Some chemistry of the Periodic Table

Electronic configuration and oxidation states of the transition metals

Electronic configuration

The d-block transition metals are defined as metals with an incomplete d subshell in at least one of their ions. When a transition metal atom loses electrons to form a positive ion the 4s electrons are lost before the electrons occupying the 3d orbitals.

Make sure that you know this. Although 4s electrons are lower in energy than 3d, they are actually further from the nucleus and are therefore the first to be lost in a reaction.

Consider the electronic configurations of the transition elements using [Ar] to represent that of argon [$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$].

Element	**Spectroscopic notation**	**Orbital box notation**
Scandium	[Ar] $3d^1\ 4s^2$	[↑][ ][ ][ ][ ]
Titanium	[Ar] $3d^2\ 4s^2$	[↑][↑][ ][ ][ ]
Vanadium	[Ar] $3d^3\ 4s^2$	[↑][↑][↑][ ][ ]
Chromium	[Ar] $3d^5\ 4s^1$	[↑][↑][↑][↑][↑]
Manganese	[Ar] $3d^5\ 4s^2$	[↑][↑][↑][↑][↑]
Iron	[Ar] $3d^6\ 4s^2$	[↑↓][↑][↑][↑][↑]
Cobalt	[Ar] $3d^7\ 4s^2$	[↑↓][↑↓][↑][↑][↑]
Nickel	[Ar] $3d^8\ 4s^2$	[↑↓][↑↓][↑↓][↑][↑]
Copper	[Ar] $3d^{10}\ 4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓]
Zinc	[Ar] $3d^{10}\ 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓]

As can be seen from the table, the filling of the d orbitals follows the aufbau principle, with the exception of chromium and copper atoms.

These exceptions are due to a special stability associated with all the d orbitals being half filled, as in the case of chromium, or completely filled, as in the case of copper.

This is best illustrated with the orbital box notation.

Questions

1) Write down the electronic configurations in both spectroscopic and orbital box notation for the following atoms and ions.

(a) Cu (b) Mn^{2+} (c) Ti^{3+} (d) Co (e) Co^{2+}

(f) Co^{3+} (g) Ni^{2+} (h) Cu^{+} (i) Fe^{3+} (j) V^{3+}

2) Zinc invariably forms the 2+ ion and the only ion of scandium is the 3+ ion. Using spectroscopic notation, write down the electronic configurations for both these ions and use them to explain why zinc and scandium are often regarded as not being transition metals.

Oxidation states

In ionic compounds the oxidation number is equal to the charge on the ion in a compound.

For example, in iron(II) chloride, $Fe^{2+}(Cl^-)_2$, iron is in oxidation state +2 and in iron(III) chloride, $Fe^{3+}(Cl^-)_3$, iron is in oxidation state +3. The two terms, oxidation state and oxidation number, are usually interchangeable and so an element is said to be in a particular oxidation state when it has a specific oxidation number.

There are certain rules for assigning and using oxidation numbers.

These are:

1. The oxidation number in a free or uncombined element is zero.
   Thus, metallic magnesium has an oxidation number of zero as does Chlorine in chlorine gas, Cl_2.
2. For ions consisting of single atoms the oxidation number is the same as the charge on the ion.
   For example, the oxidation number of chlorine in Cl^- is -1, for oxygen in O^{2-} it is -2 and for aluminium in Al^{3+} it is +3.
3. In most compounds the oxidation number for hydrogen is +1 and for oxygen it is -2.
   Notable exceptions are metallic hydrides (-1 for hydrogen) and peroxides (-1 for oxygen).
4. In its compounds fluorine always has oxidation number -1.
5. The algebraic sum of all the oxidation numbers in a molecule must be equal to zero.
6. The algebraic sum of all the oxidation numbers in a polyatomic ion must be equal to the charge on the ion. For example, in SO_4^{2-} the sum of the oxidation numbers of the one sulphur and four oxygen atoms must equal -2.

Question

Use the rules above to find the oxidation numbers of:

(a) Mn in MnF_2
(b) S in SO_2
(c) S in SO_3
(d) C in CO_3^{2-}
(e) Mn in MnO_2
(f) S in SO_4^{2-}
(g) Mn in MnO_4^{2-}
(h) Mn in MnO_4^-
(i) Cu in $CuCl_4^{2-}$

Oxidation numbers can be used to determine whether an oxidation- reduction reaction has taken place. An increase in oxidation number means that oxidation of the species has occurred, whereas a decrease in oxidation number means that reduction has occurred.

