

Contents

Part I General Considerations

1	Solvents—Composition of Solutions	3
1.1	Definitions	3
1.2	Molecular Solvents	3
1.3	Solvation of Solutes in a Molecular Solvent	4
1.4	Water as Solvent	5
1.4.1	Ability to Give H Bonds	5
1.4.2	High Value of Its Dipolar Moment	5
1.4.3	Dissociating Power of Water	7
1.5	Definition of the Solution Composition	7
1.6	Quantity of a Substance	7
1.7	Different Expressions of the Composition	8
1.7.1	Composition Expressed in Quantity of a Substance: The Molar Composition	8
1.7.2	Molality	8
1.7.3	Molar Fraction	9
1.8	Calculation of the Molality and the Molarity of a Solution from Its Molar Fraction	9
2	Thermodynamics and Equilibrium	13
2.1	Chemical Potential	13
2.2	Gibbs Free Energy Change ΔG_{sys} and Useful Work Available from the Process	16
2.3	Molar Reaction Gibbs Function	18
2.4	Evolving Reactions and Equilibrium Conditions	19
2.5	Equilibrium Conditions and Mass Law	21
2.6	Chemical Potentials and Standard States	24
2.7	Redox Reaction: Redox Couples	25
2.8	Brief Description of an Electrochemical Cell: Daniell's Galvanic Cell	26

2.9	Electromotive Force of a Galvanic Cell, Cell Potential Difference, Maximum Work Available from a Chemical Reaction, and Nernst's Equation	28
2.10	Electrode Potentials	30
2.11	Addition of Free Enthalpies and Calculation of Standard Electrode Potentials from Other Standard Electrode Potentials	32
3	Activities and Activity Coefficients	37
3.1	Chemical Equilibrium. Mass Law and Species Activities	37
3.2	On the Physical Meaning of An Activity	37
3.3	Ionic Strength of a Solution	38
3.4	Link Between Activities and Concentrations: The Activity Coefficients	40
3.5	Standard States and Activity Coefficients	40
3.6	Different Ways to Write the Mass Law	41
3.7	Usual Conventions for Activities	42
3.8	Determination of Activities	44
3.8.1	Uncharged Solutes	44
3.8.2	Activity of An Ion: Activity of the Whole Electrolyte	44
3.9	Calculation of Activity Coefficients and of Activities	44
3.9.1	Activity Calculation of Uncharged Species	44
3.9.2	Calculation of Activity Coefficients and Activities of Ions ..	44
3.10	Justification of Debye-Hückel's Theory	47
 Part II Acids and Bases Equilibria—Analytical Applications		
4	Definitions of Acids and Bases: Strength of Acids and Bases	51
4.1	Arrhenius Definition	51
4.2	Brønsted–Lowry Definition	52
4.3	Inexistence of the Proton in Solution	53
4.4	Brønsted Acidity and Basicity in Water: Nature of the Hydrated Proton in Water	54
4.5	Nomenclature	55
4.6	About the Equivalence of the Arrhenius and Brønsted Theories in Aqueous Solutions	55
4.7	Other Theories of Acids and Bases	57
4.8	Qualitative Considerations Concerning the Strength of Acids and Bases in Water	57
4.9	Quantitative Considerations Quantifying the Strengths of Acids and Bases: Dissociation Acid Constants K_a and pK_a	58
4.9.1	Acids' Strength	58
4.9.2	Bases' Strength	60
4.10	Water Dissociation	60
4.11	Uselessness of the K_b Notion	61
4.12	A Brief View of the Concept of pH	62

