### Contents

### Chapter 1 Chemical Analysis, What, Who, and Why

- A. CHEMICAL QUANTITIES, 2
  Units Involved in the Expression of Amount, 2
- B. THE DIFFERENTIATING CHARACTERISTIC, 4
  Devising a Probe for the Differentiating Characteristic, 4
  Anticipating the Response to the Probe, 5
  Measuring the Response to the Probe, 5
- C. QUANTITATION, 6
  Assessing Errors and Interferences, 6
- D. DETECTION, 7Assessing Confidence in the Results, 7
- E. IDENTIFICATION, 8
  Identification by Deductive Reasoning, 9
  "Analyze This for Me!", 9
- F. SEPARATION, 10 Single-Step Separation, 10 Separation by Dispersion, 11
- G. CHEMICAL ANALYSIS IN SCIENCE AND SOCIETY, 12
   Challenges and Rewards, 12
   The Evolution of Chemical Analysis, 12
   PRACTICE QUESTIONS AND PROBLEMS, 13

## Chapter 2 The Elements of Measurement

- A. Measurement, Interpretation, and Observation, 15
  Measurements and Interpretations, 16
  Information from Sets of Measurement Data, 16
  Sources of Measurement Numbers, 16
  Measurement Qualities, 16
- B. ELEMENTS OF MEASUREMENT SYSTEMS, 18 Conversion Devices, 18 Input/Output Relationships, 19

- C. EXAMPLES OF MEASUREMENT SYSTEMS, 20 The Analog Thermometer, 20 The Ammeter, 20 The Analog Clock, 22 pH Paper, 23
- D. CHARACTERISTICS OF SCALAR READOUTS, 24
   Linear Scales, 24
   Scalar Readout Characteristics, 25
   Interpolation Errors, 25
   Verniers, 25
   Scales in Arcs or Circles, 26
- E. Volume-to-Length Converters, 26
  The Graduated Cylinder, 27
  Scale Indication by Liquid Level, 27
  The Buret, 27
  The Volumetric Flask, 28
  The Pipet, 28
  Effects of Temperature on Volumetric Measurements, 28
- F. CHARACTERISTICS OF DIGITAL READOUTS, 30
  The Number Register, 30
  The Stepwise form of the Transfer Function, 31
  Range and Resolution, 31
  Measurements Involving ADCs, 32
  The Discrete Nature of the Data, 32
  Stimulus–Response Measurements, 33
- G. NULL MEASUREMENTS AND CONVERSION DEVICES, 34
   Double-Pan Balance, 34
   Null Measurement Characteristics, 35
   Null Conversion Devices, 36
   The Electronic Analytical Balance, 37
- H. Measurement Accuracy and Precision, 39
   Measures of Precision, 39
   Confidence Intervals, 40
   Significant Figures, 42
   Measurement Precision in Data Processing, 42
- I. Comparing Means and Deviations, 45
   Comparing the Mean with an Accepted Value, 45
   Comparing the Means of Two Data Sets, 46

