THEORETICAL PRINCIPLES OF INORGANIC CHEMISTRY

G S MANKU

Theoretical Principles of
Inorganic Chemistry

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Preface

There has been a phenomenal growth in the field of chemistry during the past 20 years or so. Inorganic chemistry has experienced a renaissance during this period; and of late, the limits of inorganic chemistry extend into physical chemistry on the one hand, and into theoretical chemistry and biochemistry on the other. There is so much percolation of physical chemistry into inorganic chemistry, that it would be better to classify both the branches as general chemistry. As a reflection of this, many new textbooks have appeared in the recent past, each reflecting a distinctive emphasis, style and depth of presentation of the subject matter.

This book is intended to be a textbook for advanced undergraduate level students of general inorganic chemistry. Such a course should expose the readers to the challenges of the subject and unify many of the underlying principles and observed facts. Textbooks should be flexible and adaptable; I have tried to make the subject easy for both students and teachers.

A university level text cannot be encyclopaedic. The discussion presented is mainly topical, and not exhaustive. The book is not intended to be a reference book. Though I have tried to cover as many topics as possible, my views, prejudices and enthusiasms have coloured the presentation. Not all my readers will find the topics presented here treated adequately; many omissions will be observed. I will be thankful to my readers for pointing out any errors and omissions in the text and giving their suggestions.

Each chapter begins in an elementary fashion. The subject matter is developed progressively as the chapter advances. Wherever possible, I have tried to give quantitative relationships. Figures and tables are used liberally as a scientist creates mental pictures or models to organize a large body of scattered observations which form the basis for the prediction of behaviour of similar systems. Each chapter has a number of solved problems which not only show the method of calculations, but also make one realize the sense of proportionality or reality. Though no formal references are given, a list of books has been suggested at the end of the text. Each chapter ends with a set of questions dealing with the topics presented.

The atomic structure and the electronic configurations of the elements form the subject matter of Chapters 1 and 2. Chapter 1 discusses the behaviour of electrons as particles; while wave mechanics or the quantum theory is presented in Chapter 2. The periodic table (which has occupied such a hallowed position in the development of chemistry) and periodic properties like the atomic sizes, atomic volumes, ionization energies, electron affinities and electronegativities, are discussed in the third chapter.

Chapter 4 discusses the important theories of covalence: the valence bond theory (VBT), the valence shell electron pair repulsion theory (VSEPRT), the molecular orbital theory (MOT) and Linnett's NPSO theory (also called the double quartet or DQ theory). Ionic bonds are discussed in Chapter 5, while the hydrogen bonds, metallic bonds and the van der Waals forces are discussed in Chapter 6.

Chapters 7 to 10 are independent of one another, and of the other chapters present in the book. Nevertheless, they are important in their own right. The views regarding the acid-base behaviour of substances is discussed in Chapter 7, while the problem of whether the given reaction involving oxidation and reduction (the redox reaction) will proceed or not is given in Chapter 8. The electrode potentials have been used for the prediction of a large amount of reactions. Chapter 9 describes the most commonly used nonaqueous solvents—the protonic, nonprotic and the organic solvents. The general chemical principles involved in the preparation of a pure element or a compound including concentration, roasting, hydrolytic metallurgy, reduction and purification of the metal, form Chapter 10 of the book.

The fast expanding field of the coordination compounds is considered in Chapters 11, 12 and 13. Werner's nomenclature and stereochemistry are part of Chapter 11. VBT theory involving hybridization of orbitals, the MOT for the metal complexes and the nature of bonding in the transition metal complexes with pi-bonding ligands, are discussed in Chapter 12. The spectral, thermodynamical, kinetic and magnetic properties of the complexes are discussed in Chapter 13.

Throughout the text, I have used the SI units. At many places, corresponding values in the conventional cgs units are also given. Wherever values in both the units are given, it is implied that wherever order of the values is sufficient, only the order is calculated; otherwise the exact equivalent is given. The unit of weight and length in SI units being kg and m, density would be expressed in terms of kg m^{-3} which would mean multiplying the accepted density values by 1000; whereas the wave numbers should be in m^{-1} necessitating multiplication of the values in cm^{-1} by 100.

