ESSENTIALS OF QUANTITATIVE ANALYSIS

,

C. .,

۲

C. David West

McGraw-Hill Book Company

New York St. Louis San Francisco Auckland Bogotá Hamburg Johannesburg London Madrid Mexico Montreal New Delhi Panama Paris São Paulo Singapore Sydney Tokyo Toronto

CONTENTS

Preface	•		xvii
CHAPTER 1	Stoichic	ometry and Gravimetric Analysis	1
	1.1 1.2	Basic Solubility Rules Basic Weight Relationships	1 2
		Gravimetric Factors	
,	1.3 1.4 1.5	Solubility and Solubility Product Will Something Precipitate? Factors That Influence Solubilities	4 7 8
		Effect of Activity Coefficients/Intrinsic Solubility/Competing Equilibria/Particle Size	
	1.6	Mechanism of Precipitate Formation	9
		The Process of Nucleation/Crystal Formation	
	1.7	Aging of Precipitates	10
		Ostwald Ripening/Thermal Aging	
	1.8 1.9 1.10 1.11	Colloidal Properties of Precipitates Contamination of Precipitates The Sensitivity and Selectivity of Gravimetric Analysis Practical Techniques of Gravimetric Analysis	11 12 12 14
		General Rules/Precipitation from Homogeneous Solution/Drying and Ignition of Precipitates	
	1.12	Three Examples of Practical Gravimetric Analyses	16
		Silver Chloride/Gravimetric Determination of Sulfate/Determination of Lead by Homogeneous Precipitation	

1

	1.13	Selected Applications of Gravimetric Analysis	19
		Bibliography	24
		Problems	24
CHAPTER 2	Statisti	cal Concepts and Tests	27
	2.1	Precision and Accuracy	27
		Determinate and Indeterminate Errors	
	2.2	The Mean	28
	2.3	The Normal Curve of Error	29
	2.4	The u-Test	32
	2.5	The Standard Deviation of a Sample	33
	2.6	The Standard Deviation of the Mean	34
	2.7	Determinate Errors	35
	2.8	The t Test	36
	2.9	Confidence Limits and Control Charts	40
		The F-Test	42
		The Q-Test	<i>43</i>
		Variance and the Propagation of Error	45
		Maximum Expected Error	46
		Errors Associated with Normal Laboratory Equipment	48
		Significant Figures	50
	2.16	Other Statistical Tests and Concepts	52
		Bibliography	52
		Problems	<i>. 53</i>
CHAPTER 3	Therm	odynamic Basis for Equilibrium	58
·	3.1	Free Energy	58
	3.2	Standard States	60
	3.3	Concentration and Activity	61
	3.4	The Equilibrium Constant	62
	3.5	Variation of Equilibrium Constant with Temperature	64
	3.6	Calculation of Activities	64
		Experimental Values for Activity Coefficients	
		Bibliography *	69
		Problems	69
CHAPTER 4	Monop	rotic Acid Equilibria	71
	4.1	Definitions of Acids and Bases	71
	4.2	The Definition of pH	72
	4.3	Solutions of Strong Acids and Bases	73

•

. 4

	4.4 4.5	The Leveling Effect Calculation of the pH of Solutions of Strong Acids and Bases	74 74
	4.6 4.7	General Approach to Equilibrium Calculations Solutions of Weak Acid, Conjugate Base, or Both	77 78
	u	Pure Weak Acid in Water/Pure Weak Base in Water/Mixture of Weak Acid and Conjugate Base: A "Buffer" Solution/Weak Base and Conjugate Acid	
	4.8	Solutions of Salts of Strong Acids and Weak Bases, and of Strong Bases and Weak Acids	83
	4.9	Acid-Base Titrations	85
		Neutralization Equivalents and Normality	<i>91</i>
		Indicators and Equivalence Point Determination Buffer Solutions Problems	93 96 97
CHAPTER 5	Polypro	otic Acids	101
	5.1	General Relationships	101
,		 A Pure Solution of Weak Polyprotic Acid/ Weak Polyprotic Acid and Conjugate Base/ Pure Solution of Ampholyte 	
	5.2 5.3	A General Equation for the Determination of the Fractional Amount of Each Species in a Mixture Titration of Phosphoric Acid	108 110
		Point A/Point B/Point C/Point D/Point E/ Point F/Point G	
	5.4	Titration of Carbonate Species	115
	5.5	The Case of Sulfuric Acid	119
	5.6	Calculation of the Concentration of All Constituents	
		of a Polyprotic Acid Family	· 120
	5.7	Amino Acids, The Salt of a Week Acid and a Week Disc	121
	5.8 5.9	The Salt of a Weak Acid and a Weak Base Practical Aspects and Selected Applications	123
	5.9	of Aqueous Acid-Base Titrations	125
		Standard Solutions of Strong Acids/Standard Solutions of Strong Bases/Applications of Aqueous Acid-Base Titrations	
	5.10	Acid-Base Titrations in Nonaqueous Solutions: The Leveling Effect	127

.