Limit of Detection, 47 C. QUANTITATION BY ACID-BASE TITRATION, 98 Comparing the Deviations of Two Data Sets, 48 Making the Standard Titrant, 98 Rejection of Data, 48 Adding Known Volumes of Standard Solution, 100 Detecting the Response to the Titrant, 102 J. LEAST SQUARES METHOD FOR LINEAR PLOTS, 51 Using an Indicator, 103 The Straight Line, 52 Using a pH Meter, 105 Linear Regression, 52 Precision of the Regression Results, 52 Concentration Effect in Strong Acid-Base Titration, 106 Precision of Values Calculated from the Working Curve, 56 D. WEAK ACIDS, WEAK BASES, AND BUFFERS, 109 Titration of Weak Acids, 109 PRACTICE QUESTIONS AND PROBLEMS, 58 Buffer Solutions, 111 Titration of Weak Bases, 113 E. LOGARITHMIC CONCENTRATION PLOTS, 115 Chapter 3 Constructing Logarithmic Concentration Acidity, Activity, and pH 61 Diagrams, 116 Solving Problems with Log Plots, 117 A. ACIDS, BASES, AND THEIR REACTIONS, 61 Obtaining Titration Curve Points from Log Plots, 120 Conjugate Acid-Base Pairs, 61 F. QUANTITATION IN POLYPROTIC SYSTEMS, 124 Relative Strengths of Acids and Bases, 62 Alpha Plots for Polyprotic Systems, 125 Equilibrium Constants, 62 Logarithmic Concentration Diagrams, 127 B. ACIDS AND BASES IN WATER, 64 Titration Curves in Polyprotic Systems, 128 Reactions of Acids with Water, 64 Titrations of Acid Mixtures, 130 Relationship Between [H<sub>3</sub>O<sup>+</sup>] and [OH<sup>-</sup>] in Water, 64 G. OTHER ANALYSES BY ACID-BASE REACTION, 133 Reactions of Bases with Water, 66 Identification by Acid–Base Reactivity, 133 Logarithmic Concentration Expressions, 67 Detection by Acid-Base Reactivity, 134 Other Amphiprotic Solvents, 68 Separation by Acid-Base Reactivity, 134 C. CONCENTRATIONS, ACTIVITIES, AND PH, 70 PRACTICE QUESTIONS AND PROBLEMS, 134 Chemical Potential, 70 Chemical Activity, 72 Activity Coefficients, 74 Chapter 5 Mean Ionic Activities, 77 Analysis by Absorption of Light 138 Activity Coefficients of Neutral Species, 77 D. EQUILIBRIUM CONSTANTS, 79 A. COLORED SOLUTIONS AND WHITE LIGHT, 138 The Equilibrium State, 80 The Wave Nature of Light, 139 Thermodynamic and Formal Equilibrium Constants, 80 The Particle Nature of Light, 140 The Effect of Ionic Strength on  $K'_a$ , 81 Sources of Light, 140 Using Formal Equilibrium Constants, 82 Light Absorbing Solutions, 141 E. PH ELECTRODE AND THE DEFINITION OF PH, 84 B. Measuring the Absorption of Light, 143 The pH Electrode, 84 Developing the Probe, 143 pH Standards, 85 Anticipating the Response to the Probe, 145 The Definition of pH, 85 Detecting the Response to the Probe, 145 The Measurement of pH, 86 Obtaining the Fraction of Light Transmitted, 146 PRACTICE QUESTIONS AND PROBLEMS, 88 C. RELATING LIGHT ABSORPTION TO CONCENTRATION, 148 Rationalizing the Working Curve, 149 Chapter 4 The Absorbance-Concentration Relationship, 150 Analysis by Acid—Base Reactivity Calibration of the Working Curve, 152 D. Instruments for Absorption Measurements, 154 A. EQUILIBRIUM CONCENTRATIONS, 90 Photometers, 154

