

8.1: Chemistry of the Transition Metals

This page explains what a transition metal is in terms of its electronic structure, and then goes on to look at the general features of transition metal chemistry. These include variable oxidation state (oxidation number), complex ion formation, colored ions, and catalytic activity.

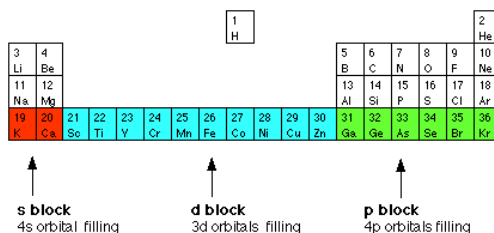
What is a transition metal?

The terms transition metal (or element) and d block element are sometimes used as if they mean the same thing. They don't - there's a subtle difference between the two terms. We'll explore d block elements first:

d-block elements

You will remember that when you are building the [Periodic Table](#) and working out where to put the electrons using the [Aufbau Principle](#), something odd happens after argon.

At argon, the 3s and 3p levels are full, but rather than fill up the 3d levels next, the 4s level fills instead to give potassium and then calcium. Only after that do the 3d levels fill. The elements in the Periodic Table which correspond to the d levels filling are called **d block elements**. The first row of these is shown in the shortened form of the Periodic Table below.



s block d block p block
 4s orbital filling 3d orbitals filling 4p orbitals filling

The electronic structures of the d block elements shown are:

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

You will notice that the pattern of filling is not entirely tidy! It is broken at both chromium and copper.

Transition metals

Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:

The official IUPAC definition:

A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.

The older definition:

A transition metal is one which forms one or more stable ions which have *incompletely* filled d orbitals.

Notice how similar these two definitions are. The only difference is that the IUPAC definition allows for the atom itself having incompletely filled d levels as well as the ions.

The problem lies only at the extreme left-hand end of the d block with, for example, scandium: Scandium has the electronic structure $[\text{Ar}] 3d^1 4s^2$. When it forms ions, it always loses the 3 outer electrons and ends up with an argon structure. The Sc^{3+} ion has **no d electrons** and so does not meet the second (older) definition.

Zinc has the electronic structure $[\text{Ar}] 3d^{10} 4s^2$. When it forms ions, it always loses the two 4s electrons to give a $2+$ ion with the electronic structure $[\text{Ar}] 3d^{10}$. The zinc ion has **full d levels** and does not meet either definition.

By contrast, copper, $[\text{Ar}] 3d^{10} 4s^1$, forms two ions. In the Cu^+ ion the electronic structure is $[\text{Ar}] 3d^{10}$. However, the more common Cu^{2+} ion has the structure $[\text{Ar}] 3d^9$. Copper is definitely a transition metal because the Cu^{2+} ion has an incomplete d level.

Transition metal ions

Here you are faced with one of the most irritating facts in chemistry at this level! When you work out the electronic structures of the first transition series (from scandium to zinc) using the [Aufbau Principle](#), you do it on the basis that the 3d orbitals have higher energies than the 4s orbitals.

That means that you work on the assumption that the 3d electrons are added after the 4s ones. However, in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.

It is important to note that when d block elements form ions, the 4s electrons are always lost first.

To write the electronic structure for Co^{2+} :

Co		$[\text{Ar}] 3d^7 4s^2$
Co^{2+}		$[\text{Ar}] 3d^7$

The $2+$ ion is formed by the loss of the two 4s electrons.

To write the electronic structure for V^{3+} :

V		$[\text{Ar}] 3d^3 4s^2$
V^{3+}		$[\text{Ar}] 3d^2$

The 4s electrons are lost first followed by one of the 3d electrons.

Variable oxidation state (number)

One of the key features of transition metal chemistry is the wide range of [oxidation states](#) (oxidation numbers) that the metals can show. It would be wrong, though, to give the impression that only transition metals can have variable oxidation states. For example, elements like Sulfur or nitrogen or chlorine have a very wide range of oxidation states in their compounds - and these obviously aren't transition metals. However, this variability is less common in metals apart from the transition elements. Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.

Examples of variable oxidation states in the transition metals

- Iron:** Iron has two common oxidation states (+2 and +3) in, for example, Fe^{2+} and Fe^{3+} . It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-} .
- Manganese:** Manganese has a very wide range of oxidation states in its compounds. For example:

+2	in Mn^{2+}
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+3	in Mn_2O_3
+4	in MnO_2
+6	in MnO_4^{2-}
+7	in MnO_4^-

You will find the above examples and others looked at in detail if you explore the chemistry of individual metals from the transition metal menu. There is a link to this menu at the bottom of the page.

