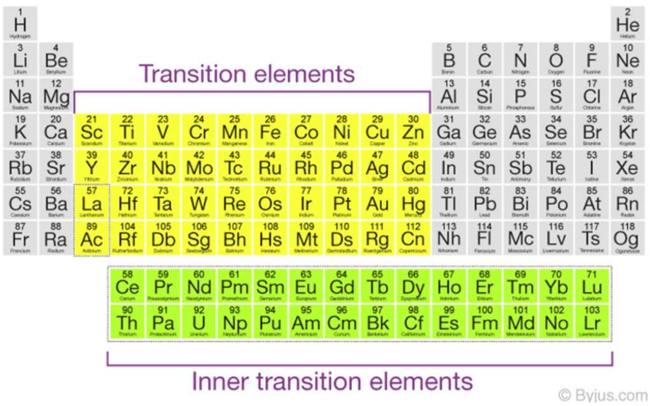
Chapter 6: D-block elements

D-block elements are the elements in which the last electron enters the d subshell. d Block elements are situated at the middle of the periodic table. These elements, also known as transition elements (transition metals) are elements that have partially filled d orbitals.

In general, any element which corresponds to the d-block of the periodic table (which consists of groups 3-12) is considered to be a transition element. Even the f-block elements comprising the lanthanides and the actinides can be considered as transition metals (inner transition elements or inner transition metals).



Why d Block Elements Are Called Transition Elements?

The name "transition elements" these elements act as a bridge, transitioning from the highly reactive s-block elements to the less reactive p-block elements. Their unique ability to exhibit multiple oxidation states and form complex compounds positions them as essential components in various chemical reactions.

Electronic Configuration of Transition Elements

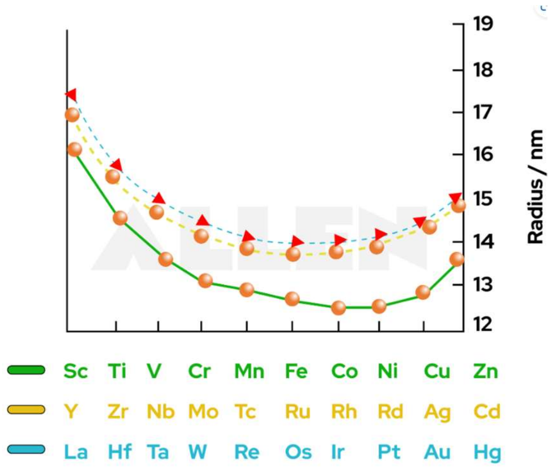
The electronic configurations of the transition elements correspond is $(n-1)d^{1-10}\ ns^{1-2}$. we can be noted that in some of these elements, the configuration of electrons corresponds to $(n\text{-}1)d^5\ ns^1$ or $(n\text{-}1)d^{10}\ ns^1$. This is because of the stability provided by the half-filled or completely filled electron orbitals.

The general electronic configuration for d-block elements in the 3d, 4d, 5d, and 6d series is as follows:

- 3d series: [Ar] $3d^{1\text{-}10}\ 4s^2$
- 4d series: [Kr] $4d^{1\text{-}10}\ 5s^2$
- 5d series: [Xe] $5d^{1\text{-}10}\ 6s^2$
- 6d series: [Rn] $6d^{1\text{-}10}\ 7s_2$
- 7d series: [Og] $7d^{1\text{-}10}\ 8s^2$

Atomic Radii of d Block Elements

The atomic radius typically decreases across a period (from left to right in the periodic table) due to increasing nuclear charge and effective nuclear charge, which attracts the electrons closer to the nucleus. However, the atomic radii generally increase down a group (from top to bottom) because of the addition of new energy levels, leading to larger electron clouds. The ionic radii of transition metals and their ions can be crucial in understanding their chemical behaviour and role in various compounds.



Trends in atomic radii of transition elements

General Properties

All transition elements exhibit similar properties because of the identical electronic configuration of their peripheral shell.

- form stable complexes
- Have high melting and boiling points
- Contain large charge/radius ratio
- Form compounds which are often paramagnetic
- Are hard and possess high densities
- Form compounds with profound catalytic activity
- Show variable oxidation states
- form coloured ions and compounds.