1

		/	
		Bibliography Problems	128 129
CHAPTER 6	Precipi	tation and Complexometric Titrations	133
	6.1 6.2	Precipitation Titrations Indicators for Precipitation Titrations	133 136
· · · ·		A. The Mohr Method/B. The Volhard Titration/ C. The Adsorption Indicator, Fajan's Method	
	6.3	Complexometric Titrations	138
		Conditional Constants/Conditional Constants with Competing Ligands	
	6.4 6.5 6.6	Indicators for Complexometric Titrations Other Complexometric Titrations Competing Reactions	147 147 148
-	,	A. Precipitations by H ₂ S Gas/B. Solubility of Salts of Weak Acids and Bases/C. Competing Complex-Formation Reactions/D. The Use of Masking Agents	
		Bibliography Problems	154 154
CHAPTER 7	Voltaic	c Cells and Direct Potentiometry	157
	7.1	Voltaic Cells	157
		Schematic Representation of Cells	
	7.2	Electrochemical Potentials, Free Energy, and Work	160
		Electrical Work	
	7.3	The Variation of E with Concentration: The Nernst	
		Equation	160
	7.4	The Determination of E^0	161
	7.5 7.6	Calculations Involving the Nernst Equation Single Electrode Potentials and Reference Electrodes	165 167
		The Ag-AgCl Electrode/The Saturated Calomel Electrode	
	7.7	Direct Potentiometry	170
	7.8	Specific Ion Electrodes	170

		The Glass Electrode/Other Glass Electrodes/ The Nicolsky Equation/Solid Crystal Electrodes/ Ion Exchange Membrane Electrodes/ Enzyme Electrodes	
	7.9	Techniques and Errors Associated with Direct Potentiometry	175
		Calibration Techniques/The Standard Addition Method	
		Bibliography Problems	177 177
CHAPTER 8	Potent	iometric and Redox Titrations	180
	8.1	Potentiometric Titration Theory	180
		Determination of the Equivalence Point/Types of Potentiometric Titrations	
	8.2	Redox Titrations Using Visual Indicators	189
	,	Redox Equivalents and Normality	
	8.3 8.4	Formal Potentials Applications of Redox Titrations	192 192
		Permanganate Oxidations/Dichromate Oxidations/Ceric Oxidations/Methods Involving Iodine/The Thiosulfate Ion/Other Reducing Agents	
		Bibliography Problems	197 197
CHAPTER 9	Electro	olysis and Coulometry	202
	9.1	Current-Voltage Curves	202
		Reversibility and Overpotential/Overpotentials/ The Necessary Applied Voltage	
	9.2	Separation and Determination of Metals by Electrolysis	208
		Controlled Potential Electrolysis/Constant Current Electrolysis/Applications and Limitations of Electrogravimetric Analysis	

1

-.

	,		
	9.3	Coulometric Analysis	212
		Constant Potential Coulometry	
	9.4	Coulometric Titrations	215
		Constant Potential Coulometric Titrations/Advantages of Coulometric Titrations	
,	9.5	Applications of Coulometric Analysis Bibliography Problems	219 220 220
CHAPTER 10	Polarog	graphy and Amperometry	223
	10.1 10.2 10.3 10.4	Polarography The Use of a Supporting Electrolyte The Shape of the Polarographic Wave The Ilkovic Equation	223 226 226 230
		Polarographic Maxima/Elimination of Oxygen	
-	10.5 10.6	Advantages and Disadvantages of the DME Modern Polarographic Techniques	232 232
	•	AC Polarography/Differential Pulse Polarography	
	10.7	Quantitative Analysis via Polarography	236
		Analysis of Mixtures	
	10.8	Applications of Quantitative Polarography	238
		Use of Polarography to Study Complexes/Inorganic Ions/Organic Ions	
	10.9	Voltammetry	240
		Some Specific Practical Applications	
	10.10 10.11 10.12	Amperometric Titrations The Two-Electrode Amperometric Titration Applications of Amperometric Titrations Bibliography Problems	242 246 251 251 252
		1	
CHAPTER 11	Atomic	Spectroscopy	256
	11.1 11.2 11.3	Wave Properties of Light Atomic Transitions Atomic Emission Spectroscopy	256 258 261