I have used the SI units strictly giving equivalence in parentheses at the proper places. Appendix A gives the rules of nomenclature of inorganic compounds, while the SI units and useful constants and conversion factors are given in Appendix B. The bond energies are given in Appendix C, while the colours of the solutions and the broad relationship of colour to the wavelength of absorption is given in Appendix D.

There is a cliche in the sciences that everyone feels that he knows "everything" in his field for about 15 minutes after submitting his Ph.D. thesis. And then, as time passes he begins to realize the limitations and the inadequacy of his knowledge. One realizes this the moment one sits down to write a book. About 99 per cent of the material to be presented in a book (or in a classroom when faced with a group of eager students willing to learn) comes from stimulating associates, directly or indirectly. I am grateful to my students and to my colleagues for their help and suggestions without which this book would never have come to be written. I am particularly thankful to Dr R.C. Rastogi, Dr. B.R. Thukral, Dr. P.S. Jaiswal and Dr. P.S. Sindhu for the discussions and suggestions, and to Mr. V.B. Agarwal for his advice and constant encouragement. I am particularly grateful to Dr. D.B. Gupta, Reader, Institute of Economic Growth, Delhi, for his interest and advice.

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Symbols and Abbreviations

A	abundance
A	atomic weight
A	energy state A_{1g} etc.
A	Madelung's constant
a	acceleration
a_{1g}	symmetry of orbitals
a_0	Bohr's radius
a_X	activity of species X
ACFT	adjusted crystal field theory
AO	atomic orbital
AV	atomic volume
B	magnetic field strength
B	Racah parameter
b_{1g}	symmetry of orbitals
BP	bonded pair of electrons
C	Coulomb
C	Curie's constant (Eq. 13.65)
C	Racah parameter
c	velocity of light in vacuum
c_X	concentration of the species X
CD	circular dichroism
CFT	crystal field theory for coordinate bond
CB	conduction bands in metals
cis	geometrical isomers
cp	*cyclo*pentadienyl ligand ($C_5H_5^-$)
D	bond dissociation energy
D	distribution ratio of metal in two solvents
D	energy states with $L=2$
D	absolute configuration of complexes
D_{np}	nonpolar contribution to the bond energy
D_p	polar contribution to the bond energy
d	complete differentiation of a variable e.g., dx/dt
d	d orbital which may be further specified as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, and d_{z^2}
Dd	dodecahedron

DQ	double quartet (Linnett's theory)
Dq	unit of the crystal field splitting in octahedral field (=10Dq)
diphos	ethylenediphosphine ligand $H_2P.CH_2.CH_2.PH_2$
E	electric field strength
E	energy
E	per cent metal extracted in solvent extraction systems
e	charge of the electron
E^0	standard electrode potential
$E_A{}^0$	standard electrode potential in acid solutions (1 M acids)
$E_B{}^0$	standard electrode potential in base solutions (1 M base)
E_{cell}	cell potentials$=E^0{}_R-E^0{}_L$
E_D	Debye energy of dipole–induced dipole interactions
Es	energy states
E_K	Keesam energy of dipole–dipole interactions
E_L	London dispersion forces
$E_L{}^0$	standard electrode potential of the left hand half-cell in a cell
$E_N{}^0$	standard electrode potential in neutral solutions (pH=7)
$E_R{}^0$	standard electrode potential of the right hand half-cell in a cell
E_{rep}	repulsion energies in a system
$E\lambda$	the monochromatic emmissive power for the radiation having wavelength λ
e_g	symmetry of the orbitals
e_j	liquid junction potentials in a cell
emf	electromotive force of a cell
en	ethylenediamine ligand ($NH_2CH_2CH_2NH_2$)
eV	electron-volt
EA	electron affinity
EAN	effective atomic number
EDTA	ethylenediaminetetraacetate anion $(^-O_2CCH_2)_2N.CH_2.CH_2.N(CH_2CO_2^-)$
ESR	electron spin resonance
exp	exponential
F	Faraday
F	force, which may be further specified as F_{elec}, F_{mag}, etc.
F	state, energy level
F	formal (1 F=activity of 1 molar)
f	f orbital
f	Jørgenson's field factor for the ligands
F_n	Slater's integrals for the energy states in atoms and ions
FB	forbidden energy bands in metals
fac	isomers in octahedral complexes $[MA_3B_3]$
G	free energy
G	the energy state
g	acceleration due to gravity
g	even state (from *gerade* state)