4.13	The Polyacid Case	62
4.14	Distribution Diagrams	63
4.15	Macroscopic and Microscopic Equilibrium Constants	66
4.16	Predominant Species Area	68
4.17	Prevision of Acid–Base Reactions: Equilibrium Constant of Acid–Base Reaction	69
4.18	Acidity Scale in Water	70
4.19	Leveling of Acids and Bases in Water	72
5	Calculations of pH Values in Aqueous Solutions	77
5.1	Analytical Concentration	77
5.2	pH of Pure Water	78
5.3	Calculation of pH in Solutions of Strong Acids	78
5.3.1	General Relation	78
5.3.2	Simplified Equations	79
5.3.3	Logarithmic Diagram	80
5.4	pH in Solutions of Strong Bases	81
5.5	pH in Solutions of Salts of Strong Acids and Bases	82
5.6	Ostwald's Dilution Law	82
5.7	pH in Solutions of Weak Acids	83
5.7.1	General Equation Permitting the pH Calculation	83
5.7.2	pH Calculations by Approximations	84
5.7.3	Calculations with Hägg's Diagrams	86
5.8	pH in a Weak Base Solution	88
5.8.1	The Base Concentration Is High	88
5.8.2	The Basic Solution Is Highly Diluted	89
5.9	pH of a Mixture of Strong Acids	91
5.10	pH of a Mixture of Strong Bases	92
5.11	pH of a Mixture of a Strong and a Weak Acid: Ionization Repression	92
5.12	pH of a Mixture of a Strong and a Weak Base	93
5.13	pH of an Equimolecular Mixture of a Weak Base and a Weak Acid	93
5.14	pH of Polyacid and Polybase Solutions	94
5.15	pH of a Monosalt of a Diacid Solution—pH of an Ampholyte Solution	95
5.16	pH of a Solution of an Amino-Acid	96
5.17	pH of a Mixture of Two Weak Acids	100
5.18	pH of a Mixture of a Weak Acid and a Weak Base in Any Proportion: Interest in the Principal Reaction Concept	100
5.19	pH Calculations Taking Activities into Account	104
6	Buffer Solutions	107
6.1	pH of a Buffer Solution Before Addition of a Strong Acid or Base	107
6.2	pH of a Buffer Solution After a Proton Addition	109

6.3	Mechanism of the Buffer Effect	110
6.3.1	Chemical Standpoint	110
6.3.2	Mathematical Standpoint	110
6.4	Buffer Capacity—Buffer Index	111
6.5	Mathematical Expression of the Buffer Index	111
6.6	Buffer Range	113
6.7	Mixtures of Several Buffers	114
6.8	Buffer Capacity of a Polyacid	115
6.9	Some Buffers	116
7	Some General Points Concerning Titrations	119
7.1	General Principle of Titrimetric Methods	119
7.2	Terminology	120
7.3	Titration Error	120
7.4	Equivalents and Normal Solutions	121
7.5	Some Titration Forms	122
7.6	Types of Chemical Reactions Used in Titrations and Titration Designations	123
7.7	Conditions That the Titration Reaction Must Fulfill	123
7.8	Glassware Used in Titrimetry	125
7.9	Titrations and Microinformatics: Current Trends	125
8	Neutralization or Acid-Base Indicators	127
8.1	General Considerations on Neutralization Indicators	127
8.2	Origin of the Color Change	128
8.3	Categories of Neutralization Indicators	130
8.4	Some Indicators	130
8.5	Conditions for Use of Color Indicators	131
8.5.1	Color-Change Interval	131
8.5.2	Influence of the Indicator Concentration on the Color-Change Interval	132
8.5.3	pH Change of the Solution Under Study by Addition of the Indicator	132
8.5.4	Ionic Strength of the Solution	133
8.5.5	Nature of the Other Substances Present in Solution	134
8.5.6	Temperature	134
8.6	Uses of Neutralization Indicators	134
9	Acid–Base Titration Curves	135
9.1	Terminology of Acid–Base Titrations	135
9.2	General Considerations Concerning Acid–Base Titration Curves: Fraction Titrated	135
9.3	Neutralization of a Strong Acid with a Strong Base and Vice Versa	136
9.3.1	Shape of the Titration Curve	136