For example, consider the oxidation number of manganese as it changes from MnO_4^- to Mn^{2+}.

The oxidation number of manganese in MnO_4^- is +7, but in Mn^{2+} manganese is in oxidation state +2.

This means that when MnO_4^- is changed to Mn^{2+} a reduction reaction has taken place.

This fits in with the more familiar definition that reduction is a gain of electrons, as shown in the ion-electron equation

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

It can also be written as

$$Mn^{+7} + 5e \longrightarrow Mn^{+2}$$

Notice that oxidation numbers are written with the plus sign first, to distinguish oxidation state from ion charge. Manganese does *not* exist as the ion Mn^{7+} in permanganate.
It is a general rule that metals with high oxidation states are oxidising agents and metals with low oxidation states are often reducing agents. Fe^{2+} will easily oxidise to Fe^{3+} for example.

Questions

1. Write an ion-electron equation for Fe^{2+} acting as:
   (i) an oxidising agent
   (ii) a reducing agent.

2. Work out the oxidation number of Cr in $Cr_2O_7^{2-}$ and decide whether the conversion of $Cr_2O_7^{2-}$ to Cr^{3+} is oxidation or reduction.
   Is the $Cr_2O_7^{2-}$ ion acting as an oxidising agent or a reducing agent in this reaction?
   Confirm your answer by writing the appropriate ion-electron equation.

3. Work out the oxidation number of chromium in $Cr_2O_7^{2-}$ and in CrO_4^{2-} and decide whether the conversion of $Cr_2O_7^{2-}$ to CrO_4^{2-} is oxidation or reduction.

4. The most common oxidation states of iron are +2 and +3.
   Using orbital box notation, draw out their respective electronic configurations and suggest which of the two ions is the more stable.

Transition metals exhibit variable oxidation states of differing stability.
A common oxidation state of most of these elements is +2 when the atom has lost its 4s electrons.
However, because the 3d subshells have energy levels very close to that of the 4s subshell, it is fairly easy for the 3d electrons to be also lost to form other oxidation states.
The different ions in different oxidation states have different stabilities, as in the case of Fe^{2+} and Fe^{3+} (see question 4 above).
Changing from one oxidation state to another is an important aspect of transition metal chemistry, often characterised by a distinct colour change, as shown in the table below.

The oxidation states of vanadium

Ion	**Oxidation state (or number)**	**Colour**
VO_2^{+}	+5	Yellow
VO^{2+}	+4	Blue
V^{3+}	+3	Green
V^{2+}	+2	Violet

Notice the similarity in formula of the top two ions

The multiplicity of different oxidation states shown by some transition metals is shown in the table below. The most stable oxidation states are in bold type.

Element	Oxidation states	Familiar compounds
Ti	+2, +3, +4	Ti_2O_3, TiO_2
V	+2, +3, +4, +5	VCl_3, V_2O_5
Cr	+1, +2, +3, +4, +5, +6	Cr_2O_3, K_2CrO_4
Mn	+1, +2, +3, +4, +5, +6, +7	MnO, MnO_2, $KMnO_4$
Fe	+1, +2, +3, +4, +6	FeO, $FeCl_3$
Co	+1, +2, +3, +4, +5	$CoCl_2$, $CoCl_3$
Ni	+1, +2, +3, +4	$NiSO_4$, $NiCl_2$
Cu	+1, +2, +3	Cu_2O, $CuSO_4$

Transition metal complexes

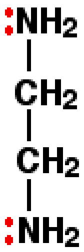
A complex consists of a central metal ion surrounded by **ligands**.

A ligand is a molecule or negative ion which bonds to the metal ion by the donation of one or more electron pairs into unfilled metal orbitals.

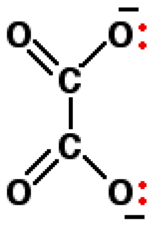
The most common neutral compound to act as a ligand is water, which bonds to the central metal ion through one of the lone pairs on the oxygen atom. Ammonia, (NH_3), is also a neutral ligand, bonding through the lone pair on the nitrogen atom.

Common ligands that are negative ions include:
- cyanide ion, CN^-
- halides, F^-, Cl^-, Br^- and I^-
- nitrite ion, NO_2^-
- hydroxide ion, OH^-.

