

❖ Magnetic Exchange Coupling and Spin State Cross Over

There are two most remarkable phenomena in the magnetochemistry of transition metal complexes which are pretty much unusual too. The first one is the magnetic exchange interactions, responsible for ferromagnetism and antiferromagnetism; and the other one is the high-spin low-spin equilibria, responsible for the oxygen-carrying capacity of the blood. In this section, we will discuss the fundamental concepts and underlying mechanisms of both the phenomenon.

➤ *Magnetic Exchange Coupling*

The magnetic materials can be broadly classified into two categories; magnetically dilute and magnetically concentrated. Magnetically dilute substances simply refer to the magnetic materials in which individual paramagnetic centers cannot interact with each other due to a large distance of separation. On the other hand, the total-electron-spin of paramagnetic centers do interact through direct-exchange or superexchange interactions in magnetically concentrated substances, which is obviously due to the small inter-micromagnetic separation. In the direct-exchange, there is a coupling between nearest neighboring cations without involving any intermediary anion; while the superexchange is generally a strong magnetic exchange interaction between two nearest neighboring cations through a non-magnetic anion. Now although the orbital contribution to the magnetic moment can be of considerable magnitude, it can be neglected in magnetically concentrated materials for a simplified approach to the rationalization of overall magnetic profile. Therefore, we will consider the spin-only magnetic moment ($\mu_{s.o.}$) as an effective magnetic moment (μ_{eff}) in these cases. The energy of total-spin interactions of paramagnetic centers (ΔE) in magnetically concentrated material can be given by the following relation.

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$$\Delta E = 2J(S)_i(S)_k \quad (63)$$

Where J is the exchange-coupling constant and is a measure of the magnitude of total electron spin interaction between various paramagnetic centers. The symbols $(S)_i$ and $(S)_k$ simply represent the total-electron-spin of i^{th} and k^{th} metal centers, respectively. For ferromagnetic substances, the value of J is positive which simply implies that the total electronic spins of all paramagnetic centers are aligned parallel to each other. For antiferromagnetic substances, the value of J is negative which simply indicates that the total electronic spins of all paramagnetic centers are aligned antiparallel to each other. The important features of both of the behaviors are discussed in detail.

1. Ferromagnetic interactions: The magnetic susceptibility in ferromagnetic materials increases very rapidly with the decrease of temperature if measurements are carried out below a certain value of temperature. Moreover, the magnetic susceptibility in ferromagnetic materials also depends upon the strength of the magnetic field applied. The comparison of variation of magnetic susceptibility with temperature for ferromagnetic and paramagnetic substances is given below.

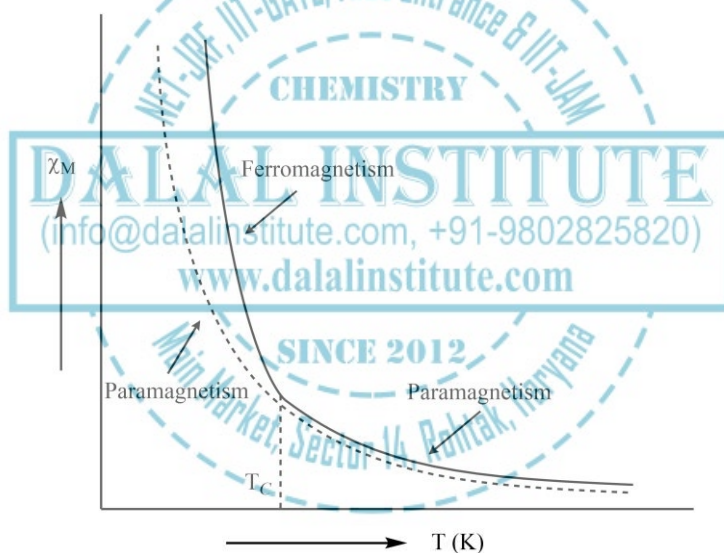


Figure 12. Plots of χ vs T for ferromagnetic and paramagnetic materials.

It can be clearly seen that the magnetic susceptibility of paramagnetic materials follows the Curie law over the complete range of temperature. On the other hand, the ferromagnetic materials obey the Curie law only up to the T_C ; but if the temperature is further lowered down, we see an abrupt gain the magnetic susceptibility. Now although the ferromagnetism generally arises from direct-exchange the superexchange can also result in the same if the paramagnetic centers connected to the diamagnetic bridge are at 90° to each other. Moreover, the ferromagnetism may also arise if the two metal ions are not identical; one having an electron in e_g and the other one in t_{2g} . The corresponding modes of orbital interactions are shown below.