Spectrometers, 156

Flow Injection Analysis, 157

E. THE ABSORBANCE SPECTRUM, 161

Rationalizing the Absorbance Spectrum, 161

B. Exact Equilibrium Expressions, 95

The Fraction of the Conjugate Pair in Each Form, 91

Solving for [H<sub>3</sub>O<sup>+</sup>] in Solutions of Acids, 92

Solving for [H<sub>3</sub>O<sup>+</sup>] in Solutions of Bases, 93

F. OBTAINING AN ABSORBANCE SPECTRUM, 164 Scanning Spectrometers, 164 Array Detector Spectrometers, 166 Fourier Transform Spectrometers, 167 Attenuated Reflectance Spectroscopy, 169 G. SPECTRAL PRECISION AND ACCURACY, 171	B. EQUILIBRIUM CONCENTRATIONS, 216 Formation of a 1:1 Complex, 216 Solving for Concentrations in Complexation Systems, 218 Formation of Higher Order Complexes, 220 Alpha Plots, 220
H. IDENTIFICATION BY THE ABSORPTION OF LIGHT, 172	C. THE EFFECT OF [H <sub>3</sub> O <sup>+</sup> ] ON COMPLEX EQUILIBRIA, 223
Compound Identification by Spectral Matching, 173 Deduction of Molecular Structure and Composition, 174  I. Separation by the Absorption of Light, 176	Hydrolysis of the Coordination Center, 224 Hydrolysis of the Ligand, 225 Hydrolysis of Ligand and Coordination Center, 227
Mixture Spectra, 176 Resolution by Simultaneous Equations, 176 Study Questions, Section I, 178 PRACTICE QUESTIONS AND PROBLEMS, 179	D. QUANTITATION BY COMPLEXATION TITRATION, 230 Standard Titrants, 230 Titration Curves, 230 Achieving Selectivity with EDTA Titrations, 233
257 moneman evolution of the property of the state of the	E. Equivalence Point Detection, 235
	Indicators, 235
Chapter 6	Displacement Titration, 236 Back Titrations, 237
Analysis by Photon Emission	Specific Ion Electrodes for Equivalence Point
<ul> <li>A. Photon Excitation of Molecular Species, 183 Photon Absorption, 184 Scattering of the Excitation Radiation, 184 Vibrational Relaxation, 185 Molecular Fluorescence, 186 Phosphorescence, 187</li> <li>B. Fluorescence and Phosphorescence</li> <li>Spectrometry, 188</li> </ul>	Detection, 237 Light Absorption for Equivalence Point Detection, 237 F. Log Concentration Plots, 241 1:1 Complex Formation, 241 Stepwise Complex Formation Systems, 243 Prediction of Titration Curves, 244 G. Spot Tests, Test Strips, Flow Injection Analysis, AND IMMUNOASSAYS, 247
Quantitation, 190	Spot Tests, 247 Test Strips, 248
Excitation and Emission Spectra, 192 Phosphorescence Measurements, 194	Flow Injection Analysis, 248
C. RAMAN SPECTROMETRY, 195	Immunoassays, 249
D. Excitation from Chemical Reactivity, 198 Chemiluminescence Measurements, 199	Practice Questions and Problems, 250
Chemiluminescence Applications, 199	Chapter 8
E. THERMAL EXCITATION AND ATOMIC EMISSION, 201 Flame Excitation, 203 Plasma Excitation, 204	Analysis by Precipitation Reactivity 25
Creating the Aerosol, 206	A. Precipitation Reactions, 253
F. PHOTON EXCITATION OF ATOMIC SPECIES, 207 Flames for use with Photon Excitation, 208 Furnaces for Sample Atomization, 208	The Equilibrium Expressions, 254 The Crystallization of Precipitates, 255 The Nucleation of Precipitates, 257

# Chapter 7 Analysis by Complexation Reactivity 214

Atomic Fluorescence Spectroscopy, 208

PRACTICE QUESTIONS AND PROBLEMS, 211

Atomic Absorption Spectroscopy, 209

A. Complexation Reactions, 214
Bonds Formed in Complexation, 215
Complexing Species, 215
Reaction Rates, 215

Chapter 8

Analysis by Precipitation Reactivity

A. Precipitation Reactions, 253
The Equilibrium Expressions, 254
The Crystallization of Precipitates, 255
The Nucleation of Precipitates, 257

B. Equilibrium Concentrations, 259
Simple Solubility Calculations, 259
Effect of Hydrolysis on Solubility, 259
Effect of Complexation on Solubility, 261

C. Quantitation by Precipitation Titration, 262
Frequently Used Reactions, 243
Titration Curves, 262
Equivalence Point Detection, 265