Explaining the variable oxidation states in the transition metals

We'll look at the formation of simple ions like Fe^{2+} and Fe^{3+} . When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process. On the whole, the compound formed is the one in which most energy is released. The more energy released, the more stable the compound. There are several energy terms to think about, but the key ones are:

- The amount of energy needed to ionize the metal (the sum of the various ionization energies)
- The amount of energy released when the compound forms. This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

The more highly charged the ion, the more electrons you have to remove and the more ionization energy you will have to provide. But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

Thinking about a typical non-transition metal (calcium)

The formula for Calcium chloride is CaCl_2 . Why is that? If you tried to make CaCl , (containing a Ca^+ ion), the overall process is slightly exothermic. By making a Ca^{2+} ion instead, you have to supply more ionization energy, but you get out lots more lattice energy. There is much more attraction between chloride ions and Ca^{2+} ions than there is if you only have a $1+$ ion. The overall process is very exothermic. Because the formation of CaCl_2 releases much more energy than making CaCl , then CaCl_2 is more stable - and so forms instead.

What about CaCl_3 ? This time you have to remove yet another electron from calcium. The first two come from the 4s level. The third one comes from the 3p. That is much closer to the nucleus and therefore much more difficult to remove. There is a large jump in ionization energy between the second and third electron removed. Although there will be a gain in lattice enthalpy, it is not anything like enough to compensate for the extra ionization energy, and the overall process is very endothermic. It definitely is not energetically sensible to make CaCl_3 !

Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the $2+$ or the $3+$ ion.

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

The 4s orbital and the 3d orbitals have very similar energies. There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second. The figures for the first three ionization energies (in kJ mol^{-1}) for iron compared with those of calcium are:

metal	1st IE	2nd IE	3rd IE
Ca	590	1150	4940
Fe	762	1560	2960

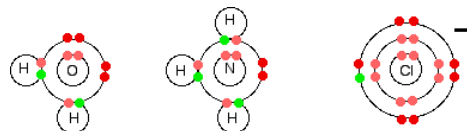
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

In the iron case, the extra ionization energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made. The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say, FeCl_2 or FeCl_3 . That means that it is not too difficult to convert between the two compounds.

The formation of complex ions

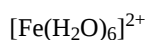
What is a complex ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion.

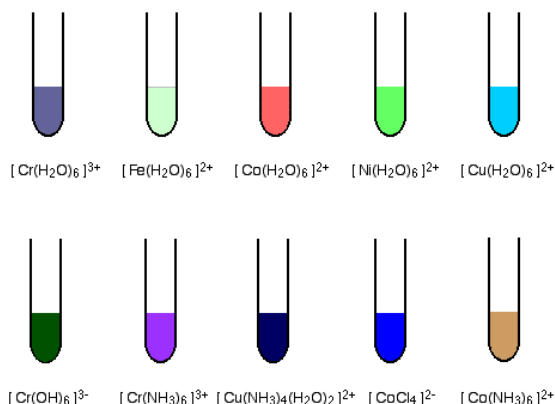
Some examples of complex ions formed by transition metals



Other metals also form complex ions - it is not something that only transition metals do. Transition metals do, however, form a very wide range of complex ions.

The formation of colored compounds

The diagrams show approximate colors for some common transition metal complex ions.



You will find these and others discussed if you follow links to individual metals from the transition metal menu (link at the bottom of the page). Alternatively, you could explore the complex ions menu (follow the link in the help box which has just disappeared off the top of the screen).

The origin of color in the transition metal ions

When white light passes through a solution of one of these ions, or is reflected off it, some colors in the light are absorbed. The color you see is how your eye perceives what is left. Attaching ligands to a metal ion has an effect on the energies of the d orbitals.

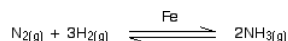
Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

Catalytic Activity

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The [Haber Process](#) combines hydrogen and nitrogen to make ammonia using an iron catalyst.



Nickel in the hydrogenation of C=C bonds

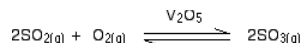
This reaction is at the heart of the manufacture of [margarine](#) from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.



Transition metal compounds as catalysts

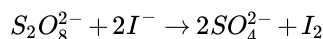
Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.



Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $\text{S}_2\text{O}_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.



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