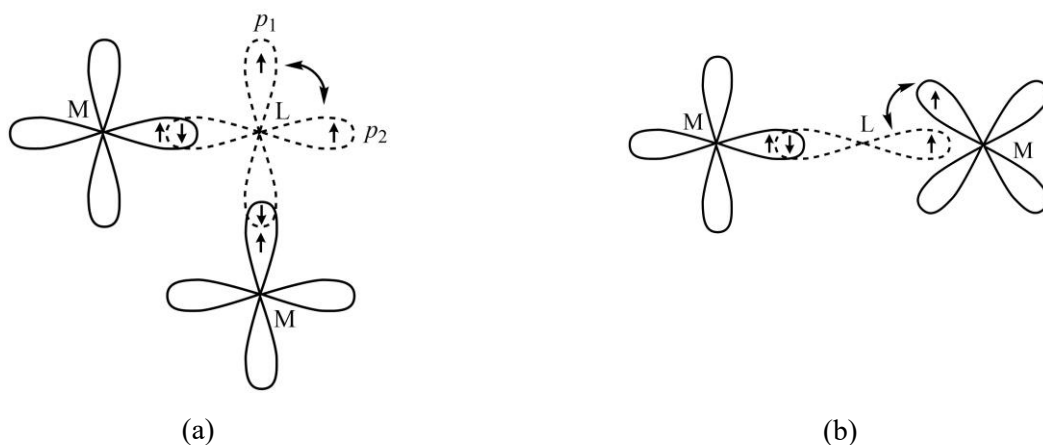


Figure 13. The ferromagnetic coupling via superexchange interactions; when (a) metal centers are at 90° , or (b) non-identical in respect of electronic configuration.

Now it's the time to discuss one of the most interesting properties of ferromagnetic materials, "the hysteresis"; which is actually responsible for the making of permanent magnets. In ferromagnetic substances, total-electron-spins of paramagnetic centers tend to align themselves parallel to each other; however, if the temperature of the system is above the Curie temperature (T_C), the thermal energy (kT) is enough to randomize the individual micro-magnets, and thus forbid them to do so. Consequently, all ferromagnetic substances behave in a paramagnetic fashion above the Curie temperature. However, if the temperature is lowered than T_C , the thermal energy would not be sufficient to decouple the individual total-electron-spins. This, in turn, would result in the creation of small magnetic domains, each of which will be having a parallel alignment of individual paramagnetic centers. Now although the magnetic moments of individual paramagnetic centers in a single "magnetic domain" are parallel to each other, the resultant magnetic moments of these "magnetic domain" are still randomly oriented; which, therefore, would not give any net magnetic moment in the absence of external magnetic field. However, when the external magnetic field is applied, the resultant magnetic moments of all magnetic domains start aligning themselves along the direction of the applied magnetic field.

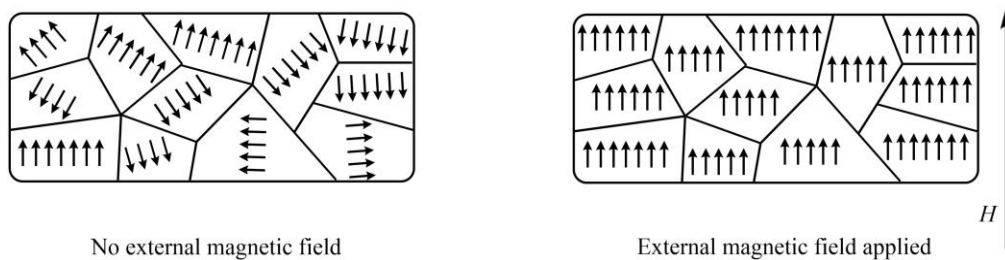


Figure 14. The alignment of magnetic domains in ferromagnetic materials when the external magnetic field is applied.

The magnitude of this domain alignment rises with the increase in the strength of the applied magnetic field, and this will continue to happen till all magnetic domains are aligned. The further increase in the magnetic field strength will not be able to enhance the magnetic susceptibility. Now though the thermal energy is continuously trying to randomize this alignment of “magnetic domains”, it would not always be able to do so completely even if the external magnetic field is turned off.