. •

		Arc and Spark Emission/Flame Photometry/Inductively-Coupled Plasma Emission	
	11.4	Principles of Atomic Absorption	264
		Line Widths	
	11.5 11.6 11.7 11.8	Beer's Law Instrumentation for Atomic Absorption Spectroscopy The Hollow Cathode Lamp Atom Reservoirs	265 267 268 271
		Flames	
	11.9	The Burner, Nebulizer, and Spray Chamber Effect of Flame Temperature/Effect of Flame Composition/Effect of Burner Position and Rotation	272
	11.10 11.11	Carbon Furnace System Optical Systems	275 276
		Monochromator Systems	
	11.12 11.13	Detectors and Readout Systems—The Photomultiplier Tube More Sophisticated Optics and Read-Out Systems	278 279
		Double Beam Systems/Zeeman Effect Background Correction/Smith-Hieftje Background Correction/Microprocessor Instruments	•
	11.14	Interferences	282
·		Physical Interferences/Chemical Interferences/Ionization/Spectral Interferences	
	11.15	Quantitative Analysis Schemes	285
		Flame Analysis/Standard Addition	
	11.16 11.17	Applications and Limitations of Atomic Absorption Comparison of Atomic Spectroscopic Techniques Bibliography Problems	286 287 287 288
CHAPTER 12		lar Spectrophotometry in the olet-Visible Region	292
•	12.1 12.2	Introduction Molecular Absorption and Emission Pathways	292 292

·

,

.

.

	,	The Absorption Process/Fluorescence Emission	
	12.3	Instrumentation for UV-Visible Spectroscopy	296
		Light Sources for UV-Visible Absorption/Monochromators/Double-Beam Systems/Sample Cells/Detectors/Modern, "Rapid-Scan" Spectrometer Systems	
• •	12.4 12.5	Beer's Law Qualitative Aspects	300 301
		Chromophoric Groups	
	12.6	Quantitative Analysis	303
		Apparent Deviations From Beer's Law/Use of Isosbestic Points/Errors in Absorption Measurements/Differential Methods	
	12.7	Applications of UV-Visible Absorption Methods	308
-	,	Analysis of Mixtures/Photometric Titrations/Other Applications of UV-Visible Methods/Determination of the Formula of a Complex/Advantages and Disadvantages of UV-Visible Absorption for Quantitative Analysis	
	12.8	Fluorescence Analysis	314
		Equation for Fluorescence	
	12.9	Phosphorescence Analysis	317
		Bibliography	319
		Problems	319
CHAPTER 13	Princip	oles of Solvent Extraction and Chromatography	323
	13.1	Basic Principles of Liquid-Liquid Extraction	323
	13.2	Craig Countercurrent Extractions	327
	13.3	Applications of Solvent Extractions	331
	13.4	Liquid Chromatography	333
		Some Definitions	
	13.5 13.6	Theoretical Aspects of Liquid Chromatography Column Efficiency	335 336
		Theoretical Plates/Measurement of Theoretical Plates/Differing Paths/Diffusion Effects/Mass Transfer Effects	

.•

	13.7 13.8	Column Selectivity Sample Capacity Bibliography Problems	339 341 341 342
CHAPTER 14	High P	erformance Liquid Chromatography	344
	14.1 14.2	Review of Theoretical Principles Apparatus	344 345
		Pumps/Gradient Elution Devices/Sample Injection Systems/Columns	
	14.3 14.4	Liquid-Solid Adsorption Chromatography Reverse Phase/Bonded Phase Liquid-Liquid Partition Chromatography	349 350
	14.5	Ion Exchange Chromatography	350
		Ion-Pair Chromatography/Ion Chromatography	
	14.6 14.7 14.8	Exclusion Chromatography Flow Programming and Gradient Elution Detectors for HPLC	355 356 357
•		Refractive Index Detector/UV Detector/Electrochemical Detectors	
	14.9 14.10	Techniques of Qualitative Analysis Quantitative Analysis by HPLC Bibliography Problems	360 361 362 362
CHAPTER 15	Gas Cl	nromatography	365
	15.1	Apparatus for GC	365
		Gas Supply/Flow Control and Measurement/Sample Introduction Systems	
	15.2	Basic Principles of Gas Chromatography	368
	15.3 15.4	Effect of Temperature Columns and Stationary Phases	371 372
	15.5	Detectors for Gas Chromatography	372
		The Thermal Conductivity Detector/The Flame Ionization Detector (FID)/The Electron Capture Detector (ECD)/Other Detectors	

•

1

, 15.6	Applications of Gas Chromatography	380
•	Qualitative Analysis/Quantitative Analysis/Specific Applications	
15.7 15.8	Microprocessor Gas Chromatography Ancillary Techniques	382 382
	GC-IR/GC-MS	
15.9	Comparison: GC and LC Problems	384 385

Appendixes

.

I	Solubility Product Constants at Room Temperature	388
II	Dissociation Constants of Acids and Bases	391
III	Logarithms of Stepwise and Overall Formation	
	Constants for Metal Ion Complexes	395
IV	Elemental List of Standard Reduction Potentials at 25°C	<i>39</i> 8
V	Detailed Solutions to Odd-Numbered Problems	405
1		151

۰,

`• t 451

١,

•

Index

-