The periodic table gives very helpful clues about the structure and configuration of electrons for a given atom. The table’s order is convenient for counting, and in most cases, the easiest way to solve a problem is to take a standard case and alter it. In general, neutral atoms are defined as having equal numbers of electrons and protons; charge “cancels out” and the atoms are stable. However, in the formation of compounds, valence electrons, or electrons in the outermost shells of an atom, can form bonds to reduce the overall energy of the system. For transition metals, the partial loss of these diffused electrons is called oxidation. Please review oxidation-reduction reactions if this concept is unfamiliar.

**Introduction**

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

<table>
<thead>
<tr>
<th>s Orbital</th>
<th>p Orbitals</th>
<th>d Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 orbital, 2 electrons</td>
<td>3 orbitals: px, py, pz; 6 electrons</td>
<td>5 orbitals: dx^2-y^2, d_z^2, d_xy, d_yz, d_xz; 10 electrons</td>
</tr>
</tbody>
</table>

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

**Neutral-Atom Electron Configuration**

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.

For example, if we were interested in determining the electronic organization of Vanadium (atomic number 23), we would start from hydrogen and make our way down (refer to the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

Referring to the periodic table below confirms this organization. We have 3 elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.
The neutral atom configurations of the fourth period transition metals are in Table 2.

**Table 2:**

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
<td>[Ar]</td>
</tr>
<tr>
<td></td>
<td>4s(^2)3d(^1)</td>
<td>4s(^2)3d(^2)</td>
<td>4s(^2)3d(^3)</td>
<td>4s(^2)3d(^4)</td>
<td>4s(^2)3d(^5)</td>
<td>4s(^2)3d(^6)</td>
<td>4s(^2)3d(^7)</td>
<td>4s(^2)3d(^8)</td>
<td>4s(^2)3d(^9)</td>
<td>4s(^2)3d(^10)</td>
</tr>
<tr>
<td></td>
<td>[Ar]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4s(^1)3d(^5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What may appear anomalous is the case that takes advantage of the degeneracy.

Take a brief look at where the element Chromium (atomic number 24) lies on the Periodic Table (found below). The electronic configuration for chromium is not

\[ 4s^2 \quad ([\text{Ar}] \ 4s^2 3d^4) \]

\[ 3d^4 x^2-y^2 \ z^2 \ xy \ yz \ xz \]

but instead it is

\[ 4s^1 \quad ([\text{Ar}] \ 4s^1 3d^5) \]

\[ 3d^5 \ x^2-y^2 \ z^2 \ xy \ yz \ xz \]

especially because of the degeneracy of the s and d orbitals. There is no error in assuming that a s-orbital electron will be displaced to fill the place of a d-orbital electron because their associated energies are equal. After all, the **Aufbau Principle** states that the lowest energy configuration is of unpaired electrons in the most space possible. Electrostatic force is inversely proportional to distance according to Coulomb’s Law; this unnecessarily paired s-orbital electron can be relieved of its excess energy.

Lastly, for the two above **energy diagrams** to be true in nature, the distance between the 4s and the 3d orbitals would be neglected. There is a slight separation for transition metals on the right of the block, but for the purpose of discussing ionization, the order indicated is true. More energetic orbitals are labeled above lesser ones.

---

**Oxidation States of Transition Metal Ions**

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose its s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see **formation of coordination complexes**.
Example 1

Write the electronic configurations of:

a. neutral iron,
   b. iron(II) ion, and
   c. iron(III) ion.

**SOLUTION**

The atomic number of iron is 26 so there are 26 protons in the species.

a. \( \text{Fe: } [\text{Ar}] 4s^2 3d^6 \)
   
b. \( \text{Fe}^{2+}: [\text{Ar}] 3d^6 \)
   
c. \( \text{Fe}^{3+}: [\text{Ar}] 3d^5 \)

Note that the s-orbital electrons are lost first, then the d-orbital electrons.

Example 2

Determine the more stable configuration between the following pair:

a. \([\text{Kr}] 5s^2 4d^6 \) vs. \([\text{Kr}] 5s^1 4d^7 \)
   
b. \( \text{Ag}^{1+} \) vs. \( \text{Ag}^{2+} \)

**SOLUTION**

a. This describes Ruthenium. There is only one 5s electron.
   
b. Once-oxidized silver \([\text{Kr}] 4d^{10} \) is more stable than twice- \([\text{Kr}] 4d^9 \).

