Pearson

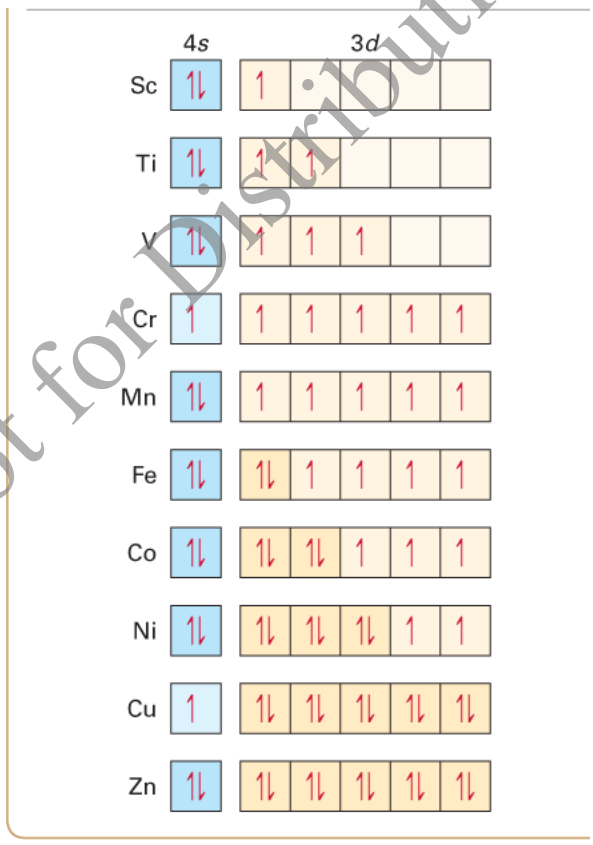
22.2: Properties of Transition Metals

Transition metals have more uniform properties than the main-group elements. For example, almost all transition metals have moderate to high densities, good electrical conductivity, high melting points, and moderate to extreme hardness. Their similar properties are related to their similar electron configurations: They all have electrons in *d* orbitals that can be involved in metallic bonding. In spite of their similarities, however, each element is also unique, and they exhibit a wide variety of chemical behavior. Before we examine some of the periodic properties of the transition metals, let's review the electron configurations of these elements, first discussed in Chapter 3.

Electron Configuration

Recall from Section 3.4 that, as we move to the right across a row of transition elements, electrons are added to $(n - 1)d$ orbitals (where n is the row number in the periodic table and also the quantum number of the highest occupied principal level). For example, as we move across the fourth-period transition metals, electrons are added to the $3d$ orbitals, as shown in Table 22.1.

Table 22.1 First-Row Transition Metal Orbital Occupancy



In general, the ground state electron configuration for the first two rows of transition elements is [noble gas] $ns^2\,(n-1)\,d^x$, and for the third and fourth rows it is [noble gas] $ns^2\,(n-2)\,f^{14}\,(n-1)\,d^x$, where x ranges from 1 to 10. Recall also from Section 3.4, however, that because the ns and $(n - 1)d$ sublevels are close in energy, many exceptions occur. For example, in the first transition series of the d block, the outer configuration is $4s^2 3d^x$ with two exceptions: Cr is $4s^1 3d^5$ and Cu is $4s^1 3d^{10}$. This behavior is related to the closely spaced $3d$ and $4s$

energy levels and the stability associated with a half-filled or completely filled *d* sublevel.

Recall from Section 3.7 that the transition metals form ions by losing electrons from the *ns* orbital *before* losing electrons from the $(n - 1)d$ orbitals. For example, Fe^{2+} has an electron configuration of [Ar] $3d^6$ because it has lost both of the 4*s* electrons to form the 2+ charge. Examples 22.1 and 22.2 review the steps in writing electron configurations for transition metals and their ions.

Example 22.1 Writing Electron Configurations for Transition Metals

Write the ground state electron configuration for Zr.

PROCEDURE Identify the noble gas that precedes the element and write it in square brackets.

SOLUTION [Kr]

PROCEDURE Count down the periods to determine the outer principal quantum level—this is the quantum level for the *s* orbital. Subtract one to obtain the quantum level for the *d* orbital. If the element is in the third or fourth transition series, include $(n - 2)\,f^{14}$ electrons in the configuration.

SOLUTION Zr is in the fifth period, so the orbitals used are

$$[\text{Kr}]\ 5s4d$$

PROCEDURE Count across the row to see how many electrons are in the neutral atom and fill the orbitals accordingly.

SOLUTION Zr has four more electrons than Kr.

$$[\text{Kr}]\ 5s^2 4d^2$$

FOR PRACTICE 22.1 Write the ground state electron configuration for Os.

Example 22.2 Writing Electron Configurations for Transition Metals

Write the ground state electron configuration for Co^{3+}.