Oxidation State of d Block Elements

D-block elements are renowned for their capacity to display variable oxidation states. For instance, manganese (Mn) can exhibit oxidation states ranging from +2 to +7.

Here is a table illustrating the possible oxidation states for some famous d-block elements:

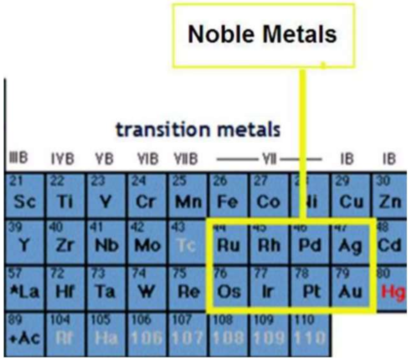
Elements	Oxidation States
Scandium (Sc)	+2, +3
Vanadium (V)	-1, +2, +3, +4, +5
Titanium (Ti)	+2, +3, +4
Chromium (Cr)	-2, -1, +1, +2, +3, +4, +5, +6, +7
Iron (Fe)	-2, -1, +2, +3, +4, +5, +6
Zinc (Zn)	+2
Manganese (Mn)	-3, -2, -1, +1, +2, +3, +4, +5, +6, +7
Gold (Au)	+1, +3
Mercury (Hg)	+1, +2

This variability allows them to engage in a wide range of redox reactions and complex formation.

Which Transition Elements Are Noble Metals?

In the three transition series,

As you move from left to right in the 3d series to the right corner where 5d transition elements are located, various properties change. The density, electronegativity, and electrical and thermal conductivities increase, while the enthalpies of hydration of metal cations decrease. This shift indicates that transition metals become less reactive and more "noble" as you go towards the lower right corner of the d block. Metals like Pt and Au in this region are so unreactive that they're often called "noble metals."



Example of d Block Elements

Scandium (Sc): Scandium is a d-block element appreciated for its lightweight and high strength. It is used in aerospace applications, where its combination of properties makes it an ideal choice for lightweight structural components in aircraft.

Vanadium (V): Vanadium finds use in steel alloys, where its addition enhances strength and corrosion resistance. It's commonly used in manufacturing high-strength steel for applications like tools, springs, and engine components.

Titanium (Ti): Titanium is known for its remarkable strength-to-weight ratio and corrosion resistance. It's extensively used in aerospace and medical implants due to its biocompatibility, as well as in sports equipment, such as bicycles and golf clubs.

Chromium (Cr): Chromium's ability to resist corrosion is a key component in stainless steel production. This type of steel is used in various applications, including kitchen appliances, cutlery, and architectural structures.

Iron (Fe): Iron, one of the most abundant d-block elements, plays a pivotal role in the production of steel used in construction, transportation, and machinery. Additionally, iron is vital in transporting oxygen in the bloodstream as part of haemoglobin.

Zinc (Zn): Zinc is widely used as a protective coating for iron and steel to prevent corrosion. It's used in galvanization processes for structures like bridges, electrical towers, and automotive parts.

Manganese (Mn): Manganese is a critical element in steel production, where it helps remove impurities and improve the strength and durability of steel. It's also used in the production of aluminium alloys.

Gold (Au): Gold is known for its beauty and resistance to corrosion. It is highly prized in jewellery and as a store of value, often used in coins and bullion.

Mercury (Hg): Mercury's unique property of being a liquid at room temperature finds application in barometers, thermometers, and some electrical switches. However, its toxicity has led to a decline in its use in recent years.

Important Compounds of Transition Elements

Some crucial compounds of transition elements include:

- **Potassium Dichromate (K2Cr2O7):** Used in the leather industry and as an oxidizing agent in azo compound preparation. It has a unique structure with a strong oxidizing ability.
- **Potassium Permanganate (KMnO4):** Known for its intense purple color, KMnO4 is used as an oxidant in organic chemistry, bleaching textiles, and decolorizing oils due to its strong oxidizing properties. It exhibits diamagnetic and weak paramagnetic properties based on temperature.

Complex Compounds

D-block elements ability to form complexes and coordination compounds is fundamental to their utility. These compounds are pivotal in catalysis, influencing various industrial processes. They form complex compounds by accepting electron pairs from ligands and forming coordinate bonds with them.