D. Logarithmic concentration plots, 267

Unsymmetrical Log Plots, 269

Estimation of Titration Curves, 271

E. SEPARATION BY PRECIPITATION, 275

xviii CONTENTS

F. QUANTITATION BY WEIGHING THE PRECIPITATE, 277 G. SPOT TESTS AND TEST STRIPS, 279 PRACTICE QUESTIONS AND PROBLEMS, 280	Chapter 10 Analysis by Oxidation—Reduction Reactivity 319
Chapter 9 Analysis by Electrode Potential 282	A. OXIDATION–REDUCTION REACTIONS, 319 Combining Electron Half-Reactions, 320 Balancing Complete Redox Reactions, 321 Equilibrium Constants for Redox Reactions, 322 Formal and Thermodynamic Equilibrium Constants, 323
A. ELECTRON EXCHANGE AT METALS, 282 The Equilibrium Potential Difference, 283 Metal-Solution Potentials from Two Related Ionic Species, 285	B. EQUILIBRIUM CONCENTRATIONS, 324 Approximation Method for Equilibrium Concentrations, 325 Algebraic Method for Equilibrium Calculations, 326
B. CALCULATING REDOX EQUILIBRIUM ELECTRODE POTENTIALS, 288 Formal and Thermodynamic Standard Potentials, 289 Relating Redox Concentrations to Equilibrium Potentials, 290 The pH Dependence of Equilibrium Potentials, 290	C. QUANTITATION BY REDOX TITRATION, 327 Titration with Ce(IV), 328 Assuring Analyte Oxidation State Before Titration, 328 Titration Curves, 329 Multiple Equivalence Point Titrations, 331 Equivalence Point Detection, 332
The Hydrogen Electrode, 291  C. MEASUREMENT OF ELECTRODE POTENTIALS, 293 The Necessity of a Reference Electrode, 293 Calculating the Expected Measurement Voltage, 294 Relating Electrode Voltage to Activity and Concentration, 295 Electrodes of the Second Kind, 296	<ul> <li>D. Iodine and Thiosulfate, 334</li> <li>E. Log Concentration Plots, 337</li> <li>Redox Log Plots with a Constant Activity Reactant, 338</li> <li>Log Plots with Asymmetry and pH Complications, 339</li> <li>The Iodine, Iodide System, 340</li> <li>Points on Titration Curves from Log Concentration Plots, 341</li> </ul>
D. Log Concentration Plots for Redox Couples, 298 Lines for the Case Where Ox and Red are Dissolved, 299 Lines for the Case Where Only Ox or Red is Dissolved, 299 Lines for Secondary Reaction Species, 300 Using Log Plots for Cell Equilibrium Potentials, 300 Log Plots of Unsymmetrical Couples, 301	F. KARL FISCHER TITRATION FOR WATER, 345 G. QUANTITATION BY ELECTROLYTIC REDOX REACTION, 347 Electrolytic Reactions, 347 Coulombs and Moles, 349 Coulometry, 350 H. ELECTROGRAVIMETRY, 353 I. COULOMETRIC TITRATION, 356
E. Ion Reactions on Membrane Surfaces, 304 H <sup>+</sup> Reaction with a Glass Surface, 305 Calculation of the Interfacial Potential, 305 Measurement of Interfacial Potential, 306 Use of the Measured Voltage to Calculate pH, 307 Transistor Chemical Sensors, 307 Interfering Electrode Reactions, 308	J. DIFFUSION-LIMITED ELECTRODES, 359 K. TEST STRIPS, SPOT TESTS AND FIA, 361 PRACTICE QUESTIONS AND PROBLEMS, 362  Chapter 11 Analysis by Interphase Partition 365
Gas-sensing Electrodes, 308  The Use of Ion-Surface Interactions for Ions Other than H <sup>+</sup> , 309  F. Ion Diffusion Through Porous Membranes, 311  Development of Electrical Potential Difference, 312  Measurement of Membrane Potential, 312  Electrode Types and Interferents, 313	A. THE LIQUID-LIQUID INTERFACE: EXTRACTION, 366 B. THE GAS-LIQUID INTERFACE: DISTILLATION, 371 C. THE GAS-Solid Interface: Adsorption, 375 Adsorption Isotherms, 376 Solid Phase Extraction, 377 D. Continuous Partition: Chromatography, 378

