

❖ Magnetic Properties of Free Ions

The resultant magnetic behavior of free ions; whether we talk about transition metals or lanthanides; arises as a result of spin-spin, orbital-orbital and spin-orbital interactions. Now stating more precisely, after considering the effect of spin-spin coupling and orbital-orbital coupling, the further degeneracy removal of the free ion terms is carried out by spin-orbital interaction (L-S coupling) that mainly leads to three different cases depending upon its relative magnitude with thermal energy. The determination of magnetic moment or magnetic susceptibility in these three situations is discussed below.

➤ *Magnitude of L-S Coupling in Ground State is Much Greater Than Thermal Energy*

If the J states after spin-orbital interaction are very far from each other energetically, the thermal energy (kT) would not be adequate to populate all J -levels of ^{2S+1}L state. This, in turn, would result in a Boltzmann distribution in which almost all of the population density is lying in the ground state ($^{2S+1}L_J$). Consequently, the effective magnetic moment will be given by equation (43) as:

$$\mu_{\text{eff}} = g\sqrt{J(J+1)} \text{ B. M.} \quad (43)$$

Where g is the Lande splitting factor or gyromagnetic ratio whose value can be found as follows:

$$g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \quad (44)$$

In case the resultant orbital angular momentum quantum number is zero i.e. $L = 0$, The value of $J = S$ and equation (43) will become:

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \text{ B. M.} \quad (45)$$

Now because the value of the gyromagnetic ratio or Lande splitting factor for free-electron is 2, equation (45) takes the following form.

$$\mu_{\text{eff}} = 2\sqrt{S(S+1)} \text{ B. M.} \quad (46)$$

Owing to the relationship between resultant spin quantum number and number of unpaired electrons ($S = n/2$), equation (46) can also be written in the form given below.

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B. M.} \quad (47)$$

Where S is the resultant spin quantum number and n is the number of unpaired electrons. The equation (45 – 47) is also called as spin only formula as they do not include any contribution from the orbital motion.

This type of magnetic behavior is generally shown by lanthanide ions. A comparison of theoretically calculated magnetic moments of various lanthanide ions with their experimental observed values is presented in the following table.

Table 3. The comparison of theoretically calculated and experimental magnetic moments (B.M.) of trivalent lanthanide ions.

| Metal ion | Electronic configuration | Ground state term symbol | Gyromagnetic ratio | $\mu_{\text{eff}} = g[J(J+1)]^{1/2}$ | μ_{eff} (experimental) |
|------------------|--------------------------|--------------------------------|--------------------|--------------------------------------|-----------------------------------|
| La ³⁺ | f^0 | ¹ S ₀ | – | 0 | 0 |
| Ce ³⁺ | f^1 | ² F _{5/2} | 6/7 | 2.54 | 2.3 – 2.5 |
| Pr ³⁺ | f^2 | ³ H ₄ | 4/5 | 3.58 | 3.4 – 3.6 |
| Nd ³⁺ | f^3 | ⁴ I _{9/2} | 8/11 | 3.62 | 3.5 – 3.6 |
| Pm ³⁺ | f^4 | ⁵ I ₄ | 3/5 | 2.68 | 2.7 – 2.8 |
| Sm ³⁺ | f^5 | ⁶ H _{5/2} | 2/7 | 0.84 | 1.5 – 1.6 |
| Eu ³⁺ | f^6 | ⁷ F ₀ | – | 0 | 3.4 – 3.6 |
| Gd ³⁺ | f^7 | ⁸ S _{7/2} | – | 7.94 | 7.8 – 8.0 |
| Tb ³⁺ | f^8 | ⁷ F ₆ | 3/2 | 9.72 | 9.4 – 9.6 |
| Dy ³⁺ | f^9 | ⁶ H _{15/2} | 4/3 | 10.63 | 10.4 – 10.5 |
| Ho ³⁺ | f^{10} | ⁵ I ₈ | 5/4 | 10.60 | 10.3 – 10.5 |
| Er ³⁺ | f^{11} | ⁴ I _{15/2} | 6/5 | 9.57 | 9.4 – 9.6 |
| Tm ³⁺ | f^{12} | ³ H ₆ | 7/6 | 7.63 | 7.1 – 7.4 |
| Yb ³⁺ | f^{13} | ² F _{7/2} | 8/7 | 4.50 | 4.4 – 4.9 |
| Lu ³⁺ | f^{14} | ¹ S ₀ | – | 0 | 0 |