Ligands such as CN^-, H_2O, NH_3 and other molecules or negative ions donating one electron pair to the metal ion are said to be **monodentate**. The term ‘dentate’ is derived from the Latin word for tooth and so monodentate ligands can be considered as one-toothed ligands. Ligands are also said to be chelating, from the Greek word meaning a claw.
If the ligand has two lone pairs, it is called a **bidentate** ligand. Common bidentate ligands are the ethanedioate (oxalate) ion and 1,2-diaminoethane (ethylenediamine), both of which are shown below.

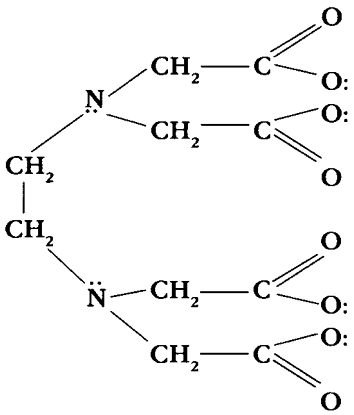


1,2-diaminoethane



ethanedioate ion

A common reagent in volumetric analysis is EDTA, ethylenediaminetetraacetic acid.
It is a hexadentate ligand which complexes with many metals in a 1:1 ratio as shown.



Structure of EDTA. Note all the electron pairs

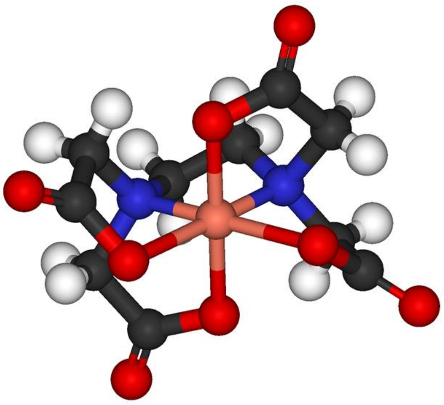


Diagram of EDTA complexing with a copper ion. Atoms with lone pairs position themselves along the x, y and z axes in an octahedral complex.

EDTA will complex with alkali metals as well as transition metals, and for this reason a solution of EDTA cannot be stored for long periods in glass containers as it complexes with the sodium ions in the glass.

The number of ligands in a complex ion varies depending on the particular ligand. For example, in $[Cu(H_2O)_6]^{2+}$ the copper(II) ion is surrounded by six water molecules and in $[CuCl_4]^{2-}$ there are four chloride ions acting as ligands around the copper(II) ion.

The number of bonds from the ligand to the central metal ion is known as the **co-ordination number** of the central ion and in the two examples given above the copper(II) ion has co-ordination numbers 6 and 4 respectively.

Naming complexes

Complex ions and complexes are written and named according to IUPAC rules.

The formula of a complex ion should be enclosed within square brackets, although common complexes such as MnO_4^- are often written without brackets. The metal symbol is written first, then the negative ligands followed by the neutral ligands, e.g. $[Fe(OH)_2(H_2O)_4]^+$.

When naming the complex ion or molecule the ligands should be named first, in alphabetical order, followed by the name of the metal.

If the ligand is a negative ion the name of which ends in -ide, the ending changes to ‘o’, e.g. chloride, Cl-, becomes chloro, cyanide, CN-, becomes cyano.

If the ligand is a negative ion the name of which ends in -ite, the final ‘e’ changes to ‘o’, e.g. nitrite, NO_2^-, changes to nitrito.

If the ligand is water it is named aqua, ammonia is named ammine and carbon monoxide is carbonyl.

If there is more than one particular ligand it is prefixed by di, tri, tetra, penta, or hexa, etc. as appropriate.

If the complex ion is an anion (negative ion) the suffix -ate is added to the name of the metal.

Sometimes the Latin name for the metal is used in this context, e.g. ferrate not ironate and cuprate rather than copperate.

The oxidation state of the metal is given in Roman numerals after its name.

For example, the complex ion $[Ni(NH_3)_6]^{2+}$ is named hexaamminenickel(II) and the negative complex ion $[Fe(CN)_6]^{3-}$ is named hexacyanoferrate(III).