9.3.2	Justifications	138
9.3.3	Practical Conclusion: Choice of the Indicator	140
9.3.4	Titration Error	140
9.3.5	Titration of a Strong Base with a Strong Acid	141
9.3.6	Concentration Conditions That Must Be Respected to Obtain Satisfactory Titrations of Strong Acids and Bases	142
9.4	Neutralization Titration Curve of a Weak Acid with a Strong Base	142
9.4.1	Shape of the Curve	142
9.4.2	Justifications	144
9.4.3	Practical Conclusions: Choice of the Indicator	145
9.4.4	Titration Error	145
9.4.5	Conditions That Must be Fulfilled for Satisfactory Titrations	146
9.5	Titration of a Weak Base with a Strong Acid	146
9.6	Titration of a Weak Acid with a Weak Base	148
9.7	Titration of a Mixture of Strong Acids with a Strong Base and Inversely	148
9.8	Titration of a Mixture of a Strong Acid and a Weak Acid with a Strong Base and Inversely	149
9.9	Titration of a Mixture of Weak Acids with a Strong Base	150
9.10	Titration of a Polyacid with a Strong Base	151
9.11	Titration of the Monosalt of a Diacid	155
10	Acid–Base Titrations: Further Theoretical Studies	157
10.1	Exact Equation of the Titration Curve of a Strong Acid with a Strong Base and Conversely; Formula Giving the Titration Error	157
10.2	Exact Equation of the Titration Curve of a Weak Acid with a Strong Base and Conversely: Titration Error	159
10.3	Exact Equations of the Titration Curves of Mixtures of Acids, Bases, Polyacids, Polybases, etc.	160
10.4	Precision of Acid–Base Titrations Related to the Sharpness Index	160
10.5	Expressions of the Sharpness Index	161
10.5.1	Titration of a Strong Acid with a Strong Base	162
10.5.2	Titration of a Weak Acid with a Strong Base	162
10.5.3	Titration of a Weak Base with a Strong Acid	162
10.5.4	Titration of a Weak Acid with a Weak Base	162
10.6	Extent of the Titration Reaction	163
10.7	Gran's Diagram	165
11	Acid–Base Reactions and Chemical Analysis	169
11.1	The Concept of pH	169
11.2	Analytical Operations and pH	169
11.3	Acidity of a Medium as an Index of Its Purity	170

11.4	On the Choice of Examples of Acid–Base Titrations	170
11.5	Direct Titrations of Acid Compounds	171
11.6	Direct Titrations of Derivatives Exhibiting a Basic Character	176
11.7	Back Titrations	179
11.8	Titration After a Chemical Reaction (After Transformation)	181
 Part III Redox Phenomena and Analytical Applications		
12	Generalities on Oxidation–Reduction	193
12.1	Definitions	193
12.2	Oxidation Numbers	197
12.3	Redox Titrations and Oxidation Numbers	199
12.4	Particular Cases of Redox Reactions: Disproportionation and Retrodisproportionation Reactions	200
12.5	Equilibration of Redox Reactions	201
13	Redox Reactions and Electrochemical Cells	205
13.1	Electrochemical Cells and Redox Reactions: Example of Daniell’s Galvanic Cell	205
13.1.1	Galvanic Cell	206
13.1.2	Electrolytic Cell	207
13.2	Nature of the Electrical Current in an Electrochemical Cell	208
13.3	The Hydrated Electron	210
13.4	Cathode, Anode, and Charges of Electrodes	211
13.5	Electrochemical Cells and Reversibility	212
13.6	Classes of Electrodes	213
13.7	Shorthand Notation for Electrochemical Cells	214
13.8	Some Examples of Cells	216
13.9	Electrode Potentials: Nernst’s Law	217
13.10	Standard Electrode Potentials and Standard Reduction Potentials of Some Redox Couples at 298 K	220
13.11	Zero-Current Electrochemical Cell Potentials—Convention	223
13.12	Formal Potentials	225
14	Predicting Redox Reactions	229
14.1	Redox Phenomena and Acidity	229
14.2	Redox Phenomena, Complexation, and Precipitation	233
14.2.1	The Stabilization of a Redox Couple by Complexation or Precipitation of One of Its Members	234
14.2.2	The Increase or Decrease in the Oxidizing Strength of One of Its Ox or Red Forms	235
14.3	Qualitative Prediction of Redox Reactions After Standard Potentials	239

