MJC-8 (T) Co-ordination Chemistry
Topic- Magnetic Properties of transition metal complexes

Basic concept of Magnetochemistry

Magnetochemistry studies how substances interact with magnetic fields. For transition metal complexes, this interaction arises primarily from **unpaired electrons** in the metal's d-orbitals.

This leads to two fundamental types of magnetic behaviour:

Paramagnetism: Caused by unpaired electrons. Substances are attracted to a magnetic field. This is a much stronger effect than diamagnetism.

Diamagnetism: Caused by all electrons being paired. Substances are weakly repelled by a magnetic field. This is a universal property of all materials but is only observable when paramagnetism is absent.

The classic way to visualize this is with a **Gouy balance**, where the sample is suspended between the poles of a magnet. The force on the sample indicates its magnetic property.

- **Diamagnetic samples are pushed out of the magnetic field.**
- **Paramagnetic samples are pulled into the magnetic field.**

1. Examples of Diamagnetism

Diamagnetic substances have no unpaired electrons in their electronic structure.

Example 1: Water (H_2O)

- **Why?** All electrons in the H_2O molecule are paired. The oxygen atom has no unpaired electrons, and the bonds (O-H) are covalent with paired electrons.
- **Demonstration:** A small stream of water from a burette will be very slightly repelled (deflected away) by a very strong magnet. This is a famously delicate experiment due to the weakness of diamagnetism.

Example 2: Sodium Chloride (NaCl) - Table Salt

- **Why?** NaCl is an ionic solid. Na^+ has the electron configuration of Neon `[Ne]` (all electrons paired). Cl^- has the electron configuration of Argon `[Ar]` (all electrons paired).
- **Observation:** NaCl crystals show no attraction to a magnet.

Example 3: Benzene (C_6H_6)

- **Why?** All electrons in the carbon-carbon and carbon-hydrogen bonds are paired. The delocalized pi-system in the aromatic ring also consists of paired electrons.
- **Famous Example:** Graphite (a stack of graphene sheets, which are like benzene rings) is actually **strongly diamagnetic**. A small piece of graphite can be levitated over a stack of strong neodymium magnets.

Example 4: Coordination Complex: $[Fe(CN)_6]^{4-}$

- **Metal Ion:** Fe^{2+} (a d^6 ion).
- **Ligand:** CN^- (cyanide), a very **strong-field ligand**.
- **Explanation:** The strong field from the CN^- ligands causes a large splitting of the iron's d-orbitals. This makes it energetically favorable for all 6 d-electrons to pair up in the lower-energy orbitals (**low-spin complex**).
- **Result: No unpaired electrons → Diamagnetic**.

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2. Examples of Paramagnetism

Paramagnetic substances have at least one unpaired electron.

Example 1: Molecular Oxygen (O_2)

- **Why?** This is the most common and surprising example. Despite being a stable molecule, O_2 has **two unpaired electrons** in its molecular orbital configuration. This is fundamental to its chemistry.
- **Demonstration:** Liquid oxygen suspended between the poles of a magnet is strongly attracted to it, creating a beautiful "bridge" of liquid O_2.

Example 2: Sodium Atom (Na)

- **Why?** The electron configuration of a sodium atom is `[Ne] 3s¹`. The single electron in the 3s orbital is unpaired.
- **Observation:** While it's hard to demonstrate with solid sodium metal (due to metallic bonding), atomic sodium vapor is paramagnetic.

Example 3: Manganese(II) Sulfate ($MnSO_4$)

- **Metal Ion:** Mn^{2+} (a d^5 ion).

- **Explanation:** The Mn^{2+} ion has five electrons in its d-orbitals. With weak-field ligands like water or sulfate around it, it is most stable with the electrons unpaired in all five orbitals (**high-spin complex**), following Hund's rule.
- **Result: 5 unpaired electrons → Strongly Paramagnetic**.

Example 4: Coordination Complex: $[Fe(H_2O)_6]^{2+}$

- **Metal Ion:** Fe^{2+} (a d^6 ion).
- **Ligand:** H_2O (water), a **weak-field ligand**.
- **Explanation:** The weak field from the H_2O ligands causes a small splitting of the d-orbitals. It is energetically favorable for the electrons to remain unpaired, leading to a **high-spin configuration** with 4 unpaired electrons.
- **Result: 4 unpaired electrons → Paramagnetic**. (This contrasts directly with the diamagnetic $[Fe(CN)_6]^{4-}$ complex).

Example 5: Gadolinium(III) Ion (Gd^{3+})

- **Why?** Gd^{3+} is an f^7 ion. The f-orbitals are very inner and are not significantly split by the ligand field. The seven electrons therefore remain unpaired to maximize stability.
- **Result: 7 unpaired electrons → Extremely Paramagnetic**. This is why Gadolinium-based compounds are used as contrast agents in MRI scans.