{J}{atom}\right) \quad (4)$$

$$E_z = \frac{\Delta H_v}{\Omega} \times \frac{8\pi^2}{3} \quad (5)$$



**Figure 3.** Young's modulus of the elements of the fourth, fifth, and sixth periods of the Periodic Table. Open points are estimated values. [1].

Equation 5 demonstrates by derivation the linear nature of the relationship between heat of evaporation and the mechanical property Young's modulus for our simplified model [2]. This is applicable to figure 2 since the bulk modulus is very similar to the elastic modulus of most of the metals, and the cohesive energy and heat of vaporization are equivalent in this context. This derivation can somewhat adequately model the behavior observed in figure 2, yet does not account for the clearly distinct empirical correlations for A1 and A3 vs A2 metals [3]. Additionally, the numerical constant for the relationship changes based on the estimate of the bond stretching at fracture, and fails to predict the elastic modulus of copper by a factor of about 2 when compared to experiments [2]

It makes conceptual sense that the Young's modulus would be linearly correlated to the thermodynamic heat of evaporation, since both properties inherently rely on the bond strength between a metal atom and its neighbors. The elastic modulus, representing the stiffness of material, should certainly depend on the bond character and strength. A higher modulus means that the material will elastically deform less than materials with a lower modulus when exposed to a tensile stress. The bond strength is such that the atoms are able to cling to each other strongly, making the material macroscopically stiff.

On the other hand, the energy required to vaporize a metal atom depends similarly on the level of attraction an atom has to its neighbors. Energetically speaking bonds represent energy, and overcoming the energy barrier to free an atom and push it into the higher energy gas phase requires an energetical input. Since both of these material properties depend on

bond strength and packing geometry it makes sense that they would be related in some way, even linearly for a given packing geometry.


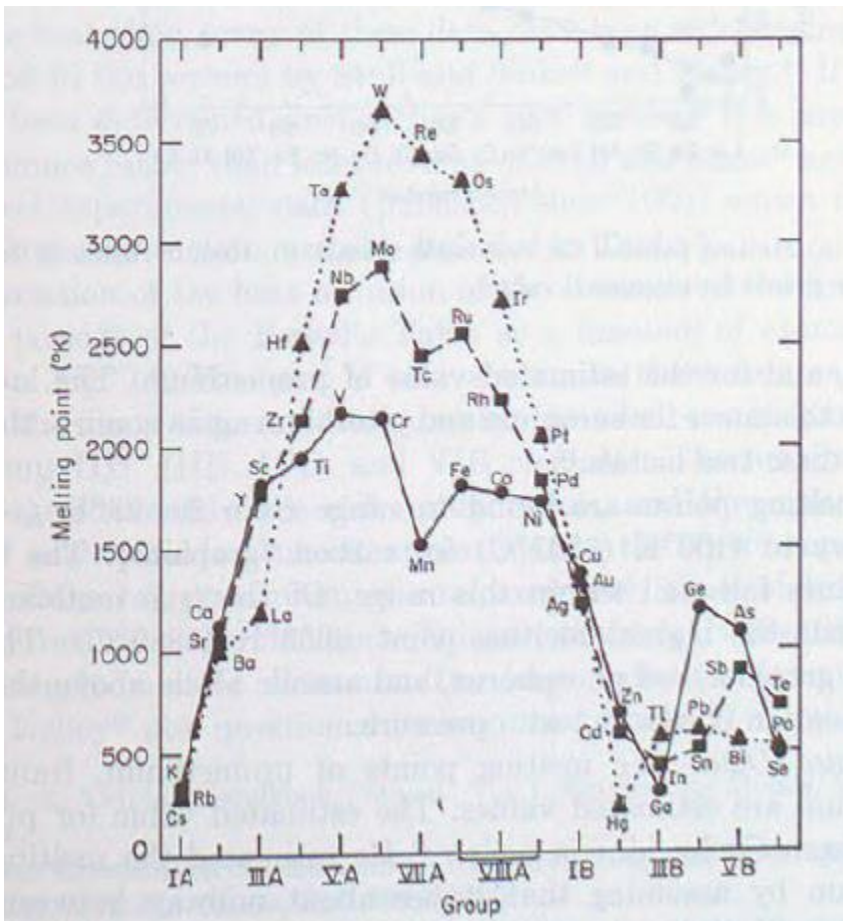
In figure 3 a plot of elemental Young's modulus vs periodic group is depicted and shows interesting trends. Each period's elements show a marked maximum of elastic modulus in the middle of the period. More specifically, those elements with many unpaired *d* orbital electrons are most likely to have a superior Young's modulus. This is due to the fact that they are able to form the largest number of bonds with neighboring atoms, thus increasing their number of tethering mechanisms to the material. 

