

Contents

Abbreviations	xi
1. Introduction	1
2. Chemical Bonds	11
2.1 Atomic Orbitals	11
2.2 Theoretical Treatments of Chemical Bonding	19
Simple Electrostatic Theory	19
Valence Bond Theory	25
Molecular Orbital Theory	28
Ligand-Field Theory	30
3. Stereochemistry and Stability of Metal Complexes	34
3.1 Examples of Ligand-Field Effects	36
Copper(II)	36
Nickel(II) and Platinum(II)	37
Cobalt(II)	37
Iron(II) and Cobalt(III)	38
Iron(III) and Manganese(II)	38
Chromium(II) and Manganese(III)	38
Copper(I)	39
3.2 Polarizability and Covalent Character	39
3.3 Steric Effects	42
3.4 Stability Constants of Metal Complexes	44
3.5 Thermodynamics of Complex Formation	49
3.6 The Chelate Effect	53
4. Effects of Complex Formation on Oxidation-Reduction Potentials.	56
4.1 Factors Determining Magnitudes of Potentials	56
4.2 Some Analytical Applications	58

4.3	Ligand-Field Stabilization Energies	59
4.4	Potentials of Some Transition Metal Cyanide Complexes	64
4.5	Potentials of Some Copper Complexes	66
4.6	Potentials of Iron Complexes	68
4.7	Some General Observations	69
5.	Factors Governing the Rates of Formation and Dissociation of Complexes, and Also Their Rates of Oxidation and Reduction	74
5.1	Reaction Mechanisms	74
5.2	"Inert" Complexes	75
5.3	Oxidation and Reduction of Metal Complexes	81
5.4	Slow Reactions and Catalysts	83
6.	Effects of Complex-Forming Species on Cation Concentrations	88
6.1	Some Quantitative Aspects	89
6.2	"Apparent" Constants	93
6.3	Some Examples Based on Differences in Stability Constants or Solubilities	94
6.4	Effects of Hydrolysis	96
6.5	Complexometric Titrations	99
6.6	Indicators for Complexometric Titrations	103
6.7	Other Reagents Used in Complexometric Titrations	114
6.8	"Masking" of Chemical Reactions	117
6.9	"Demasking"	125
7.	Surface Phenomena	130
7.1	Adsorption Indicators	131
7.2	Ion Exchange	135
7.3	Chromatography of Inorganic Substances	138
7.4	Polarography of Metal Complexes	140
8.	Visible and Ultraviolet Absorption Spectra of Metal Complexes	143
8.1	The Process of Light Absorption	143
8.2	Fluorescence	145
8.3	Types of Ultraviolet and Visible Spectra of Complexes	147
	d-d Transitions	147
	Excitations within Ligands	149
	Charge-Transfer	152
8.4	On Designing Ligands to give Colored Metal Complexes	155
8.5	Chemiluminescent Indicators	162
9.	Solubility of Complexes	165
9.1	Factors Governing Solubility in Water	165
9.2	Effect of pH on the Solubility of Metal Complexes and Salts	168

9.3	Applications to Alkali Metal Salts and Complexes .	171
9.4	Alkaline Earth Metal Species .	172
9.5	Complexes Bonding through Sulfur Anions .	173
9.6	p-Dimethylaminobenzylidene-rhodanine .	175
9.7	Precipitation of Anionic Complexes with Large Cations	176
9.8	Hydrophobic Character and Charge Neutralization in Inner Complexes. Representative Examples .	177
	Cupferron .	178
	Salicylaldoxime .	179
	β-Benzoinoxime .	182
	Arsonic Acids .	182
	8-Hydroxyquinoline .	184
	Dioximes .	186
	Nitrosophthols .	188
	Chloranilic Acid .	189
	Some Recently Introduced Precipitants .	190
9.9	Solubility in Organic Solvents .	193
9.10	Collectors .	193
9.11	Micelle Formation .	194
9.12	Factors Governing the Selection of a Precipitant for Inorganic Cations .	195
10.	Extraction into Organic Solvents	201
10.1	Types of Systems .	201
10.2	General Discussion .	203
10.3	Metal Halides and Their Complex Acids .	204
10.4	Thiocyanate Complexes .	206
10.5	Inorganic Nitrates .	207
10.6	Quantitative Aspects of Extraction Equilibria .	208
10.7	Metal Complexes with Organic Ligands .	211
	Complexes with Dioximes .	213
	Complexes with Acetylacetone and Thenoyltrifluoro- acetone .	214
	Complexes with Cupferron .	215
	Complexes with Nitrosophenols and Derivatives .	216
	Complexes Bonding through Sulfur Atoms .	218
	Complexes Bonding through Sulfur and Nitrogen .	221
	Complexes with 8-Hydroxyquinoline and Its Deriva- tives .	223
	Newer Complexes Bonding through Nitrogen and Oxygen .	224
10.8	Extraction through Ion-Pair Formation .	225

10.9	Extraction with Organic Phosphorus Compounds	228
11.	Reactions of Organic Reagents with Inorganic Anions	236
11.1	Indirect Methods for Detecting and Determining Anions	237
	Colorimetric Methods Based on Differences in Stability Constants of Complexes	237
	Methods Depending on Precipitation or Differences in Solubility of Complexes and Salts of Inorganic Cations	238
	<i>A. Colorimetric</i>	238
	<i>B. Titrimetric</i>	239
11.2	Methods Based on Precipitation with Organic Cations, Including Extraction into Organic Solvents	240
11.3	Methods Depending on Oxidation or Reduction	242
11.4	Diazotization Reactions	246
11.5	Nitration Reactions	247
11.6	Heterocyclic Syntheses	247
11.7	Complex Formation with Organic Ligands	248
11.8	Other Indirect Reactions	251
12.	Procedures for Detecting and Determining Inorganic Neutral Molecules	257
12.1	Direct Spectrophotometry	258
12.2	Oxidation Reactions	259
12.3	Substitution Reactions	263
12.4	Indirect Reactions	264
13.	Analytical Properties of the Elements	268
14.	On Seeking New Organic Reagents for Use in Inorganic Analysis	324
14.1	Organic Reagents for Metal Ions	324
	Bonding Groups in Reagents	324
	The Nature of the Metal Ion	326
14.2	Metal Complexes as Reagents	328
14.3	Some Promising Fields for Research in Analytical Methods	329
Index		337