14.4	Drawbacks of the Prediction Rule Based on the Sole Consideration of Standard Potentials	240
14.5	Quantitative Character of a Redox Reaction	242
14.6	Kinetic Considerations Concerning Redox Reactions	245
15	Predicting Redox Reactions by Graphical Means	247
15.1	Predominance Areas of a Redox Couple	247
15.2	Qualitative Prediction of Redox Reactions from the Knowledge of the Predominance Areas	250
15.3	Frost Diagrams	253
15.4	<i>E</i> /pH Diagrams or Pourbaix Diagrams	257
15.5	An Example of Application of Pourbaix Diagrams in Analytical Chemistry	261
15.6	Extension of Pourbaix Diagrams	263
16	Calculating Equilibrium Potentials of Solutions Containing Several Redox Couples	265
16.1	Equilibrium Potentials and Electrode Potentials	265
16.2	Potential of a Solution Containing Only One Redox Couple	266
16.3	General Case: Equilibrium Potential of a Solution Containing Two Redox Couples	266
16.4	Determining the Ox and Red Concentrations of a Couple from the Known Equilibrium Potential by Graphical Means	269
16.5	A Particular Case: The Exchange of Electrons is Accompanied by an Exchange of Protons or by an Exchange of Ligands	270
16.6	Case in Which One of the Species Redox is Polynuclear	271
16.7	Equilibrium Potential of a Solution When it Contains an Ampholyte	272
16.8	Potential of a Solution Containing a Mixture of the Reduced Polyfunctional Member of a Couple and of the Oxidized Member of Another Couple	274
16.9	Potential of a Solution Containing a Mixture of an Oxidized Form of a First Couple and of Two Reduced Forms Belonging to Two Other Different Redox Couples	276
16.10	General Considerations Concerning Redox Titrations	277
16.11	Thermodynamic Condition for a Redox Titration Reaction	277
16.12	Kinetic Conditions in Order to Achieve a Satisfactory Redox Titration Reaction	278
16.13	Detection of the Equivalence Point of a Redox Titration	279
16.14	General Considerations on Internal Redox Indicators	279
16.15	Some Internal Redox Indicators	280
16.15.1	1,10-Phenanthroline	280
16.15.2	Diphenylamine	282
16.15.3	Methylene Blue	283
16.15.4	Diphenylpyrazine	283

17 A Study of Some Redox Titration Curves	285
17.1 Titration of the Ferrous Ion by the Ceric Ion, One of the Simplest Examples of a Redox Titration	285
17.1.1 Common Simplified Theoretical Study	286
17.1.2 Rigorous Study	289
17.2 Further Considerations Concerning Symmetrical Titrations: Titration Error	290
17.2.1 Consideration 1	290
17.2.2 Consideration 2	290
17.2.3 Consideration 3	291
17.2.4 Consideration 4	292
17.2.5 Consideration 5	292
17.2.6 Consideration 6	292
17.2.7 Consideration 7	293
17.3 Study of the Titration Curve of Stannic Ions by Chromous Ions—Generalization to All Asymmetrical Titrations	294
17.4 Redox Titrations in Which a Simultaneous Exchange of Electrons and Protons or Other Particules Exists	297
17.5 Cases in Which the Equivalence Potential Values Depend on the Concentration of One of the Reactants	298
17.6 Titration of the Hypovanadous Ion by the Permanganate Ion	302
17.6.1 First Equivalence Point	303
17.6.2 Second Equivalence Point	306
17.6.3 Third Equivalence Point	306
17.7 Titration of a Mixture	308
18 Oxidoreductimetry: Direct and Indirect Iodometries	313
18.1 Oxidoreductimetry	313
18.2 Nomenclature of the Titration Methods Involving the Use of Iodine or the Formation of Iodine	314
18.3 Some Physicochemical Properties of Iodine	315
18.4 Predominance Areas of Some Species of Iodine	315
18.5 Interesting Features Exhibited by the Couple I_2/I^- for Its Use in Titrimetry	317
18.5.1 Stability	317
18.5.2 Coloration	317
18.5.3 Solubilities	317
18.5.4 Standard Potential Values of I_2/I^- Couples	317
18.5.5 The Influence of pH	319
18.5.6 Existence of the Fundamental Reaction of Direct and Indirect Iodometries	319
18.5.7 Detection of the Equivalence Point	319
18.6 The Fundamental Reaction of Iodometries	319
18.7 Iodine Solutions	321
18.8 Thiosulfate Solutions	323