The results clearly indicate that the experimental values of μ_{eff} for most of the lanthanide ions are pretty much comparable to their theoretical counterparts. However, the magnetic moment for Eu³⁺ and Sm³⁺ calculated using equation (43) are zero, suggesting them as diamagnetic which is quite strange as they are actually having a considerable amount of paramagnetism. This is obviously due to the fact that the energy difference between their ground state term and the first excited state is comparable to thermal energy i.e. $\Delta E \approx kT$. Therefore, even at room temperature, a part of the total population of Sm³⁺ and Eu³⁺ ions would be present in their excited states, which in turn are obviously having a different value of total angular momentum quantum number (J -value) and gyromagnetic ratio (g -value).

➤ **Magnitude of L-S Coupling in Ground State is Comparable to Thermal Energy**

If the separation between J states after spin-orbital interaction is comparable to the thermal energy (kT) available, the resultant value of the magnetic moment is governed by a complex function of temperature. In this scenario, the total magnetic susceptibility will be having contributions from first-order Zeeman effects of involved states according to their Boltzmann weights, as well as from second-order Zeeman effects from neighboring levels. Mathematically, the magnetic susceptibility will be given as follows:

$$\chi_M = \frac{N}{3kT} \sum g^2 \beta^2 J(J+1)(2J+1) e^{-\Delta E/kT} \sum (2J+1) e^{-\Delta E/kT} \quad (48)$$

It can clearly be seen from equation (48) that the magnitude of magnetic susceptibility does not depend directly on the reciprocal of temperature, and thus does not follow Curie-Weiss law. The theoretical calculation for Sm^{3+} ion, according to equation (48), yielded a magnetic moment of 1.38 B.M.; which pretty much comparable to the experimental one. Similarly, satisfactory results are also obtained for trivalent europium ions.

➤ **Magnitude of L-S Coupling in Ground State is Much Less Than Thermal Energy**

If the energy separation between J states (generated after L - S coupling) is much less than the thermal energy (kT) available, all of the J -levels of ^{2S+1}L ground state. This situation is pretty much analogs to the case when spin and orbital motion are completely decoupled from each other. In other words, L - S interaction would not be effective in distinguishing different metal ions on the basis of total motion. Therefore, the effective magnetic moment will be given by the following relation:

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.} \quad (49)$$

Hence, the relationship shown in the equation (49) does not consider any quenching of orbital magnetic moment at all. In this case, the resultant orbital angular momentum quantum number is zero i.e. $L = 0$, the L will be completely eliminated from equation (49) and we will get:

$$\mu_{\text{eff}} = \sqrt{4S(S+1)} \text{ B.M.} \quad (50)$$

Owing to the relationship between spin multiplicity and the number of unpaired electrons ($S = n/2$), equation (50) can also be written in the form given below.

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.} \quad (51)$$

Where S is the spin multiplicity and n is the number of unpaired electrons. The equations (50, 51) are also called as spin only formulas as they do not include any contribution from orbital motion. Now it is worthy to note that no free transition metal exists with very small J -separation relative to thermal energy; however, had they shown such behavior, we would have used the equation (49) to calculate their magnetic moment. In that case, a comparative analysis of the results from equation (49) and equation (51) could be used to estimate the contribution exclusively from the orbital motion.

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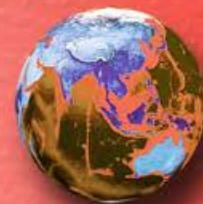
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Table of Contents

| | |
|--|-----------|
| CHAPTER 1 | 11 |
| Stereochemistry and Bonding in Main Group Compounds: | 11 |
| ❖ VSEPR Theory | 11 |
| ❖ $d\pi-p\pi$ Bonds | 23 |
| ❖ Bent Rule and Energetic of Hybridization..... | 28 |
| ❖ Problems | 42 |
| ❖ Bibliography | 43 |
| CHAPTER 2 | 44 |
| Metal-Ligand Equilibria in Solution: | 44 |
| ❖ Stepwise and Overall Formation Constants and Their Interactions | 44 |
| ❖ Trends in Stepwise Constants..... | 46 |
| ❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand..... | 49 |
| ❖ Chelate Effect and Its Thermodynamic Origin..... | 56 |
| ❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry..... | 63 |
| ❖ Problems | 68 |
| ❖ Bibliography | 69 |
| CHAPTER 3 | 70 |
| Reaction Mechanism of Transition Metal Complexes – I: | 70 |
| ❖ Inert and Labile Complexes..... | 70 |
| ❖ Mechanisms for Ligand Replacement Reactions | 77 |
| ❖ Formation of Complexes from Aquo Ions..... | 82 |
| ❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis.... | 86 |
| ❖ Racemization of Tris Chelate Complexes | 89 |
| ❖ Electrophilic Attack on Ligands | 92 |
| ❖ Problems | 94 |
| ❖ Bibliography | 95 |