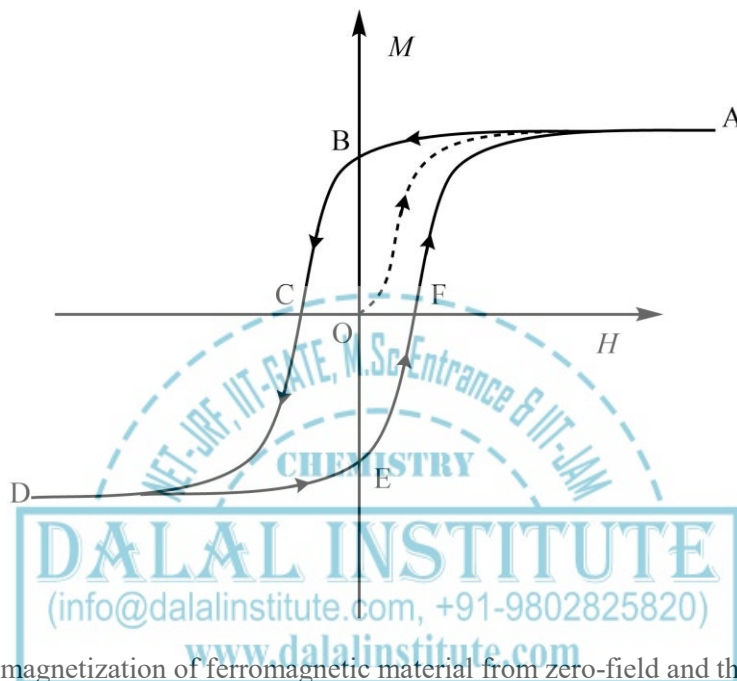


Figure 15. The magnetization of ferromagnetic material from zero-field and the hysteresis loop responsible for the retention of magnetism.

The magnetization of ferromagnetic material is governed by a non-linear curve along OA, attaining a saturation state. However, when the applied field strength decreased back to zero, the demagnetization does not follow AO but the path AB, resulting in a non-zero magnetic moment even if the applied field strength is lowered down to zero. For complete randomization of magnetic domains, the magnetic field should be applied and then increased in the opposite direction; which, consequently, would result in a decrease of magnetization along path BC. The further increase in the magnetic field strength in the opposite direction will actually induce the magnetization of the ferromagnetic material in a reversed manner with again a saturation state, represented by the path CD. Now if the reversed magnetic field is lowered down to zero, the material would again be left with non-zero magnetization (DE). For complete randomization of “magnetic domains” along EF, an increasing applied field strength in the forward direction is needed. Finally, the further increase in the magnetic field will again magnetize the material along FA, completing the hysteresis loop. This retention of “magnetic domain” alignments imparts the permanent magnetism to the ferromagnetic material and called as hysteresis, and has applications in memory-storage devices like computer hard disk drives.

2. Antiferromagnetic interactions: The magnetic susceptibility in antiferromagnetic materials decreases very rapidly with the decrease of temperature if measurements are carried below a certain value of temperature. Moreover, the magnetic susceptibility in antiferromagnetic materials also sometimes depends upon the strength of the magnetic field applied. The comparison of variation of magnetic susceptibility with temperature for antiferromagnetic and paramagnetic substances is given below.

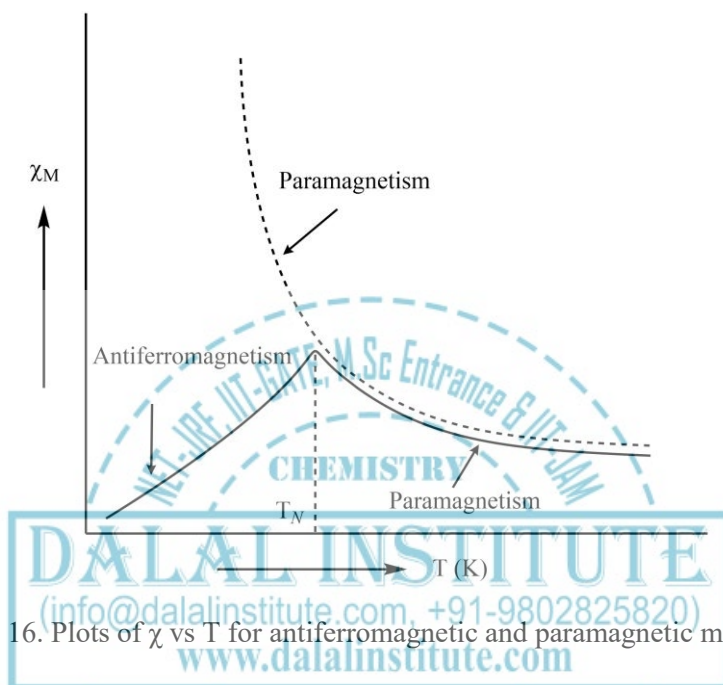


Figure 16. Plots of χ vs T for antiferromagnetic and paramagnetic materials.

