The Electron Configurations of Transition Metal Atoms and Ions
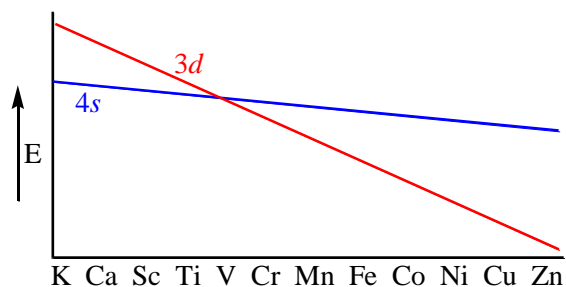
When predicting the electron configuration of an element, we begin by using the *aufbau* principle. It tells us to add electrons one at a time to the lowest energy available orbital. Through element 18 (argon) it works in an easily predictable pattern of filling: 1*s*, 2*s*, 2*p*, 3*s*, then 3*p*. When we reach potassium, something quite unexpected happens. The next electron goes into the 4*s* orbital instead of the 3*d*. Why? Furthermore, when electrons are removed from transition metals, we find the 4*s* depopulates first. This is even more surprising.

We begin by noting that for the 4th period and lower, the n*s* and (n-1)*d* orbitals lie very close in energy to one another. This is particularly true for the first 5 or 6 elements of each period. Thus, apparently minor effects can affect the energetic ordering of these orbitals.

To answer the first question posed, consider constructing a potassium atom from an argon atom. One proton will be added to the nucleus and one electron to an orbital. The question is: Which orbital? To choose the orbital, the next question that needs to be asked is "Which orbital will result in the lowest energy atom?" and there are really only two candidates 3*d* and 4*s*. This is because 3*d* is in the same subshell as the last filled orbital (3*p*) and 4*s* is the lowest energy orbital from the next principal quantum number.

The electrons in an atomic core are more tightly packed than those of the valence shell. This is because low principal quantum number orbitals are inherently smaller than those with larger principal quantum numbers and because added protons (as one moves through the periodic table) pull them even closer together. The result is that as one approaches the nucleus from a point far from the nucleus, electron-electron repulsions increase considerably as one gets close to the nucleus. With that in mind, look at the n = 3 level in Figure 2.4 (p. 13). Drop a perpendicular to the radial axis (*x*-axis) through the maximum on the *d* orbital ($\ell = 2$) and extend it up to the *s* orbital ($\ell = 0$). You can see there is more area under the *d* orbital curve, than the *s* orbital curve. This will be even more pronounced for the 4*s* orbital. Thus, although a 3*d* orbital is lower in energy than a 4*s* orbital in a one electron atom, when they are filled in a multi-electron atom electron-electron repulsions raise the energy of the 3*d* more than the 4*s* and the latter ends up more stable.

As more protons and electrons are added to the atom, the protons pull harder on the electrons closest to the nucleus. Since, on average, electrons in the 3*d* orbital are closer than those in the 4*s*, the energy of the 3*d* falls more rapidly and eventually drops below that of the 4*s* (see Figure) The

crossover point is near vanadium. This is why the electron configuration of chromium is [Ar] $4s^1$ $3d^5$. In this configuration, there are 6 unpaired electrons whose spins will align. The energy released from aligning all of these spins is greater than the energy difference between the orbitals.

From the previous discussion, we can conclude that the $3d$ orbital on scandium (for example) is higher in energy than its $4s$ orbital, yet the scandium(II) ion has an electron configuration of [Ar] $3d^1$. We now need to reconcile this apparent discrepancy. The error commonly made here is tying together the atom and ion. The question here is actually which orbital is more stable in the ion, not the atom. In all transition metal ions, the valence (n-1)d orbital is lower in energy than the ns orbital. Removing electrons has two effects. The first is the same as adding protons (albeit somewhat muted), the second is reduced electron-electron repulsions. Both of these effects favor stabilizing the (n-1)d over the ns.

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