PROCEDURE Identify the noble gas that precedes the element and write it in square brackets.

SOLUTION [Ar]

PROCEDURE Count down the periods to determine the outer principal quantum level—this is the quantum level for the *s* orbital. Subtract one to obtain the quantum level for the *d* orbital. If the element is in the third or fourth transition series, include $(n - 2)\,f^{14}$ electrons in the configuration.

SOLUTION Co is in the fourth period, so the orbitals used are

$$[\text{Ar}]\ 4s3d$$

PROCEDURE Count across the row to see how many electrons are in the neutral atom and fill the orbitals accordingly.

SOLUTION Co has nine more electrons than Ar.

$[\mathrm{Ar}]\ 4s^2 3d^7$

PROCEDURE For an ion, remove the required number of electrons, first from the *s* and then from the *d* orbitals.

SOLUTION Co^{3+} has lost three electrons relative to the Co atom.

$$[\mathrm{Ar}]\ 4s^0 3d^6 \text{ or } [\mathrm{Ar}]\ 3d^6$$

FOR PRACTICE 22.2 Write the ground state electron configuration for Nb^{2+}.

Atomic Size

As we discussed in Section 3.6, for main-group elements, the size of atoms decreases across a period and increases down a column. For transition metals, however, there is little variation in size across a row (other than for the first two elements in each transition metal row, such as Sc and Ti in the first row), as shown in Figure 22.1. The reason for the difference is that, across a row of transition elements, the number of electrons in the outermost principal energy level (highest *n* value) is nearly constant. As another proton is added to the nucleus with each successive element,

Figure 22.1 Trends in Atomic Radius

With the exception of a decrease in radius from the first to the second element, there is only a small variation in atomic radius across each transition metal row. There is a small and expected increase in radius from the first to the second transition metal row but virtually no difference in radius from the second to the third.

another electron is added as well, but the electron goes into an $n - 1$ orbital. The number of outermost electrons thus stays the same, and the electrons experience a roughly constant effective nuclear charge as we move across the row, keeping the radii approximately constant.

Looking down a group, we see a small but expected increase in size from the first transition metal row to the second, but the size of elements in the third row is about the same as it is for those in the second row. This pattern is also different from that of the main-group elements, especially when we consider that in any given column, the third transition row has 32 more electrons than the second row. The third transition row elements are not larger because 14 of the 32 electrons are in a $(n - 2)f$ sublevel, and while electrons in *f* orbitals are in lower principal quantum levels, they are not very effective at shielding the outer electrons from nuclear charge. Consequently, the outer electrons are held more tightly by the nucleus, offsetting the typical increase in size between the periods. This effect is called the **lanthanide contraction**.

Conceptual Connection 22.1 Atomic Size

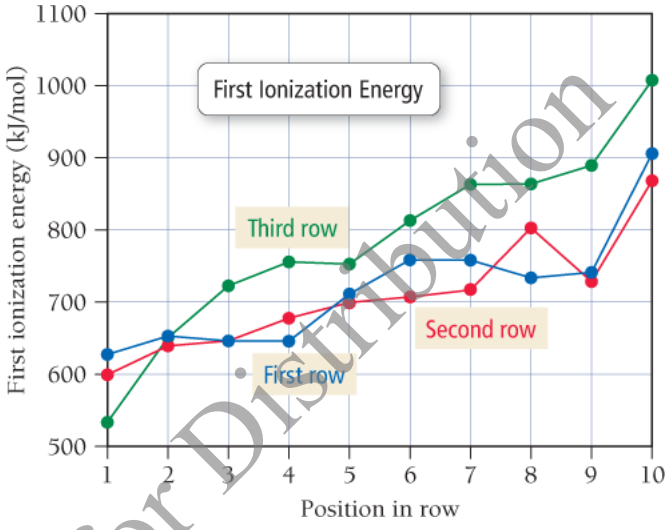
Ionization Energy

Interactive

The first ionization energies of transition elements follow the expected main-group periodic trend and slowly increase across each transition metal row (Figure 22.2), but the increase is smaller than for main-group elements. As we move down a group, we see that the third transition row generally has a higher ionization energy than do the first two rows, a trend counter to that observed in the main-group elements. In the transition elements the charge of the nucleus increases substantially from one row to the next, but there is only a small increase in atomic size between the first and second rows, and no increase in size is observed between the second and third rows. The outer electrons are therefore held more tightly in the third transition row than in the first two rows.

Figure 22.2 Trends in First Ionization Energy

First ionization energy generally increases across each transition metal row, following the main-group trend. However, in contrast to the main-group trend, the third transition metal row has a greater ionization energy than the first and second rows.