18.9	Examples of Titration by Direct Iodometry	325
18.9.1	Determination of Sulfurous Acid, Hydrogen Sulfitcs, and Sulfitcs	325
18.9.2	Determination of Hydrogen Sulfide, Hydrogen Sulfides, and Sulfides	326
18.9.3	Determination of Alkaline Cyanides: Fordos and Gelis's Method	326
18.9.4	Determination of Hydrazine and Its Derivatives	327
18.9.5	Determination of Arsenicals	328
18.9.6	Determination of Derivatives of Antimony +III	328
18.9.7	Determination of Stannous Tin	328
18.9.8	Determination of Mercurous Salts: Extension to the Determination of Mercuric Salts and to That of Reducing Organic Substances	329
18.9.9	Determination of Thiocyanates	330
18.9.10	Determination of Thiols	330
18.9.11	Determination of Xanthogenates and Derivatives: Determination of Hydrazoic Acid and of Azides	331
18.9.12	Determination of Hydroquinol	332
18.9.13	Determination of Vitamin C	333
18.10	Examples of Titrations by Indirect Iodometry	336
18.10.1	Recall of Information	336
18.10.2	Titration of Nitrous Acid and Nitrites	336
18.10.3	Determination of Halogens	337
18.10.4	Determination of Hypochlorites	337
18.10.5	Determination of Halogens at Oxidation Numbers +III, +V, +VII	340
18.10.6	Determination of Metallic Salts "at Their Maximum" ..	340
18.10.7	Determinations of Arsenic and Antimony at Oxidation State +V	342
18.10.8	Determination of Hydrogen Peroxide and of Peroxy Salts	343
18.10.9	Determination of Aqueous Dioxygen by Winkler's Method	344
18.10.10	Determination of Peroxides and Hydroperoxides	344
18.10.11	Determination of Diverse Organic Compounds	344
19	Iodometry in Alkaline Medium, Iodatometry, Periodimetry, and Bromometry	347
19.1	Iodometry in Alkaline Medium	347
19.1.1	General Considerations	347
19.1.2	Applications	351
19.2	Iodatometry	352
19.2.1	General Considerations	352
19.2.2	Applications	355
19.3	Periodimetry	358

19.4	Bromatometry, Hypobromometry, and Bromometry	366
19.4.1	General Considerations	366
19.4.2	Oxidization Reactions	368
19.4.3	Determinations by Fixing bromine into an Organic Substrate Either by Substitution or by Addition	373
20	Oxidizations with Permanganate, Dichromate, and Ceric Ions	
	Some Titration Methods Involving a Reduction Reaction	377
20.1	Oxidization with Permanganate Ions	377
20.1.1	General Considerations	377
20.1.2	Applications of Manganimetry in Acidic Medium	382
20.1.3	Manganimetry in Neutral and Weakly Alkaline Media....	386
20.1.4	Manganimetry in Strongly Alkaline Medium	388
20.1.5	Determination of Organic Matters in Water	389
20.2	Titration with Dichromate Ions: Chromimetry	390
20.2.1	Definition	390
20.2.2	General Considerations	390
20.2.3	Applications	393
20.3	Titration with Ceric Ions	394
20.3.1	Some Properties of Cerous and Ceric Salts	395
20.3.2	Advantages of Cerimetry	396
20.3.3	Standardized Solutions	397
20.3.4	Applications of Cerimetry	398
20.4	Some Other Oxydoreductimetric Titration Methods	402
20.4.1	Titration with Titanium III Salts	402
20.4.2	Titration with Chromium II Salts	403
20.4.3	Titration with Ascorbic Acid	403
21	Some Applications of Redox Reactions in Qualitative Analysis	405
21.1	Organic Analysis	405
21.1.1	Colorimetric Analysis	405
21.1.2	Detection in Chromatography	410
21.1.3	Titration Reactions for Which the Equivalence Point Is Detected Through the Occurrence of a Redox Reaction...	411
21.1.4	Functional Analysis	412
21.2	Inorganic Analysis	412
Part IV	Complexation Reactions—Analytical Applications	
22	General Definitions Concerning Complexes Rules of Nomenclature and Writing	423
22.1	General Definition of Complexes	423
22.2	Complexes as Compounds Resulting from the Interaction of Electron-Donating and Electron-Accepting Species	424
22.3	Limits of the Set of Complexes	425