It can be clearly seen that the magnetic susceptibility of paramagnetic materials follows the Curie law over the complete range of temperature. On the other hand, the antiferromagnetic materials obey the Curie law only up to the T_N ; but if the temperature is further lowered down, we see an abrupt decline the magnetic susceptibility.

Now if the antiparallel alignment of total-electronic-spins of individual paramagnetic centers wants to occur without any interference of a diamagnetic center, it would be possible only via the formation of normal covalent bond in which half-filled orbitals of the participating paramagnetic centers overlap with each other. Sometimes, the pairing of electrons occurs without the formation of any covalent bond. For instance, recent studies have shown that there is no direct metal–metal bond in $\text{Fe}_2(\text{CO})_9$, and the individual iron centers have one unpaired electron but the pairing results in a net-zero total-electron-spin. However, in most of the cases, the pairing of total-electron spins of paramagnetic centers in antiferromagnetic materials occurs via the mediation of a diamagnetic atom or ion. The second mechanism is so profound that even if the distance of separation between paramagnetic centers is very small, the pairing of total-electron-spin takes place via the diamagnetic bridge. The diamagnetic mediation is usually done by O^{2-} or halide ions. The classic example of this kind of antiferromagnetism is MnO ; in which oxide ions serve in bridging.

Hence, in antiferromagnetic substances, total-electron-spins of paramagnetic centers tend to align themselves antiparallel to each other; however, if the temperature of the system is above the Neel temperature (T_N), the thermal energy (kT) is enough to randomize the individual micro-magnets, and thus forbid them to do so. Consequently, all antiferromagnetic substances behave in a paramagnetic fashion above the Neel temperature. However, if the temperature is lowered than T_N , the thermal energy would not be sufficient to decouple the individual total-electron-spins. This, in turn, would result in the creation of antiferromagnetic lattice, in which total-electron-spins of individual paramagnetic centers are aligned antiparallel to each other. The antiferromagnetic coupling is temperature-dependent and sometimes field-dependent too. Furthermore, the phenomena of antiferromagnetism can also occur within the same molecule, and that what we call intramolecular antiferromagnetism. This kind of antiferromagnetism generally arises through a direct metal-metal bond like $[\text{Cu}_2(\text{OAc})_4] \cdot (\text{H}_2\text{O})_2$ and $\text{K}_4[\text{Cl}_5\text{Ru}-\text{RuCl}_5]$; however, in some compounds like $\text{K}_4[\text{Cl}_5\text{Ru}-\text{O}-\text{RuCl}_5]$, the mediation via diamagnetic center does exist.

The antiparallel alignment of total-electron-spins may also lead to a different type of material “ferrimagnetic”, which have the have the magnetic profile just like ferromagnets. The magnetic susceptibility in ferrimagnetic materials increases rapidly (but at a slightly lower rate than ferromagnetic) with the decrease of temperature if measurements are carried below a certain value of temperature (T_C). Moreover, like ferromagnetic materials, the magnetic susceptibility in ferrimagnetic materials also depends upon the strength of the magnetic field applied. Now though the magnetic behavior of a ferrimagnetic material resembles ferromagnetic materials, the ferrimagnetic materials do have an antiparallel alignment of total-electron-spins like in antiferromagnetic materials. However, these paramagnetic ions are present in two different sets of lattice sites. In other words, the ferrimagnetic materials also have the antiparallel alignment of total-electronic-spins, but unlike antiferromagnetism, they do not cancel each other completely, resulting in a permanent magnetism.

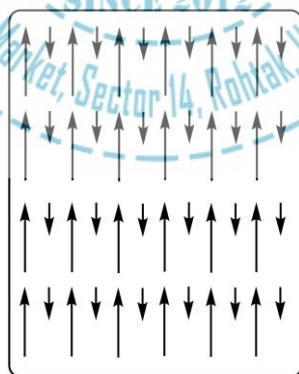


Figure 20. The ordering of total-electron-spins in Ferrimagnetic materials.

Owing to the resemblance in overall magnetic profile ferromagnetism, the oldest known magnetic substance, “loadstone” was originally classified as a ferromagnetic in nature. However, only after Neel's discovery of ferrimagnetism and antiferromagnetism in 1948, we came to know that Fe_3O_4 is actually a ferrimagnet substance.

