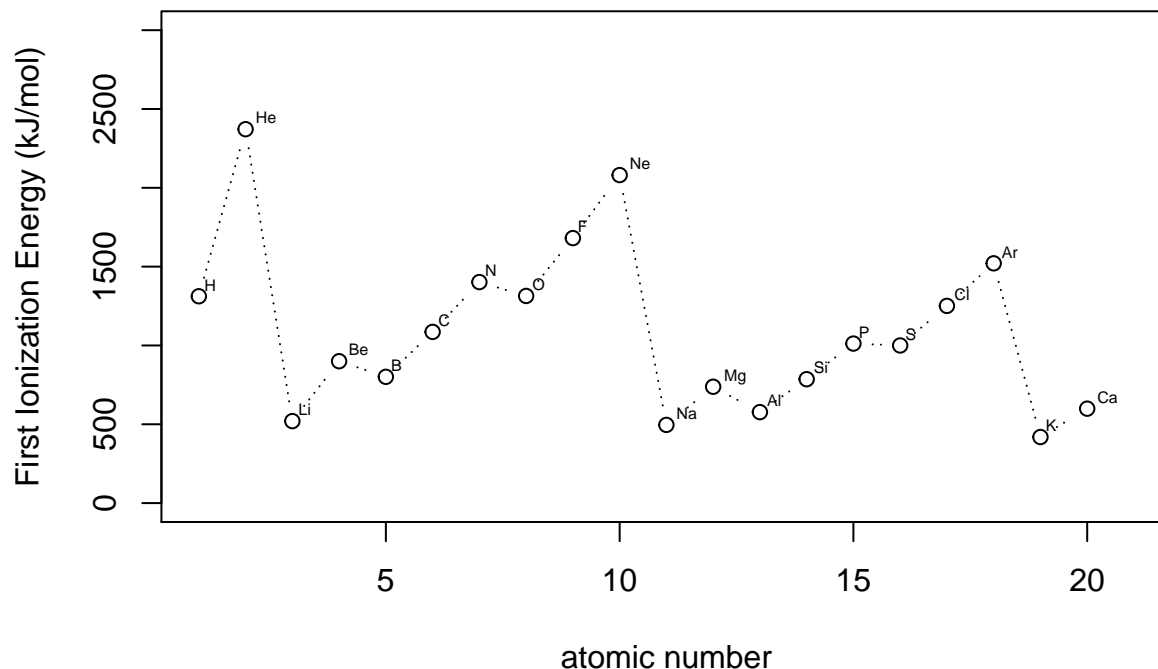


Key for Periodic Trends in Properties of Elements I

The following figure shows the first ionization energies, IE_1 , for the elements H \rightarrow Ca as a function of their atomic numbers, Z .



We know that IE_1 is proportional to Z , and yet the data do not show a steady increase in IE_1 as a function of Z . For each decrease in IE_1 that you see in this figure—for example, there is a decrease in IE_1 from helium to lithium—explain the source of the decrease.

- The decrease from He to Li, from Ne to Na, or from Ar to K is explained by a change in the shell that holds the electron: from $n = 1$ to $n = 2$ for He and Li, from $n = 2$ to $n = 3$ for Ne and Na, or from $n = 3$ to $n = 4$ for Ar and K. An increase in n implies an increase in the distance of the electron from the nucleus, r . As IE is inversely proportional to r , this decreases IE_1 .
- The decrease from Be to B, or from Mg to Al is explained by a change in the subshell that holds the electron: from $2s$ to $2p$ for Be and B, or from $3s$ to $3p$ for Mg and Al. As an ns electron screens an np electron more than an np electron screens an ns electron, Z_{eff} is greater from an ns electron. As IE is directly proportional to Z_{eff} , this decreases IE_1 .
- The decrease from N to O, or from P to S is explained by how electrons enter orbitals of the same subshell. The first three electrons in the $2p$ orbital for N and the $3p$ orbital for P occupy separate orbitals; the additional $2p$ electron for O and $3p$ electron for S must pair up with another electron. The repulsion between the electrons makes them easier to remove, which decreases IE_1 .

The photoelectron spectrum for scandium, Sc, has seven peaks with the following ionization energies, IE , and relative heights:

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7
IE (MJ/mol)	433	48.5	39.2	5.44	3.24	0.77	0.63
relative height	2	2	6	2	6	1	2
orbital	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^1$	$4s^2$

Complete the table by completing the row giving the orbital designation for each peak. Explain how you made your decisions.