| | |
|--|------------|
| CHAPTER 4 | 96 |
| Reaction Mechanism of Transition Metal Complexes – II: | 96 |
| ❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes..... | 96 |
| ❖ The Trans Effect..... | 98 |
| ❖ Theories of Trans Effect..... | 103 |
| ❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism..... | 106 |
| ❖ Electron Exchange..... | 117 |
| ❖ Problems..... | 121 |
| ❖ Bibliography..... | 122 |
| CHAPTER 5 | 123 |
| Isopoly and Heteropoly Acids and Salts: | 123 |
| ❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions..... | 123 |
| ❖ Problems..... | 152 |
| ❖ Bibliography..... | 153 |
| CHAPTER 6 | 154 |
| Crystal Structures: | 154 |
| ❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI ₂ , BiI ₃ ; ReO ₃ , Mn ₂ O ₃ , Corundum, Pervoskite, Ilmenite and Calcite..... | 154 |
| ❖ Problems..... | 178 |
| ❖ Bibliography..... | 179 |
| CHAPTER 7 | 180 |
| Metal-Ligand Bonding: | 180 |
| ❖ Limitation of Crystal Field Theory..... | 180 |
| ❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes..... | 184 |
| ❖ π -Bonding and Molecular Orbital Theory..... | 198 |
| ❖ Problems..... | 212 |
| ❖ Bibliography..... | 213 |

| | |
|--|------------|
| CHAPTER 8 | 214 |
| Electronic Spectra of Transition Metal Complexes: | 214 |
| ❖ Spectroscopic Ground States | 214 |
| ❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals..... | 243 |
| ❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States)..... | 248 |
| ❖ Calculation of Dq , B and β Parameters | 280 |
| ❖ Effect of Distortion on the d -Orbital Energy Levels | 300 |
| ❖ Structural Evidence from Electronic Spectrum | 307 |
| ❖ Jahn-Teller Effect | 312 |
| ❖ Spectrochemical and Nephelauxetic Series | 324 |
| ❖ Charge Transfer Spectra | 328 |
| ❖ Electronic Spectra of Molecular Addition Compounds..... | 336 |
| ❖ Problems | 340 |
| ❖ Bibliography | 341 |
| CHAPTER 9 | 342 |
| Magnetic Properties of Transition Metal Complexes: | 342 |
| ❖ Elementary Theory of Magneto-Chemistry | 342 |
| ❖ Guoy's Method for Determination of Magnetic Susceptibility | 351 |
| ❖ Calculation of Magnetic Moments | 354 |
| ❖ Magnetic Properties of Free Ions..... | 359 |
| ❖ Orbital Contribution: Effect of Ligand-Field | 362 |
| ❖ Application of Magneto-Chemistry in Structure Determination | 370 |
| ❖ Magnetic Exchange Coupling and Spin State Cross Over | 375 |
| ❖ Problems | 384 |
| ❖ Bibliography | 385 |
| CHAPTER 10 | 386 |
| Metal Clusters: | 386 |
| ❖ Structure and Bonding in Higher Boranes..... | 386 |
| ❖ Wade's Rules..... | 401 |

| | |
|--|------------|
| ❖ Carboranes..... | 407 |
| ❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters..... | 412 |
| ❖ Total Electron Count (TEC)..... | 417 |
| ❖ Problems..... | 424 |
| ❖ Bibliography..... | 425 |
| CHAPTER 11..... | 426 |
| Metal-II Complexes: | 426 |
| ❖ Metal Carbonyls: Structure and Bonding..... | 426 |
| ❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation..... | 439 |
| ❖ Important Reactions of Metal Carbonyls..... | 446 |
| ❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes..... | 450 |
| ❖ Tertiary Phosphine as Ligand..... | 463 |
| ❖ Problems..... | 469 |
| ❖ Bibliography..... | 470 |
| INDEX..... | 471 |



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