Question

Name the following complexes:

(a) $[CoCl_4]^{2-}$
(b) $[Ni(H_2O)_6]^{2+}$
(c) $[Fe(CN)_6]^{4-}$
(d) $[Ti(NH_3)_6]^{3+}$
(e) $[Ni(CN)_6]^{4-}$
(f) MnO_4^-
(g) $[PtCl_6]^{2-}$
(h) $Ni(CO)_4$
(i) $[Co(NH_3)_4]^{2+}$

Colour in transition metal complexes

Simple ions and complex ions of the transition metals are often coloured. This is because they **absorb** light in certain parts of the visible spectrum. The colour seen is the **complementary** colour to that absorbed, i.e. it is a combination of the colours not absorbed.

To help understand this, we can consider white light to be a combination of the three primary colours red, blue and green.

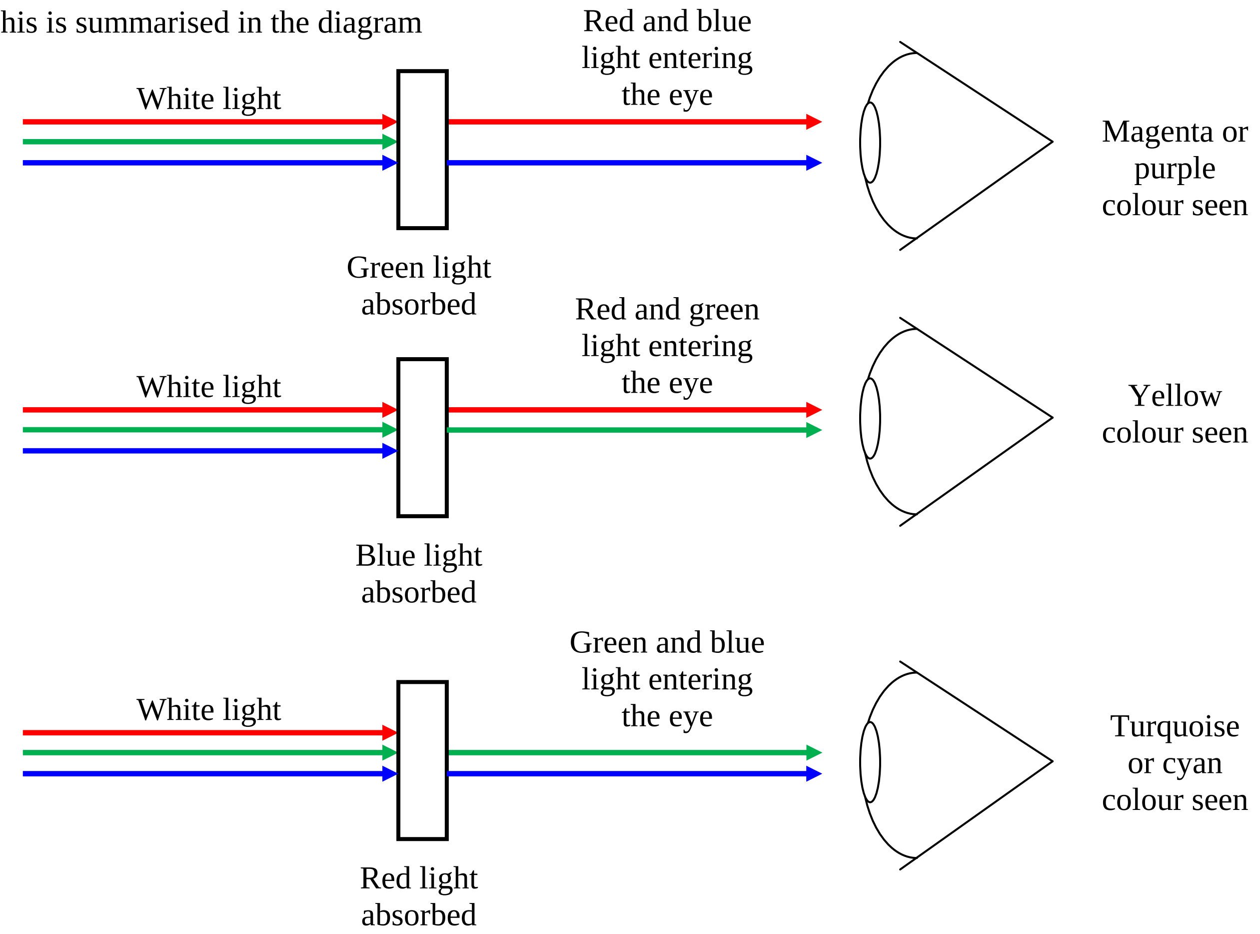
If red light is absorbed, the colours transmitted are blue and green, which is seen as green/blue or cyan.

