

## 8.2: Bonding in Simple Molecules That Contain Transition Metals

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 oxidation states experimentally observed.

### 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 8.2.1

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: $p_x$ , $p_y$ , $p_z$ ; 6 electrons	5 orbitals: $d_{x^2-y^2}$ , $d_{z^2}$ , $d_{xy}$ , $d_{yz}$ , $d_{xz}$ ; 10 electrons
	Highest energy orbital for a given quantum number $n$	Degenerate with s-orbital of quantum number $n+1$

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 Configurations

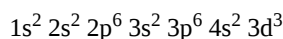
Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down 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).

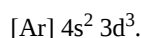
If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on [electron configuration](#).

Figure 8.2.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.



or



The neutral atom configurations of the fourth period transition metals are in Table 8.2.2.

Table 8.2.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] 4s <sup>2</sup> 3d <sup>1</sup>	[Ar] 4s <sup>2</sup> 3d <sup>2</sup>	[Ar] 4s <sup>2</sup> 3d <sup>3</sup>	[Ar] 4s <sup>2</sup> 3d <sup>4</sup>	[Ar] 4s <sup>2</sup> 3d <sup>5</sup>	[Ar] 4s <sup>2</sup> 3d <sup>6</sup>	[Ar] 4s <sup>2</sup> 3d <sup>7</sup>	[Ar] 4s <sup>2</sup> 3d <sup>8</sup>	[Ar] 4s <sup>2</sup> 3d <sup>9</sup>	[Ar] 4s <sup>2</sup> 3d <sup>10</sup>
			[Ar] 4s <sup>1</sup> 3d <sup>5</sup>					[Ar] 4s <sup>1</sup> 3d <sup>10</sup>	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 8.2.1). The electronic configuration for chromium is not [Ar] 4s<sup>2</sup>3d<sup>4</sup> but instead it is [Ar] 4s<sup>1</sup>3d<sup>5</sup>. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 8.2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

## 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 8.2.1

Write the electronic configurations of:

- neutral iron,
- iron(II) ion, and
- iron(III) ion.

**Answer**

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

- Fe:  $[\text{Ar}] 4s^2 3d^6$
- $\text{Fe}^{2+}$ :  $[\text{Ar}] 3d^6$
- $\text{Fe}^{3+}$ :  $[\text{Ar}] 3d^5$

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

## ✓ Example 8.2.2

Determine the more stable configuration between the following pair:

- $[\text{Kr}] 5s^2 4d^6$  vs.  $[\text{Kr}] 5s^1 4d^7$
- $\text{Ag}^{1+}$  vs.  $\text{Ag}^{2+}$

**Answer**

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

## Multiple Oxidation States

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 their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

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

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).

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.

### ✓ Example 8.2.3

What makes zinc stable as Zn<sup>2+</sup>? What makes scandium stable as Sc<sup>3+</sup>?

#### Answer

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

### ✓ Example 8.2.4

Why is iron almost always Fe<sup>2+</sup> or Fe<sup>3+</sup>?

#### Answer

Iron is written as [Ar]4s<sup>2</sup>3d<sup>6</sup>. Losing 2 electrons from the s-orbital (3d<sup>6</sup>) or 2 s- and 1 d-orbital (3d<sup>5</sup>) electron are fairly stable oxidation states.

### ✓ Example 8.2.5

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

#### Answer

Although  $\text{Mn}^{+2}$  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  $\text{Mn}_{(s)}$ , Mn(II) as  $\text{MnO}$ , Mn(II,III) as  $\text{Mn}_3\text{O}_4$ , Mn(IV) as  $\text{MnO}_2$ , or manganese dioxide, Mn(VII) in the permanganate ion  $\text{MnO}_4^-$ , and so on.

## Oxidation State of Transition Metals in Compounds

When given an ionic compound such as  $\text{AgCl}$ , 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  $\text{Cl}^-$ . In addition, by seeing that there is no overall charge for  $\text{AgCl}$ , (which is determined by looking at the top right of the compound, i.e.,  $\text{AgCl}^\#$ , where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us  $\text{Ag}^+$  and  $\text{Cl}^-$ , 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 8.2.6

Determine the oxidation state of cobalt in  $\text{CoBr}_2$ .

#### Answer

Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 ( $\text{Br}^-$ ). Since there are two bromines each with a charge of -1. In addition, we know that  $\text{CoBr}_2$  has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

### ✓ Example 8.2.7

What is the oxidation state of zinc in  $\text{ZnCO}_3$ . (Note: the  $\text{CO}_3$  anion has a charge state of -2)

#### Answer

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

## 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 must have an oxidation state of +7. This gives us  $\text{Mn}^{7+}$  and  $4\text{O}^{2-}$ , 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.*

### 📌 Manganese: A Case Study

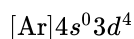
**Manganese** is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular 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.



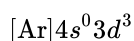
Figure 8.2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

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.

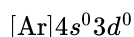
$\text{Mn}_2\text{O}_3$  is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.



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



$\text{KMnO}_4$  is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.



Since the 3p orbitals are all paired, this complex is diamagnetic.

## 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.

## Questions

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

(A) <u>Copper</u> (I) Chloride: $\text{CuCl}$	(B) <u>Copper</u> (II) Nitrate: $\text{Cu}(\text{NO}_3)_2$	(C) <u>Gold</u> (V) Fluoride: $\text{AuF}_5$
(D) <u>Iron</u> (II) Oxide: $\text{FeO}$	(E) <u>Iron</u> (III) Oxide: $\text{Fe}_2\text{O}_3$	(F) <u>Lead</u> (II) Chloride: $\text{PbCl}_2$
(G) <u>Lead</u> (II) Nitrate: $\text{Pb}(\text{NO}_3)_2$	(H) <u>Manganese</u> (II) Chloride: $\text{MnCl}_2$	(I) <u>Molybdenum</u> trioxide: $\text{MoO}_3$
(J) <u>Nickel</u> (II) Hydroxide: $\text{Ni}(\text{OH})_2$	(K) <u>Platinum</u> (IV) Chloride: $\text{PtCl}_4$	(L) <u>Silver</u> Sulfide: $\text{Ag}_2\text{S}$
(M) <u>Tungsten</u> (VI) Fluoride: $\text{WF}_6$	(N) <u>Vanadium</u> (III) Nitride: $\text{VN}$	(O) <u>Zirconium</u> Hydroxide: $\text{Zr}(\text{OH})_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate ( $\text{MnO}_4^{2-}$ )
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?

## References

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