Transition metals can attract electrons and accept lone pairs from other molecules, forming what's called coordinate bonding. They often create complex molecules with various substances like CO, NO^-, NH_3, H_2O, F^-, Cl^-, and CN^-. Examples of such complexes include

$Co(NH_3)_6^{3+}$, $Cu(NH_3)_4^{2+}$, $Fe(CN)_6^{4-}$, FeF_6^{3-}, $Ni(CO)_4$.

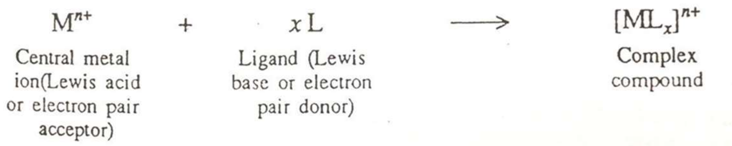
Chapter 7: Complexes

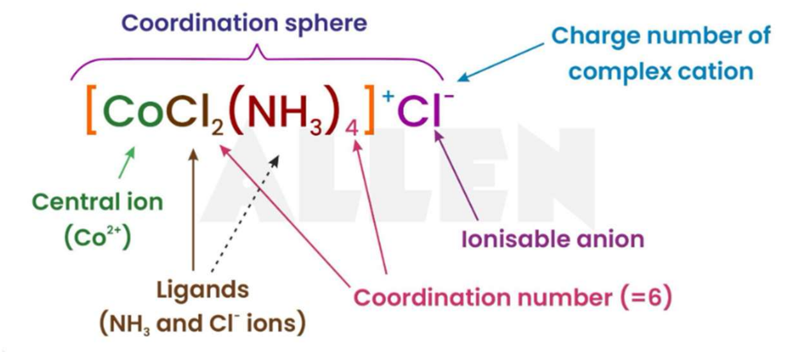
Introduction

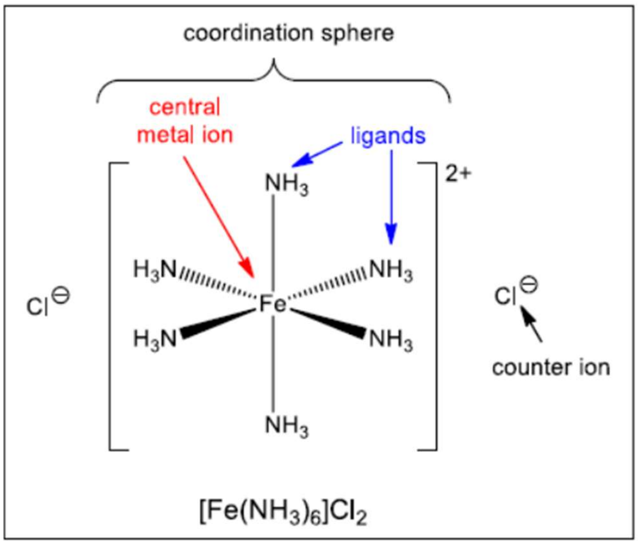
According to the Lewis Acid-Base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. Coordination complexes consist of a ligand and a metal center cation and their charge can be positive, negative, or neutral. Coordination compounds are neutral compounds that contain at least one complex ions. Example of coordination complexes and compounds are:

- Complex Cation: $[Co(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is **monodentate** or **polydentate**.







Central Metal Atom or Ion:

- In coordination chemistry, the central atom or ion is typically a metal (such as transition metals like iron, copper, or platinum), which has empty orbitals that can accept electron pairs.
- The metal atom or ion usually carries a positive charge, and its oxidation state can vary, which influences the overall properties and reactivity of the coordination compound.

Ligands:

The atoms, molecules, or ions that are bound to the coordination centre or the central atom/ion are referred to as ligands. These ligands can either be a simple ion or molecule (such as Cl^- or NH_3) or in the form of relatively large molecules, such as ethane-1,2-diamine (NH_2-CH_2-CH_2-NH_2).

Types of Ligands Based on the nature of the bond between the ligand and the central atom, ligands are classified as follows:

- Anionic ligands: CN^-, Br^-, Cl^-
- Cationic ligands: NO^+
- Neutral ligands: CO, H_2O, NH_3

Coordination Number The coordination number of the central atom in the coordination compound refers to the total number of sigma bonds through which the ligands are bound to the coordination centre.