If blue light is absorbed, the colours transmitted are red and green, which is seen as yellow.

If green light is absorbed, the colours transmitted are red and blue, which is seen as magenta (purple).

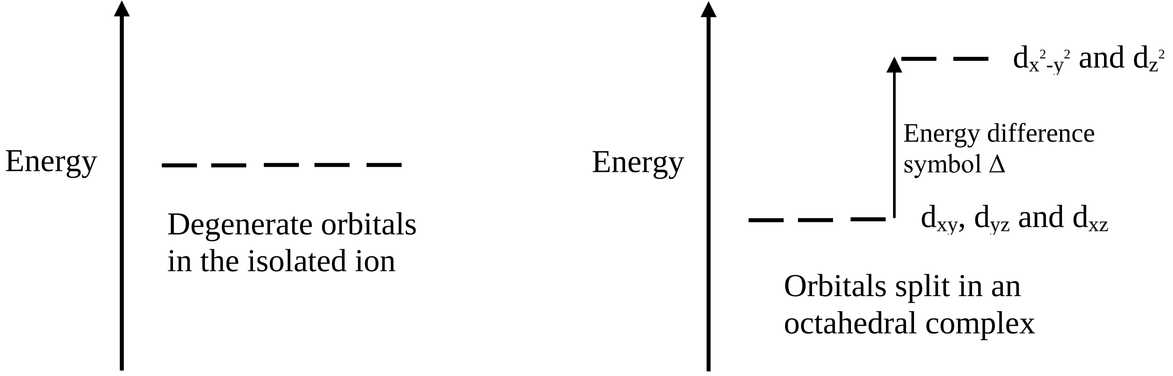
The best example of this is the permanganate ion, which absorbs green light very strongly.

This is summarised in the diagram



The reason that compounds of transition metals absorb white light is the loss of degeneracy of the d orbitals in these compounds.
In the free ion, the five different 5d orbitals (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}) are **degenerate**, i.e. of equal energy. However, in a complex such as $[Ti(H_2O)_6]^{3+}$ the metal ion is no longer isolated but is surrounded by the six water molecules acting as ligands. The complex has an octahedral shape and the water molecules can be considered to approach the central Ti^{3+} ion along the x, y and z axes.

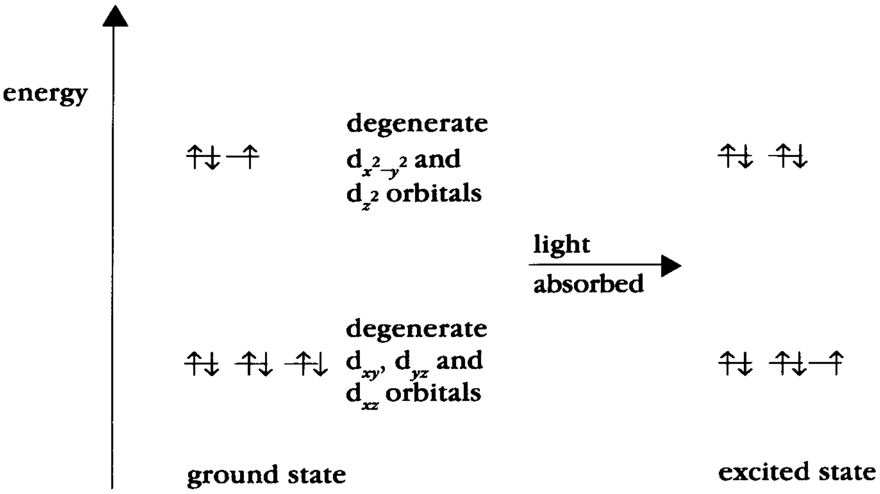
Due to electrostatic repulsion, the orbitals that lie on these axes will be raised to higher energy than those orbitals that lie between the axes.
The d_{xy}, d_{yz} and d_{xz} orbitals lie between the axes.
The $d_{x^2-y^2}$ and d_{z^2} orbitals lie along the axes and electrostatic repulsion causes these orbitals to have higher energy than the other three. This is shown in the diagram:



In many transition metal complexes, Δ has an energy value corresponding to visible light. Its actual value depends on how strongly the ligands are attracted to the central metal ion.