➤ **Spin State Cross Over**

In transition metal chemistry, most of the compounds for a given stereochemistry are either high-spin or low-spin for a wide range of conditions like temperature, pressure, or the replacement of ligands, etc. However, there are complexes which show a transformation from high-spin to low-spin state with keeping its stereochemistry somewhat more or less the same. Now It is a quite well-known fact that metal complexes from d^4 to d^7 electronic configurations in octahedral crystal fields may result in a high or low-spin system depending on the strength of the surrounding crystal field. Most of the complexes with aforementioned configurations are either high-spin or low-spin over a wide range of temperature, pressure or other conditions like a slight variation in ligand field. However, in some of the complexes, the strength of the ligand field is such that the separation of high-multiplicity term and low-multiplicity terms is very small and quite comparable to the thermal energy available. Now though the high-spin–low-spin crossover can occur, and does occur, in d^4 – d^7 complexes, ninety percent of the reported cases belong to Fe^{2+} (d^6) complexes. This can be better understood from the partial correlation diagram of d^6 octahedral complexes.



Figure 21. The partial correlation diagram of d^6 octahedral complexes showing the transformation of the ground state from ${}^5T_{2g}$ to ${}^1A_{1g}$ as the ligand-field increases.

It can be clearly seen that the energy gap between high-spin and low-spin states near the crossover point is quite small and comparable to the thermal energy; therefore, the temperature does have a great effect on the position of the high-spin–low-spin equilibria.

The study of these spin-crossover phenomena is pretty easy to do as the number of unpaired electron in the two states are different. For instance, the d^6 complexes of Fe^{2+} are diamagnetic in the low-spin state while having four unpaired electrons in the high-spin state. Thus, a variation in the magnitude of the magnetic moment is expected as we after spin crossover. Consider the example of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$; in which the high-spin state transforms into to low-spin with the decrease of temperature. Both of these complexes exist in the high-spin $^5\text{T}_{2g}$ ground state with effective magnetic moments slightly greater than the spin-only value for four unpaired electrons. However, the moment of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ at 174 K suddenly drops to below 1 B.M. Similarly, the same thing does happen in $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ but at 232 K. As the temperature is lowered than these specific temperatures, the complexes start to exist in the $^1\text{A}_{1g}$ ground state.

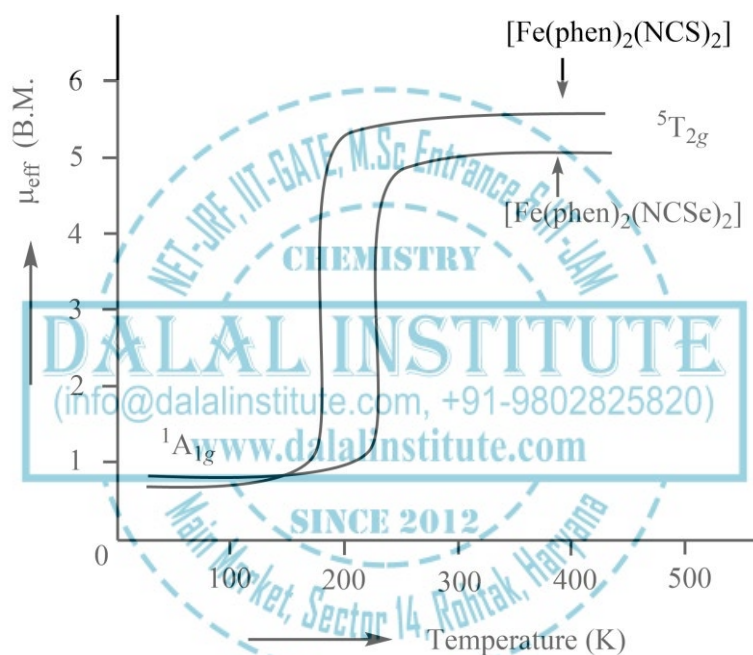


Figure 21. The partial correlation diagram of d^6 octahedral complexes.

Other examples of this include Fe^{3+} surrounded by six sulfur ligands in $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$ complex. The preference of low-spin state at lower temperatures and higher pressure can be explained in terms of the volume factor. High-spin octahedral complexes have larger volumes due to the presence of electron in e_g orbitals; while low-spin octahedral complexes have electron density concentrated in t_{2g} orbitals. Now because of the lowering of temperature and increment of pressure support the lower volume, the low-spin state is also favored at the lower value of temperature. In hemoglobin, the replacement of water molecule by dioxygen also induces a spin-crossover, which in turn results in the phenomenon of cooperativity, which is essential for our life.

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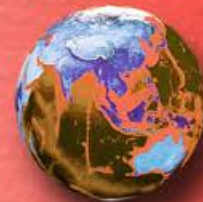
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Table of Contents

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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