The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple potential oxidation states.

### Introduction

Oxidation results in an increase in the oxidation state. Reduction results in a decrease in the oxidation state. If an atom is reduced, it has a higher number of valence shell electrons, and therefore a higher oxidation state, and is a strong oxidant. For example, oxygen (O) and fluorine (F) are very strong oxidants. On the other hand, lithium (Li) and sodium (Na) are incredibly strong reducing agents (likes to be oxidized), meaning that they easily lose electrons. In this module, we will precisely go over the oxidation states of transition metals.

### Unpaired Electrons of d-orbitals

To fully understand the phenomena of oxidation states of transition metals, we have to understand how the unpaired d-orbital electrons bond. There are five orbitals in the d subshell manifold. As the number of unpaired valence electrons increases, the d-orbital increases, the highest oxidation state increases. This is because unpaired valence electrons are unstable and eager to bond with other chemical species. This means that the oxidation states would be the highest in the very middle of the transition metal periods due to the presence of the highest number of unpaired valence electrons.

To determine the oxidation state, unpaired d-orbital electrons are added to the 2s orbital electrons since the 3d orbital is located before the 4s orbital in the periodic table.

For example: Scandium has one unpaired electron in the d-orbital. It is added to the 2 electrons of the s-orbital and therefore the oxidation state is +3. So that would mathematically look like: 1s electron + 1s electron + 1d electron = 3 total electrons = oxidation state of +3. The formula for determining oxidation states would be (with the exception of copper and chromium):

\[
\text{Highest Oxidation State for a Transition metal} = \text{Number of Unpaired d-electrons} + \text{Two s-orbital electrons}
\]

The number of d-electrons range from 1 (in Sc) to 10 (in Cu and Zn). See Periodic Table below:
In the image above, the blue-boxed area is the d block, or also known as transition metals.

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

It was mentioned previously that both copper and chromium do not follow the general formula for transition metal oxidation states. This is because copper has 9 d-electrons, which would produce 4 paired d-electrons and 1 unpaired d-electron. Since copper is just 1 electron short of having a completely full d-orbital, it steals an electron from the s-orbital, allowing it to have 10 d-electrons. Likewise, chromium has 4 d-electrons, only 1 short of having a half-filled d-orbital, so it steals an electron from the s-orbital, allowing chromium to have 5 d-electrons.

Rules About Transition Metals

1. Free elements (elements that are not combined with other elements) have an oxidation state of zero, e.g., the oxidation state of Cr (chromium) is 0.

2. For ions, the oxidation state is equal to the charge of the ion, e.g., the ion Fe^{3+} (ferric ion) has an oxidation state of +3.

3. The oxidation state of a neutral compound is zero, e.g., What is the oxidation state of Fe in FeCl_3?

   4. Answer: Cl has an oxidation state of -1. Since there are 3 Cl atoms the negative charge is -3. Since FeCl_3 has no overall charge, the compound have a neutral charge, and therefore the oxidation state of Fe is +3.

   In other words, it is: Fe^{3+} and 3Cl^{-}, which makes up FeCl_3 with a neutral charge.

Multiple Oxidation States

As stated above, most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and therefore their oxidation state is almost always +1 (from losing it) and alkaline earth metals have two electrons in their valencers-orbital, resulting with an oxidation state of +2 (from losing both). This is not the case for transition metals since transition metals have 5 d-orbitals. The d-orbital has a variety of oxidation states. The s-orbital also...
contributes to determining the oxidation states.

Example

Iron has 4 unpaired electrons and 2 paired electrons. To find one of its oxidation states, we can use the formula:

\[
\text{Oxidation State of Fe} = 4 + 2 = +6
\]

Indeed, +6 is one of the oxidation states of iron, but it is very rare. Other possible oxidation states for iron includes: +5, +4, +3, and +2.

Since there are many exceptions to the formula, it would be better just to memorize the oxidation states for the fourth period transition metals, since they are more commonly used. Here is a chart which shows the most common oxidation states for first row transition metals. See table in this module for more information about the most common oxidation states.

<table>
<thead>
<tr>
<th>Element Name and Symbol</th>
<th>Atomic Number</th>
<th>Common Oxidation States</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium (Sc)</td>
<td>21</td>
<td>+3</td>
<td>Sc: [Ar] 4s(^1)3d(^{\frac{5}{2}})</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>22</td>
<td>+4</td>
<td>Ti: [Ar] 4s(^2)3d(^{\frac{5}{2}})</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>23</td>
<td>+2, +3, +4, +5</td>
<td>V: [Ar] 4s(^2)3d(^{\frac{5}{2}})</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>24</td>
<td>+2, +3, +6</td>
<td>Cr: [Ar] 4s(^2)3d(^{\frac{5}{2}})</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>25</td>
<td>+2, +3, +4, +6, +7</td>
<td>Mn: [Ar] 4s(^2)3d(^{\frac{7}{2}})</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>26</td>
<td>+2, +3</td>
<td>Fe: [Ar] 4s(^2)3d(^{\frac{6}{2}})</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>27</td>
<td>+2, +3</td>
<td>Co: [Ar] 4s(^2)3d(^{\frac{7}{2}})</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>28</td>
<td>+2</td>
<td>Ni: [Ar] 4s(^2)3d(^{\frac{8}{2}})</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>29</td>
<td>+1, +2</td>
<td>Cu: [Ar] 4s(^2)3d(^{10})</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>30</td>
<td>+2</td>
<td>Zn: [Ar] 4s(^2)3d(^{10})</td>
</tr>
</tbody>
</table>