g	Jφrgenson's field factor for the metals
g	Lande's splitting factor (=2.0023)
H	energy state
H	magnetic field strength
h	Planck's constant
ΔH	enthalpy of the reaction, further classified as ΔH_f (formation), ΔH_s (sublimation), ΔH_r (reaction), ΔH_{solv} (solvation), etc.
I	intensity of light
I	ionization energy
IE	ionization energy
IP	ionization potential
IR	infrared region of spectrum (wavelength greater than 10^{-6} μm)
i	$(-1)^{\frac{1}{2}}$
J	exchange energy integrals
J	Joule
J	total angular momentum quantum number
K	Kelvin
K	K shell, the first shell of electrons
k	Boltzman's constant$=$R$/N$
k	Sommerffeld's quantum number for the elliptical orbits
k	zone refining separation factor (ideal)
k'	zone refining actual separation factor (less than k)
K_a	acid dissociation constant
K_b	base dissociation constant
K_{eq}	equilibrium constant for a reaction
K_{SP}	solubility product for sparingly soluble compounds
K_{ext}	extraction constant for the solvent extraction systems
K_w	ionic product for water$=1.02\times10^{-14}$ at 298 K
K_α	characteristic x-rays
K_β	characteristic x-rays
k_{M}	nephelauxetic factor for the metals
L	ligand
L	shell, second from the nucleus
L	total value of the l values of the electrons in an atom
L	L configuration (absolute) for the metal complexes
l	quantum number, the azimuthal number for orbital
L_α	characteristic x-rays
L_β	characteristic x-rays
LP	lone pair of electrons
ln	log to the base e, the natural or Naperian logarithm
lel	absolute configuration of chelate rings in complexes
LGO	ligand group orbitals (in MOT of complexes)
M	minus rotation of the octahedral complexes
$\dot{M}$	molecular weight
m	mass of the electron or of any other particle of interest

m	metre
m	molality
M_L	total angular momentum of electrons in atom
M_S	total spin momentum in an atom
M_e-	methyl group CH_3
m_0	rest mass (of the electron)
m_l	magnetic quantum number
m_s	spin quantum number
MO	molecular orbitals
MOT	molecular orbital theory
mer	geometrical isomer of octahedral $[MA_3B_3]$
N	Avogadro's number
N	Normalizing factor for the wave function
n	an integer
n	Bohr's orbit number
n	Born exponent for the ions
n	quantum number, the principal number
n	refractive index$=c/c_0$, ratio of velocity of light in medium to vacuum
n	Slater's orbital number
N_a	normalizing factor for the antibonding MO
N_b	normalizing factor for the bonding MO
Oh	octahedral
ORD	optical rotatory dispersion
ob	conformation of the tris chelate rings
P	energy state with $L=1$
P	pairing energy
P	per cent ionic character of a covalent bond
P	positive rotation of octahedral complex
P	pressure (in equation of state)
p	$-\log$, *e.g.* pH, pK
p	momentum of the particle$=mv$ or mu
p	p orbital
P_{HA}	partition coefficient for HA
P_{MLc}	partition coefficient for the species ML_c
P_m	molar polarization
P_{H_2}	partial pressure of H_2; similarly p_{O_2} for oxygen
PA	proton affinity
pn	propylenediamine ligand $CH_3 \cdot CH(NH_2) \cdot CH_2NH_2$
Q	concentration quotient for a reaction
q	interionic distance for the ion pair association [(9.15)]
q	ionic charge
R	gas constant$=8.314\ 41_2$ J mol^{-1} K^{-1}
R	molar refraction of the compound
R	radial distribution function for the electrons
r	polar coordinate