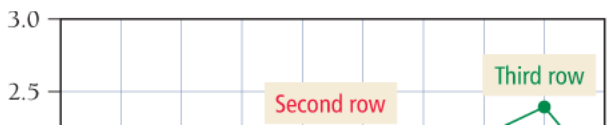


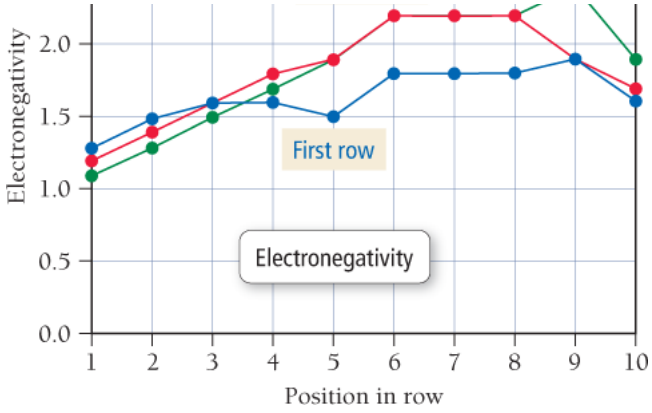
Electronegativity

The electronegativity values of the transition metals, like their ionization energies, follow the main-group trend and slowly increase across a row, as shown in Figure 22.3. The increase is smaller than the increase that occurs in the main-group elements, but we would expect that given the similarity in the sizes of the atoms across the transition metal rows. The trend in electronegativity values down a group (or column) is another example of the transition metals behaving differently from the main-group elements. The electronegativity values generally increase from the first transition metal row to the second, but there is no further increase for the third row. In the main-group elements, by contrast, we see a *decrease* in electronegativity down a group.

Figure 22.3 Trends in Electronegativity

The electronegativity of the transition metal elements generally increases across a row, following the main-group trend. However, in contrast to the main-group trend, electronegativity increases from the first transition metal row to the second. There is little electronegativity difference between the second and third transition rows.





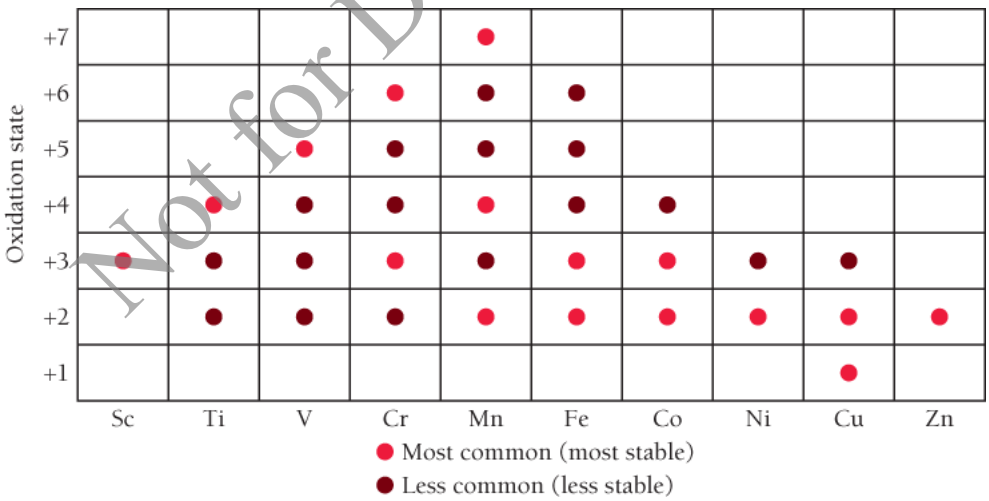
The difference is again caused by the relatively small change in atomic size as we move down a column for the transition elements, accompanied by a large increase in nuclear charge. One of the heaviest metals, gold (Au), is also the most electronegative metal. Its electronegativity value (EN = 2.4) is even higher than that of some nonmetals (EN of P is 2.1), and compounds of an Au^- ion have been observed.

Oxidation State

Unlike main-group metals, which tend to exhibit only one oxidation state, the transition metals often exhibit a variety of oxidation states (Figure 22.4). The highest oxidation state for a transition metal is +7 for manganese (Mn). The electron configuration of manganese in this oxidation state corresponds to the loss of all the electrons in the 4*s* and 3*d* orbitals, leaving a noble gas electron configuration ([Ar]). This is the same configuration we see for all of the highest oxidation states of the elements to the left of Mn. To the right of manganese, the oxidation states are all lower, mostly +2 or +3. A +2 oxidation state for a transition metal is not surprising, since 4*s* electrons are readily lost.

Figure 22.4 First-Row Transition Metal Oxidation States

The transition metals exhibit many more oxidation states than the main-group elements. These oxidation states range from +7 to +1.



In some rare cases, oxidation states higher than +7 have been observed.

Metals in high-oxidation states, such as +7, exist only when the metal is bound to a highly electronegative element such as oxygen; they do not exist as bare ions.