The strongest ligand is the cyanide ion. Some cyano complexes do not have a colour because the value of Δ falls into the ultraviolet region.
The order of bonding attraction of ligands is:
cyanide > water > ammonia > halide ions.

Electrons can be promoted from a low-energy orbital to a higher energy one, absorbing photons of visible light as it does so.
This results in the complex having a colour corresponding to (white light – colour absorbed) i.e. the complementary colour.
The diagram below shows what happens to the d electrons in a copper (II) ion with an electron arrangement of $3d^9$:



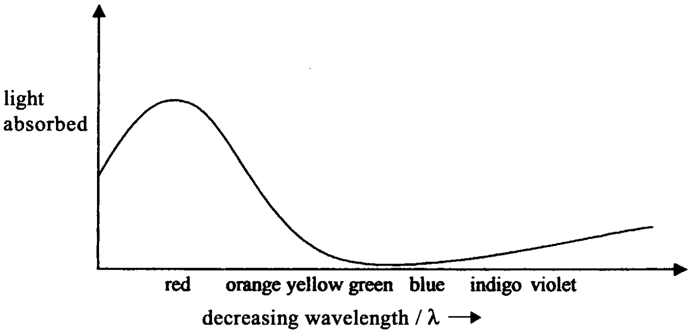
Copper (II) compounds have a blue to blue-green colour. This means that they are absorbing light from the red end of the visible spectrum.
The colour of many transition metal complexes can be explained by this promotion of d electrons. It is known as **d-d transitions**.
There is another method of producing colour called charge-transfer and this explains colour in ions such as permanganate and dichromate which have no unbonded d electrons, but this is not within the scope of Advanced Higher Chemistry.

Ultra-violet and visible absorption spectroscopy

The effects of d-d transitions can be studied using ultra-violet and visible absorption spectroscopy. The absorption of ultra-violet or visible radiation corresponds to outer electrons becoming excited. When an atom, molecule or ion absorbs energy, electrons are promoted from their ground state to an excited state. The energy difference between these states corresponds to the ultra-violet and visible regions of the electromagnetic spectrum. For ultra-violet radiation the wavelength range is approximately 200-400 nm and for visible radiation the wavelength radiation is approximately 400-700 nm. Since ultra-violet radiation has shorter wavelengths it is of higher energy than visible radiation.

The visible absorption spectrum of $[Cu(H_2O)_6)]^{2+}$ is shown below.

Red light is absorbed more than any other colour, so the colour seen is blue-green, or cyan.



The complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ has an absorption peak between red and green. Red and green light are both absorbed and the colour seen is a darker blue.

Catalysis

Transition metals and their compounds act as catalysts in many important industrial chemical reactions, some of which are summarised in the table below.

Process	Catayst used
Haber (ammonia production)	Iron
Contact (sulphur trioxide production)	Vanadiun (V) oxide
Ostwald (ammonia oxidised to NO_2)	Platinum
Catalytic converters in cars	Platinum, palladium and rhodium
Production of methanol	Copper
Hardening of oils to fats	Nickel
Polymerisation of alkenes	Titanium compounds

Catalysts speed up chemical reactions by providing an alternative reaction pathway of lower activation energy.
Transition metals can form a variable number of bonds because of the availability of unoccupied or partially occupied d orbitals.
It is believed that the presence of unpaired electrons or unfilled d orbitals allows intermediate complexes to form, providing reaction pathways of lower energy compared to the uncatalysed reaction.

If you are interested, check out http://en.wikipedia.org/wiki/Ziegler-Natta_catalyst for an explanation on how titanium compounds are used to polymerise alkenes. Ziegler and Natta won the Nobel Prize in Chemistry in 1963 for their discovery of catalysts of this type.
You are not expected to know exactly how Ziegler-Natta catalysts work, but you can see that at one stage of the reacion, the electron-rich double bond is attracted to the positive titanium centre.

Many transition metals act as catalysts because of their ability to exist in a variety of different oxidation states. This also allows the transition metal to provide an alternative reaction pathway with lower activation energy and so speed up the reaction. The transition metal reverts to its original oxidation state once the reaction is complete.
A good example of this is the Rochelle salt experiment from Higher Grade. Pink cobalt (II) chloride turns to green cobalt (III) and when the reaction has finished, the cobalt (III) returns to cobalt (II).