22.4	Writing and Systematic Nomenclature of Complexes	427
22.5	Electrical Charge of an Ion Complex	428
23	Some Elements Concerning the Chemistry of Complexes	429
23.1	Attaining Complexes	429
23.2	Some Ligands Found in Classical Complexes	430
23.2.1	Some Monodentate Ligands	430
23.2.2	Some Polydentate Ligands	431
23.3	Some Aspects of the Chemistry of Complexes	433
23.4	State of the Ions in Aqueous Solution and Consequences	436
24	Stability of Complexes: Some Elements Concerning the Kinetics of Their Formation	439
24.1	Definition of Complexes in the Context of Analysis	439
24.2	Stability of Complexes: Perfect and Imperfect Complexes	440
24.3	Formation or Stability Constants of Complexes	441
24.4	General Methodology of Determining Stability Constants	442
24.5	Some Examples of Calculations Carried Out with Stability Constants	444
24.6	Distribution Diagrams	446
24.7	Formation Curve	448
24.8	The Complexes as Particle Donors	449
24.9	Factors Influencing the Stability of Complexes	453
24.10	Stability of Chelates: Chelate and Macrocyclic Effects	456
24.11	Kinetics of Complexes' Formation: Labile and Inert Complexes ..	459
25	Superimposition of Varied Equilibria to Complexation Equilibria ...	461
25.1	Superimposition of Several Complexation Equilibria	461
25.2	An Important Particular Case of Parasitic Reactions: Formation of the Complexes Hydroxo, Oxo, and so Forth from the Hydrolysis of Metallic Ions	462
25.2.1	Hydrolysis of Metallic Ions	462
25.2.2	Competition Between the Hydroxo Complexes and Other Ligands	464
25.2.3	Complexation—Precipitation Interaction: Formation of Insoluble Oxides and Hydroxides	468
25.3	Formation of Polynuclear Complexes; Polymerization	476
25.4	Ability of Ligands to Complex Metallic Ions and Acidity of Solution	480
26	Conditional Stability Constants	485
26.1	Species Existing in Solution When a Metallic Ion Is Titrated with EDTA	485
26.2	Conditional Constants, Parasitic Reaction Coefficients, and Apparent Concentrations	486

26.3	Examples of Conditional Constants' Calculations	489
26.4	Quantitative Changes in Coefficients α	491
26.5	Conditional Constants, Masking, and Selective Complexations in the Presence of Several Metallic Ions	493
26.6	Conditional Constants and Calculation of the Concentrations of the Different Species in Solution	494
26.7	Case of Metal Indicators	497
26.8	Extension of the Concept of Conditional Stability Constants	499
26.9	About the Interest in the Concept of Conditional Constants	500
27	Complexometry I: Mercurimetry (Votocek–Dubsky's Method)	503
27.1	The Major Difficulty Encountered During Complexometric Titrations	503
27.2	Mercurimetry: Votocek–Dubsky's Method	505
27.2.1	Principle	506
27.2.2	Equivalence Point	507
27.2.3	Standard Solutions	510
27.2.4	Applications	511
28	Complexometry II: Titrations with EDTA	513
28.1	Some Properties of EDTA	513
28.1.1	Acid Dissociation Constants of EDTA	514
28.1.2	EDTA: A Very Powerful Chelating Agent	515
28.1.3	Formation Reactions of Metal–EDTA Chelates	516
28.2	Direct Titration Curve of a Metallic Ion with EDTA	517
29	Complexometry III: Metal Cation Indicators and Types of EDTA Titrations	525
29.1	Some Metal Ion Indicators	525
29.1.1	Azo Derivatives Possessing a Phenol Function	525
29.1.2	Triphenylmethane Derivatives	527
29.1.3	Derivatives of Miscellaneous Structures	529
29.2	Types of EDTA Titrations	530
29.2.1	Direct Titrations	530
29.2.2	Back Titrations	531
29.2.3	Titrations with Indirect Metal Indicators	532
29.2.4	Replacement or Substitution Titrations	533
29.2.5	Alkalimetric Titrations	534
29.2.6	Sequential Titrations of Mixtures, Selectivity, Masking, and Demasking	535
29.3	Determination of Anions with EDTA	539
29.4	Other Complexones	540
30	Applications of the Formation of Complexes in Inorganic Analysis ...	543
30.1	Qualitative Inorganic Analysis	543
30.1.1	Cations' Characterization	544
30.1.2	Anions' Characterization	563