For example, in the coordination complex given by $[Ni(NH_3)_4]^{2+}$, the coordination number of nickel is 4.

Oxidation Number The oxidation number of the central atom can be calculated by finding the charge associated with it when all the electron pairs that are donated by the ligands are removed from it. For example, the oxidation number of the platinum atom Homoleptic and Heteroleptic Complex in the complex $[PtCl_6]^{2-}$ is +4.

Types of Coordination Complexes

• Cationic complexes: In this co-ordination sphere is a cation.

Example: $[Co(NH_3)_6]Cl_3$

• Anionic complexes: In this co-ordination sphere is Anion.

Example: $K_4[Fe(CN)_6]$

• Neutral Complexes: In this co-ordination sphere is neither cation or anion.

Example: $[Ni(CO)_4]$

• Homoleptic complex: The complex consist of a similar type of ligands.

Example: $K_4[Fe(CN)_6]$

• Heteroleptic complexes: These consists of different types of ligands.

Example: $[Co(NH_3)_5Cl]SO_4$

Properties of Coordination Compounds

The general properties of coordination compounds are discussed in this subsection.

• The coordination compounds formed by the transition elements are coloured due to the presence of unpaired electrons that absorb light in their electronic transitions. For example, the complexes containing Iron(II) can exhibit green and pale green colours, but the coordination compounds containing iron(III) have a brown or yellowish brown colour.

• When the coordination centre is a metal, the corresponding coordination complexes have a magnetic nature due to the presence of unpaired electrons.

• Coordination compounds exhibit a variety of chemical reactivity . They can be a part of inner-sphere electron transfer reactions as well as outer-sphere electron transfers.

• Complex compounds with certain ligands have the ability to aid in the transformation of molecules in a catalytic or a stoichiometric manner.

Naming Coordination Compounds

Anion Name	*Ligand Name*
Bromide, Br^-	Bromo
Carbonate, CO_3^{2-}	Carbonato
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Fluoride, F^-	Fluoro
Hydroxide, OH^-	Hydroxo
Oxalate, $C_2O_4^{2-}$	Oxalato
EDTA	Ethylenediamine tetracetato

Neutral Ligand	*Ligand Name*
Ammonia, NH3	Ammine
Water, H2O	Aqua
Carbon Monoxide, CO	Carbonyl
Ethylenediamine, en	Ethylenediamine

Metal	*Anion Name*
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Manganese	Manganate
Nickel	Nickelate
Platinum	Platinate
Zinc	Zincate

If more than one ligand is attached then,

2 = di
3 = tri
4 = tetra
5 = penta
6 = hexa

The set of rules for naming a coordination compound is:

1. When naming a complex ion, the ligands are named before the metal ion.
2. Write the names of the ligands in the following order: neutral, negative, positive. If there are multiple ligands of the same charge type, they are named in alphabetical order.
3. Multiple occurring monodentate ligands receive a prefix according to the number of occurrences: di-, tri-, tetra-, penta-, or hexa. Polydentate ligands (e.g., ethylenediamine, oxalate) receive bis-, tris-, tetrakis-, etc.
4. Anions end in -ido. This replaces the final "e" when the anion ends with "-ate" (e.g, sulfate becomes sulfato) and replaces "-ide" (cyanide becomes cyanido).
5. Neutral ligands are given their usual name, with some exceptions: NH_3 becomes ammine; H_2O becomes aqua or aquo; CO becomes carbonyl; NO becomes nitrosyl.
6. Write the name of the central atom/ion. If the complex is an anion, the central atom's name will end in -ate, and its Latin name will be used if available (except for mercury).

7. If the central atom's oxidation state needs to be specified (when it is one of several possible, or zero), write it as a Roman numeral (or 0) in parentheses.
8. End with "cation" or "anion" as separate words (if applicable).

Example:

Write a proper chemical name for each of the following coordination compounds:

a. $[NiCl_4]^{2-}$

b. $Pt(NH_3)_2Cl_4$

c. $[Pt(NH_3)_2Cl_2]Cl_2$. ----- $[Pt(NH_3)_2Cl_2]^{2+} + 2Cl^-$.

Solution:

a. Tetrachloronickelate(II) ion.

b. Diamminetetrachloroplatinum(IV).

c. Diamminedichloroplatinum(IV) chloride.