### Varying Oxidation States

The following chart describes the most common oxidation states of the period 3 elements.

**Table 3:**

<table>
<thead>
<tr>
<th>Ox. #</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>+2</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>+3</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>+4</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ox. #</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
</tr>
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<td>----</td>
</tr>
<tr>
<td>+5</td>
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<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
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</tr>
<tr>
<td>+6</td>
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<td>x</td>
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<td>x</td>
</tr>
<tr>
<td>+7</td>
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<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

This diagram brings up a few concepts illustrating the stable states for specific elements.

Example 3

What makes zinc stable as Zn$^{2+}$? What makes scandium stable as Sc$^{3+}$?

**SOLUTION**

Zinc has the neutral configuration [Ar]4s$^2$3d$^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as [Ar]4s$^2$3d$^1$. Losing 3 electrons brings the configuration to the noble state with valence 3p$^6$.

Example 4

Why is iron almost always Fe$^{2+}$ or Fe$^{3+}$?

**SOLUTION**

Iron is written as [Ar]4s$^2$3d$^6$. Losing 2 electrons from the s-orbital (3d$^6$) or 2 s- and 1 d-orbital (3d$^6$) electron are fairly stable oxidation states.

Example 5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

**SOLUTION**

Although Mn$^{+2}$ is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as Mn(s), Mn(II) as MnO, Mn(II,III) as Mn$_3$O$_4$, Mn(IV) as MnO$_2$, or manganese dioxide, Mn(VII) in the permanganate ion MnO$_4^-$, and so on.

---

**Effect of Oxidation State on Physical Properties**

Transition metals have high boiling points. The d orbitals allow electrons to become diffused and enables them to be delocalized within solid metal. This increases the attractive forces between the atoms and requires more energy to dissociate them in order to change phases. This attraction reaches a maximum in Group IV for manganese (boiling point of 2061 °C), which has 5 unpaired electrons. The potential for manganese to form strong and numerous bonds is greater than its neighbors. For this same reason, zinc has a low boiling point (907 °C): it does not have much attractive force.
between like atoms. Also in the 12th period, mercury has a low melting point (-39 °C), which allows it to be liquid at standard conditions.

The lanthanide contraction is a term that describes two different periodic trends. The first is that the Group VI transition metals are separated by 15 additional elements which are displaced to the bottom of the table. The lanthanides introduce the f orbital, which are very diffused and do not shield well. Since additional protons are now more visible to these electrons, the atomic radius of a Group VI transition metal is contracted enough to have approximately equal atomic radii to Group V transition metals. The second definition explains the general decrease in ionic radii and atomic radii as one looks at transition metals from left to right. This is due to the addition of electrons to the same diffused f orbital while protons are added. This results in greater attraction between protons and neutrons. The term refers to the same idea that f orbitals do not shield electrons efficiently, but refer to comparisons between elements horizontally and vertically.

**Manganese: A Case Study**

Manganese is widely studied because it is an important reducing agent in chemical analysis. It is also studied in biochemistry for catalysis, as well as in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese’s flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

\[ \text{Mn}_2\text{O}_3 \] is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is **paramagnetic**.

\[
\begin{align*}
\text{4s}^0 \\
\text{3d}^4 x^2-y^2 z^2 xy yz xz
\end{align*}
\]

\[ \text{MnO}_2 \] is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is **less paramagnetic** than \( \text{Mn}^{3+} \).

\[
\begin{align*}
\text{4s}^0 \\
\text{3d}^3 x^2-y^2 z^2 xy yz xz
\end{align*}
\]

\[ \text{KMnO}_4 \] is potassium permanganate, where manganese is in the +7 state. No electrons exist in the 4s and 3d orbitals. The 3p orbitals have no unpaired electrons, so this complex is **diamagnetic**.

\[
\begin{align*}
\text{4s}^0 \\
\text{3d}^0 x^2-y^2 z^2 xy yz xz
\end{align*}
\]
Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

References


Outside Links


- For more help in writing these states, all neutral and +1 cations are listed at the NIST website:
  
  external link: [http://physics.nist.gov/PhysRefData/...iguration.html](http://physics.nist.gov/PhysRefData/...iguration.html)

Contributors

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