**Chromium and Copper Exceptions**

Chromium and copper have 4s\(^1\) instead of 4s\(^2\). This is because chromium is 1 d-electron short for having a half-filled d-orbital, therefore it takes one from the s-orbital, so the electron configuration for chromium would just be: [Ar] 4s\(^1\)3d\(^{\frac{5}{2}}\). Similarly, for copper, it is 1 d-electron short for having a fully-filled d-orbital and takes one from the s-orbital, so the electron configuration for copper would simply be: [Ar] 4s\(^1\)3d\(^{10}\).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.
Oxidation State of Transition Metals in Compounds

When given an ionic compound such as AgCl, you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the halogen group of the periodic table, we then know that it has a charge of -1, or simply Cl\(^{-}\). In addition, by seeing that there is no overall charge for AgCl, (which is determined by looking at the top right of the compound, i.e., AgCl\(^{#}\), where \(\#\) represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us Ag\(^{+}\) and Cl\(^{-}\), in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

Example \(\PageIndex{2}\)
Determine the oxidation state of cobalt (Co) in CoBr\(_2\).

**SOLUTION**

Similar to chlorine, bromine (Br) is also in the halogen group, so we know that it has a charge of -1 (Br\(^{-}\)). Since there are two bromines, the anion (bromine) gives us a charge of -2. In addition, we know that CoBr\(_2\) has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 in order to neutralize the -2 charge from the two bromines. With this said, we get Co\(^{2+}\) and 2Br\(^{-}\), which would result as CoBr\(_2\).

Example \(\PageIndex{3}\)

What is the oxidation state of zinc (Zn) in ZnCO\(_3\). *(Note: CO\(_3\) in this example has an oxidation state of -2, CO\(_3\)\(^{2-}\))*

**SOLUTION**

Knowing that CO\(_3\) has an oxidation state of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc (Zn) has an oxidation state of +2. This gives us Zn\(^{2+}\) and CO\(_3\)\(^{2-}\), in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge, giving us ZnCO\(_3\).

Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate (\(\text{MnO}_4^{-}\)) ion. Since oxygen has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom (Mn) must have an oxidation state of +7. This gives us Mn\(^{7+}\) and 4 O\(^{2-}\), which will result as \(\text{MnO}_4^{-}\).

This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.

Real World Examples

Magnets are used in electric motors and generators that allow us to have computers, light, telephones, televisions, and
electric heat. Magnetism is a function of chemistry that relates to the oxidation state. The oxidation state determines if the element or compound is diamagnetic or paramagnetic. Diamagnetic substances have only paired electrons, and repel magnetic fields weakly. These substances are non-magnetic, such as wood, water, and some plastics. However, paramagnetic substances become magnetic in the presence of a magnetic field. Paramagnetic substances have at least one unpaired electron. Another stronger magnetic force is a permanent magnet called a ferromagnet. These are much stronger and do not require the presence of a magnetic field to display magnetic properties. These are the type of magnets found on your refrigerator.

Outside links

1. Periodic Table: http://commons.wikimedia.org/wiki/File:Periodic_table.svg
2. Ionic Compounds: http://lac.smccme.edu/New%20PDF%20No.../Ionrules2.pdf (Page 6 is useful)

References

3. Clentsmith, G. K., F. G. Cloke, et al. (2003). "Stabilization of low-oxidation-state early transition-metal complexes bearing 1,2,4-triphosphaclopentadienyl ligands: structure of [Sc(P3C2tBu2)2]2; Sc(II) or mixed oxidation state?" Angew Chem Int Ed Engl 42(9): 1038-41

Problems

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) Copper(I) Chloride: CuCl
(B) Copper(II) Nitrate: Cu(NO₃)₂
(C) Gold(V) Fluoride: AuF₅
(D) Iron(II) Oxide: FeO
(E) Iron(III) Oxide: Fe₂O₃
(F) Lead(II) Chloride: PbCl₂
(G) Lead(II) Nitrate: Pb(NO₃)₂
(H) Manganese(II) Chloride: MnCl₂
(I) Molybdenum trioxide: MoO₃
(J) Nickel(II) Hydroxide: Ni(OH)₂
(K) Platinum(IV) Chloride: PtCl₄
(L) Silver Sulfide: Ag₂S
1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate (MnO$_4^{2-}$)

2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?

3. Which transition metal has the most number of oxidation states?

4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

Solutions

See File Attachment for Solutions. (You will probably need Adobe Reader to open the PDF file.)

Contributors

- Joslyn Wood, Liza Chu (UCD)