r	radius of the species
R_{F}	characteristic of a solute in a solvent in chromatography
R_{H}	Rydberg's constant$=1\ 096\ 773_1 \times 10^7$ m^{-1} for hydrogen
R_{He}	Rydberg's constant for helium
RP	resonance potential
r_{a}	radius of anion
r_{c}	radius of the cation. crystal radius
r_{EL}	radius of the ion from electron density maps
r_{i}	ionic radius
r_{p}	Pauling's radius
r_1	Pauling's univalent radius
R^*	(complex) conjugate of the radial distribution function R
S	overlap integral
S	total spin of the electrons in an atom
S	energy state with$=0$
s	spin quantum number
ΔS	entropy change
S^0	entropy under standard state
S_N1	nucleophilic substitution, first order reaction
$\mathrm{S}_N1\mathrm{CB}$	nucleophilic substitution, first order reaction. conjugate base mechanism
$\mathrm{S}_N{}^2$	nucleophilic substitution, second order reaction rate
s_{Q}	strength of the soft-soft interactions (Eq. 7.65)
SAP	square antiprism
SP	square pyramidal
SR	Sanderson's stability ratio
T	kinetic energy (used in wave mechanics)
T	temperature
t	time interval
t_{1g}, t_{2g}	symmetry of the orbitals
T_{1g}	energy state
TBP	trigonal bipyramid
Td	tetrahedral
trans	geometrical isomers of complexes
u	ungerade or uneven state
u	velocity
U_0	lattice energy at 0 K
U_{c}	lattice energy at any other temperature usually at room temperature (298 K)
V	potential difference, volts
V	volume
v	velocity
V_{sp}	specific volume
VB	valence bands in metals
VBT	valence bond theory

X	electric field strength
X	electronegativity, *e.g.*, X_p (Pauling's), X_m (Mullikan's) etc.
x	cartesian coordinate
Y	total angular distribution function
y	cartesian coordinate
Z	nuclear charge or the atomic number
Z^*	effective nuclear charge
z	cartesian coordinate
$z_\pm$	ionic charge
α	polarizability of the ion
α	the degree of ionization or dissociation
α_λ^M	molar rotation of the optically active compound at wavelength λ
$[\alpha]\lambda$	specific rotation of the optically active compounds at wavelength λ
β_n	stability constant of the complex ML_n
γ	activity coefficient
Δ	change in a quantity
Δ	conformation of the octahedral complex
Δ_0	octahedral field strength $=$ 10 Dq
Δ_t	tetrahedral field strength
δ	partial charge
δ	right handed helix
∂	partial differentiation of a variable
∇	Laplacian operator
ϵ	molar extinction constant
ϵ_0	permittivity of vacuum
ϵ	permittivity of medium
ϵ_r	relative permittivity of medium $=\epsilon/\epsilon_0$
ϵ	Planck's photon energy $=h\nu$
ϕ	angle of deflection
ϕ	molecular rotation of optically active compounds
ϕ	polar coordinate
Φ	angular distribution function of the wave function for electron
Φ^*	complex conjugate of Φ
η	viscosity
Λ	conformation of the octahedral complex
λ	left handed helix
λ	wave length of the radiation
λ_C	Compton's wavelength $=2.426\ 308_9\times10^{-12}$ m
μ	bridging group in complexes
μ	dipole moment
μ	reduced mass $=mM/m+M$
μ	permeability of medium
μ_0	permeability of vacuum $=4\pi\times10^{-7}$ H m^{-1}
μ_B	Bohr magneton
μ_J	magnetic moment due to the spin-orbit coupling

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μ_L	magnetic moment due to total angular momentum of the electrons
μ_S	magnetic moment due to the total spin of the electrons
μ_{eff}	effective magnetic moment due to the presence of the electrons in an ion or a complex
μ_m	dipole moment of an ion
μ_s	magnetic moment due to spin of the electron
ν	frequency of radiation
$\bar{\nu}$	wave number of the radiation
$\nu_{\pm}$	number of ions produced by the ionization of one molecule
ν_0	frequency associated with the zero point energy
π	ratio of the circumference to the diameter of a circle
π	the pi-bonding orbital
π^*	the antibonding pi-orbital
χ_A	diamagnetic susceptibility
χ_m	magnetic susceptibility
ρ	density
σ	screening constant
σ	the sigma bond
σ	sigma bonding orbital
σ^*	sigma antibonding orbital
σ	Hammett's function
σ_A	softness factor (Eq. 7.65)
ψ	angle
ψ	amplitude of vibration for the wave in wave equation
ψ^*	complex conjugate of ψ
ψ_a	antibonding wave function
ψ_b	bonding wave function
ψ_n	nonbonding wave function
Σ	wave function for the LGO in coordinate complexes (MOT)
τ	the volume element $d\tau = dx\,dy\,dz$
θ	angle of deflection
θ	polar coordinate
Θ	angular part of the wave function
Θ^*	complex conjugate of Θ
ξ	spin-orbit coupling constant

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