Figure 4 depicts the melting point trends of elemental metals when they are plotted according to their position on the periodic table. One can observe that they are visually similar to figure 3. Similarly to the above derivation, we can make a simple model for a relationship between melting point and heat of evaporation for a given material. We start with the equation for Gibbs free energy (6) and applying it to melting of a material. At melting, the two phases are in thermodynamic equilibrium, so the change in gibbs free energy is set to zero, so the enthalpy of melting is equal to the melting temperature multiplied by the change in entropy of melting (8).



$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\Delta G_m = \Delta H_m - T_m\Delta S_m = 0 \quad (7)$$

$$\Delta H_m = T_m\Delta S_m \quad (8)$$

Making a simple assumption that the change in entropy upon melting is approximately the same for metals, we reach a relationship that shows the melting temperature is directly proportional to the  $\Delta H_m$ .

$$E_z \propto \Delta H_m \propto T_m \quad (9)$$

In figure 4 we observe that the melting point trends very similarly to elastic modulus for the same elemental metals. Conceptually this seems reasonable as melting point is also related thermodynamically to the interatomic attractions within a bulk material.

**Figure 4.** Melting point of the elements of the fourth, fifth, and sixth periods of the Periodic Table [1].

All of the trends demonstrated in these figures can be mechanistically explained by examining the concepts of cohesive energy and metallic bonding mechanisms. We see a maximum value of elastic modulus and melting temperature in the middle of each period. This is because the middle elements such as iridium and osmium have high numbers of unpaired *d* electrons which they are able to use for interatomic bonding. Metallic bonding is modelled as positively charged nuclei surrounded by a “sea of electrons” that each constituent atom contributes to. The more valence electrons available for contribution to this type of bonding, the greater the cohesive force within the material. This is the reason that transition metals have very high melting points and elastic moduli. Both the *d* and *s* orbitals are available for bonding. This explains why the middle of the period metals exhibit the trends shown in figures 3 and 4.

Furthermore, one can observe that as you go down periods in the periodic table, the maxima become higher in magnitude in figures 3 and 4. This is likely due to the increase in atomic number as you go down rows. The higher the atomic number, the more constituent proton cations the nucleus of the atom contains. This indicates that the electrostatic interactions between the nuclei and the “sea of electrons” will be stronger in atoms with larger atomic numbers, as demonstrated in figures 3 and 4.

These two factors discussed account mechanistically for the trends demonstrated in the above figures and explain why the elastic modulus can be related to various thermodynamic constants. This works because all of the material properties are inherently related to bond strength and material cohesion.

## **Summary**

Overall, this paper has presented several experimental figures from the literature and attempted to explain the results both through simple derivations, and through mechanistic examination. Elastic modulus is a representation of bond strength within a given material and can therefore be correlated to thermodynamic material properties such as the melting point, and energy of vaporization. The results of deriving from theory aren't perfect, since factors like imperfections and packing structure will play a role in determination of thermodynamic properties. However, deriving the relationships from first principles is still a valuable and educational experience.

The elastic modulus is a good predictor of all these thermodynamic properties, but ultimately is predicted by cohesive energy. This is because cohesive bond energy is the underlying root of the mechanical stiffness of a material, not the other way around. A general assessment of the elastic modulus, melting temperature, and heat of vaporization among other properties, can be made by examining the number of bonds possible in a metal matrix. Iridium and osmium have remarkably high values of the aforementioned properties due to their high number of unpaired *d* electrons. These electrons allow them to contribute a high number to the “sea of electrons” that is the nature of metallic bonding, thus

increasing the nucleus's electrostatic attraction to the material in bulk. This atomic level analysis of cohesion and bonding explain the nature of the relationship between elastic modulus and various thermodynamic material properties.



**Sources:**

[1] Gschneidner, Karl A. Physical Properties and Interrelationships of Metallic and Semimetallic Elements. *Solid State Physics*. Vol 16. 1964.

[2] Lecture notes from MCEN 5044. 2018.

[3] Wacke, S, et al. "Relations between the Cohesive Energy, Atomic Volume, Bulk Modulus and Sound Velocity in Metals." *Journal of Physics: Conference Series*, vol. 289, 2011, p. 012020., doi:10.1088/1742-6596/289/1/012020.

[4] G Grimvall and S Sjödin. Correlation of Properties of Materials to Debye and Melting Temperatures. *Journal of Physics*. Vol 10. 1974.

[5] R E McLaren. Theory of Cohesive Energy in simple metals. *Journal of Physics*. Vol 6. 1976.