30.2	Quantitative Inorganic Analysis	568
30.2.1	Titration of Ca^{2+}	568
30.2.2	Titration of Mg^{2+}	569
30.2.3	Titration of Lead	570
30.2.4	Titration of Bismuth	570
30.2.5	Titration of Aluminum	571
30.2.6	Miscellaneous Titrations	571

Part V Precipitation Phenomena—Analytical Applications

31	Applications of the Formation of Complexes in Organic Analysis	575
31.1	Formation of Complexes with Fe^{3+} and Fe^{2+}	575
31.2	Formation of Complexes with Cu^{2+}	590
31.3	Formation of Complexes with Ag^{+}	597
31.4	Formation of Complexes with Co^{2+}	599
31.5	Formation of Complexes with Hg^{2+}	601
31.6	Formation of Miscellaneous Complexes and Analytical Applications	603
32	Intrinsic, Ionic, and Total Solubilities; Solubility Product and Precipitation	609
32.1	Solubility Product and Intrinsic Solubility	609
32.2	Generalization of the Concept of Solubility Product	610
32.3	Thermodynamic Justification of the Concept of Solubility Product	612
32.4	Intrinsic Solubility, Total Solubility, and Ionic Product	613
32.5	Difficulties Encountered in the Calculations of Solubilities	617
33	Dependence of the Solubility on the Solution's Ionic Strength and on the Presence of Common Ions: Superimposition of Several Precipitation Equilibria	619
33.1	Influence of the Ionic Strength on the Solubility	619
33.2	The Common Ion Effect	622
33.3	Superimposition of Two Precipitation Equilibria: Separation by Precipitation	628
34	Solubility and pH	633
34.1	Solubility of Acidic and Basic Solutes as a Function of pH	633
34.1.1	The Monoacid or Monobasic Case	633
34.1.2	The Diacid or Dibase Case	636
34.1.3	The Ampholyte Case	637
34.2	Solubility of Poorly Soluble Salts as a Function of pH	639
34.2.1	Qualitative Aspect	639
34.2.2	Acid–Base Equilibria and Precipitation in a Buffered Medium: Quantitative Aspect	640
34.2.3	Solubility of Poorly Soluble Salts in Unbuffered Media ..	642

34.3	Fractional Precipitation of Ions as a Function of the Solution's pH Value	648
34.3.1	Qualitative Aspects	648
34.3.2	Fractional Precipitation of Metallic Ions as Sulfides	649
34.3.3	Fractional Precipitation of Metallic Ions as Hydroxides	654
34.3.4	Fractional Precipitation of Metallic Ions as Oxinates	656
35	Precipitation and Complexation	659
35.1	Dissolution of a Precipitate by Complexation of the Metal Cation Constituting it: Generalities	659
35.2	Dissolution of a Precipitate by Complexation: Quantitative Aspects	660
35.3	Dissolution of a Precipitate by Complexation: Further Calculations	662
35.3.1	Dissolution of Silver Bromide with a Sodium Thiosulfate Solution	663
35.3.2	Dissolution of a Precipitate with an Excess of Precipitating Reagent	664
35.3.3	Precipitation of Metallic Sulfides	668
35.4	Destruction of a Complex by Formation of a Precipitate	672
35.5	Separation by Complexation and Precipitation	676
36	Theoretical Study of Some Precipitation Titration Curves	679
36.1	Case of a Symmetric Titration: Titration of A Halide by Silver Ions and Inversely	679
36.1.1	Titration Reaction	679
36.1.2	General Equation of the Titration Curve	680
36.1.3	Shape of the Titration Curve	682
36.1.4	Simplified Equations of the Titration Curve	682
36.1.5	Titration Error	683
36.1.6	Inflection Point of the Titration Curve	684
36.1.7	Inverse Titration	685
36.2	Dissymmetric Titrations	686
37	Titrimetric Methods Involving a Precipitation	689
37.1	Argentometry	689
37.1.1	Definitions	689
37.1.2	Generalities	689
37.2	Argentometry in Acidic Medium: Charpentier–Volhard's Method	690
37.2.1	Principle	690
37.2.2	Theoretical Justification of the Method	690
37.2.3	Conditions in Which the Titration Must Be Carried Out	691
37.2.4	Titration Error	692