- The orbital designations are shown above. The only question to address is whether the last two peaks are $3d^1, 4s^2$ or $4s^1, 3d^2$. From Madelung's rule, we expect the electrons to fill the $4s$ orbital before they enter the $3d$ orbital; thus, we expect Sc to have two $4s$ electrons. Once filled, the electrons in the $4s$ orbital become somewhat easier to remove than a $3d$ electron. This is consistent with Slater's rules, which suggest that $3d$ electrons screen $4s$ electrons, but that $4s$ electrons do not screen $3d$ electrons.

The $1s$, $2s$, and $3s$ electrons in argon, Ar, have ionization energies of 309, 31.5, and 2.82 MJ/mol, respectively. What is the full electron configuration for Ar?

- The electron configuration for argon is $1s^2 2s^2 2p^6 3s^2 3p^6$.

We can use Slater's rules to estimate Z_{eff} for any electron in Ar. For example, for a $1s$ electron in Ar, we have

$$Z_{\text{eff}} = Z - S = 18 - (1)(0.35) = 17.65$$

Note that the electron of interest is a $1s$ electron, that there is one additional electron in the $1s$ orbital, which accounts for the term $-(1)(0.35)$, and that we ignore the electrons in all other orbitals because they have smaller ionization energies. Using Slater's rules, estimate Z_{eff} for the $2s$ and the $3s$ electrons in Ar.

- Using Slater's rules, we first group the orbitals

$$(1s^2) \quad (2s^2 2p^6) \quad (3s^2 3p^6)$$

For a $2s$ electron we have $Z_{\text{eff}} = Z - S = 18 - (5)(0.35) - (2)(0.85) = 14.55$, and for a $3s$ electron we have $Z_{\text{eff}} = Z - S = 18 - (5)(0.35) - (8)(0.85) - (2)(1.00) = 7.45$.

Based on your values for Z_{eff} , are the effective nuclear charges sufficient to explain the differences in the ionization energies for the $1s$, $2s$, and $3s$ electrons in argon? If no, then offer an additional explanation.

- The ionization energies show that it is approximately $10\times$ harder to remove a $2s$ electron than a $3s$ electron (31.5 vs. 2.82 MJ/mol). The value of Z_{eff} for a $2s$ electron relative to a $3s$ electron, however, is less than $2\times$ greater (14.55 vs. 7.45), which means we cannot explain the difference in their ionization energies based on Z_{eff} alone. It must be the case that the radius for a $2s$ electron is smaller than expected, suggesting that the greater the effective nuclear charge, the more the electrons are pulled toward the nucleus and the smaller the radius. A similar argument applies to the relative ionization energies of the $1s$ and $2s$ electrons.

An element's first ionization energy, IE_1 , is the energy needed to remove the least tightly-held electron, which we represent by the reaction $E \rightarrow E^+ + e^-$. The second ionization energy, IE_2 is the energy needed to remove the next least tightly-held electron, which we represent by the reaction $E^+ \rightarrow E^{2+} + e^-$. The third and subsequent ionization energies follow the same pattern. The first and second ionization energies for helium, He, are 2370 and 5250 kJ/mol, respectively. Given that both electrons are in the same orbital, why is IE_2 more than $2\times$ than that for IE_1 ?

- When we remove the first electron from He, we leave behind an ion with a positive charge, He^+ . Three things make the second electron harder to remove. First, the two electrons in He screen each other from seeing the full charge of the nucleus, which means $Z_{\text{eff}} < 2$; once we remove one electron, the one that remains has $Z_{\text{eff}} = 2$. Second, the increase in Z_{eff} means the radius shrinks as the one remaining electron is pulled inward. And, third, it requires more energy to remove a negative charge from an ion that carries a positive charge than to remove it from a neutral atom.

The element beryllium, Be, has four electrons and four ionization energies, which are 900, 1760, 14850, and 21000 kJ/mol, respectively. As we expect, each ionization energy is greater than the preceding ionization energy. There is, however, a significant increase from IE_2 to IE_3 . Offer an explanation for this observation.

- The electron configuration for Be is $1s^2 2s^2$. The first and second electrons removed are from the $2s$ orbital. The third and fourth electron are in a $1s$ orbital and have much greater ionization energies because they are closer to the nucleus.