37.3	Argentometry in Neutral or Weakly Alkaline Medium: Mohr's Method	693
37.3.1	Principle	693
37.3.2	Mechanism of the Endpoint Indication: Titration Error ...	694
37.3.3	pH Conditions	695
37.3.4	Applications	696
37.4	Argentometry in Weakly Acidic or Neutral Medium: Fajans' Method	696
37.4.1	Principle	696
37.4.2	Indication Mechanism	696
37.4.3	Experimental Conditions	697
37.5	Liebig–Denigés' Method	697
37.5.1	Definitions	697
37.5.2	Principle of Liebig's Method	698
37.5.3	Equations of the Titration Curve	698
37.5.4	Titration Error	700
37.5.5	Drawback to Liebig's Method	700
37.5.6	Denigés' Modification	700
37.5.7	Applications and Extensions of Liebig–Denigés' Method	702
37.5.8	Standard Solutions	702
37.6	Some Other Precipitation Methods	703
38	Gravimetry by Precipitation	705
38.1	Principle and Some Definitions	705
38.2	Conditions for the Success of a Gravimetry by Precipitation Determination	706
38.3	Insolubility of the Precipitate in the Medium	707
38.4	Composition of the Precipitate; Impurities of the Precipitate	708
38.4.1	Impurities by Coprecipitation	708
38.4.2	Impurities by a Lack of Selectivity of the Precipitation Reaction	710
38.5	Obtaining a Suitable Precipitate	712
38.5.1	Purity of Precipitates and Size of Particules	712
38.5.2	Size of Particules	712
38.6	Precipitation from Homogeneous Solution	714
38.7	The Gravimetric Factor	716
38.8	Sensitivity of Gravimetry	718
38.9	Some Experimental Details	719
38.9.1	Quantitative Filtration	719
38.9.2	Drying of Precipitates	719
38.9.3	Precision Balances	719
38.9.4	Thermobalances	719
38.10	Some Characteristics of Gravimetry by Precipitation	720

39 Some Applications of the Precipitation Phenomenon in Inorganic and Organic Qualitative and Quantitative Analysis	721
39.1 Titrations Involving the Precipitation of Insoluble Silver Salts	721
39.1.1 Determination of Organic Halogens	721
39.1.2 Determination of Hydrochlorides, Hydrobromides, and Hydroiodides	723
39.1.3 Some Examples	723
39.1.4 Zeisel's Method: Determination of Methoxy and Ethoxy Groups	726
39.1.5 Prototropic Titrations in the Presence of Silver Ions	727
39.2 Other Titrimetric Methods Involving a Precipitation Phenomenon	729
39.3 Gravimetry	731
39.3.1 Gravimetric Assays Involving Ignition	732
39.3.2 Gravimetric Assays Involving a Prior Solvent Extraction	732
39.3.3 Assay Involving Solvent Extraction and Drying to Constant Weight	733
39.3.4 Gravimetric Determinations Involving the Formation of a Precipitate that Is Weighed	733
39.4 Determination of Inorganic Ions After Precipitation with Organic Precipitants	734
39.5 Qualitative Organic Analysis	736
39.6 Inorganic Qualitative Analysis	740
Appendix A The Chain Rule or Differentiating a Function of a Function	743
Appendix B Sharpness Index for the Titration of a Strong Acid with a Strong Base	745
Appendix C Sharpness Index for the Titration of a Weak Acid with a Strong Base and Conversely	747
Appendix D Sharpness Index for the Titration of a Weak Acid with a Weak Base	749
Appendix E Finding an Approximate Expression of the Fraction α of the Added Titrant That Has Reacted	751
Appendix F A Study of Liebig–Denigés's Titration Curves	753
Bibliography	763
Index	765