Liquid Junction Potentials, 314

The Equivalence of Response Function for all

G. SELECTIVITY AND DETECTION WITH

PRACTICE QUESTIONS AND PROBLEMS, 316

Electrodes, 315

ELECTRODES, 316

D. CONTINUOUS PARTITION: CHROMATOGRAPHY, 378

The Fraction of Time Spent in Each Phase, 379

Moving One of the Phases, 379

E. GAS CHROMATOGRAPHY, 385

Effect of Mobile Phase Flow Rate, 383

Measures of Effectiveness, 381

The Instrument, 386

F. Quantitation by Weighing the Precipitate, 277 G. Spot Tests and Test Strips, 279 Practice Questions and Problems, 280	Chapter 10 Analysis by Oxidation—Reduction Reactivity 319
Chapter 9 Analysis by Electrode Potential 282	A. OXIDATION–REDUCTION REACTIONS, 319 Combining Electron Half-Reactions, 320 Balancing Complete Redox Reactions, 321 Equilibrium Constants for Redox Reactions, 322 Formal and Thermodynamic Equilibrium Constants, 323
A. ELECTRON EXCHANGE AT METALS, 282 The Equilibrium Potential Difference, 283 Metal-Solution Potentials from Two Related Ionic Species, 285	B. EQUILIBRIUM CONCENTRATIONS, 324 Approximation Method for Equilibrium Concentrations, 325 Algebraic Method for Equilibrium Calculations, 326
B. CALCULATING REDOX EQUILIBRIUM ELECTRODE POTENTIALS, 288 Formal and Thermodynamic Standard Potentials, 289 Relating Redox Concentrations to Equilibrium Potentials, 290 The pH Dependence of Equilibrium Potentials, 290	C. QUANTITATION BY REDOX TITRATION, 327 Titration with Ce(IV), 328 Assuring Analyte Oxidation State Before Titration, 328 Titration Curves, 329 Multiple Equivalence Point Titrations, 331 Equivalence Point Detection, 332
The Hydrogen Electrode, 291  C. MEASUREMENT OF ELECTRODE POTENTIALS, 293 The Necessity of a Reference Electrode, 293 Calculating the Expected Measurement Voltage, 294 Relating Electrode Voltage to Activity and Concentration, 295 Electrodes of the Second Kind, 296	<ul> <li>D. Iodine and Thiosulfate, 334</li> <li>E. Log Concentration Plots, 337</li> <li>Redox Log Plots with a Constant Activity Reactant, 338</li> <li>Log Plots with Asymmetry and pH Complications, 339</li> <li>The Iodine, Iodide System, 340</li> <li>Points on Titration Curves from Log Concentration Plots, 341</li> </ul>
D. Log Concentration Plots for Redox Couples, 298 Lines for the Case Where Ox and Red are Dissolved, 299 Lines for the Case Where Only Ox or Red is Dissolved, 299 Lines for Secondary Reaction Species, 300 Using Log Plots for Cell Equilibrium Potentials, 300 Log Plots of Unsymmetrical Couples, 301	F. Karl Fischer Titration for Water, 345 G. Quantitation by Electrolytic Redox Reaction, 347 Electrolytic Reactions, 347 Coulombs and Moles, 349 Coulometry, 350 H. Electrogravimetry, 353 I. Coulometric Titration, 356
E. Ion Reactions on Membrane Surfaces, 304 H <sup>+</sup> Reaction with a Glass Surface, 305 Calculation of the Interfacial Potential, 305 Measurement of Interfacial Potential, 306 Use of the Measured Voltage to Calculate pH, 307 Transistor Chemical Sensors, 307 Interfering Electrode Reactions, 308	J. DIFFUSION-LIMITED ELECTRODES, 359 K. TEST STRIPS, SPOT TESTS AND FIA, 361 PRACTICE QUESTIONS AND PROBLEMS, 362  Chapter 11 Analysis by Interphase Partition 361
Gas-sensing Electrodes, 308  The Use of Ion-Surface Interactions for Ions Other than H <sup>+</sup> , 309  F. Ion Diffusion Through Porous Membranes, 311  Development of Electrical Potential Difference, 312  Measurement of Membrane Potential, 312  Electrode Types and Interferents, 313  Liquid Junction Potentials, 314	<ul> <li>A. The Liquid-Liquid Interface: Extraction, 366</li> <li>B. The Gas-Liquid Interface: Distillation, 371</li> <li>C. The Gas-Solid Interface: Adsorption, 375</li></ul>

Moving One of the Phases, 379

Measures of Effectiveness, 381

The Instrument, 386

Effect of Mobile Phase Flow Rate, 383

E. GAS CHROMATOGRAPHY, 385

The Equivalence of Response Function for all

G. SELECTIVITY AND DETECTION WITH

PRACTICE QUESTIONS AND PROBLEMS, 316

Electrodes, 315

ELECTRODES, 316

Sample Injection, 387	
The Column, 388	
The Detector, 388	
The General Elution Problem, 390	
Peak Overlap, 391	
Information Obtained from Gas Chromatograms,	391
1952 N. H. G. S. S. B. G. S.	

- F. High-Performance Liquid Chromatography, 393 The HPLC System, 393 Partition Chromatography, 395
- G. Variations on the Chromatographic Theme, 396 Planar Chromatography, 397
- H. Mass Spectrometric Detection, 398
- I. Multichannel Chromatographic Detection, 399
  Practice Questions and Problems, 400

### Chapter 12 Analysis by Biochemical Reactivity

403

- A. Enzyme Reactivity, 404
  Varieties of Enzymes and Reactivity, 405
  Enzyme Activation and Inhibition, 406
  The Effect of pH, 406
  Enzyme Stability, 408
- B. KINETICS OF ENZYME REACTIONS, 409 First-Order Reaction Rates, 410 Enzyme-Catalyzed Reactions, 410 The Michaelis-Menten Equation, 412 Analytical Significance of  $K_{\rm M}$  and  $K_{\rm cat}$ , 413
- C. KINETIC METHODS OF ANALYSIS, 416
   Continuous Flow Methods, 416
   Stopped Flow Methods, 417
   Quenching Methods, 418
   Applications of Kinetic Analysis with Enzymes, 418
- D. Antigen–Antibody Reactivity, 420
  Antibodies and Their Generation, 421
  Detecting the Antibody-Antigen Reaction, 422
- E. IMMOBILIZED ENZYMES AND ANTIBODIES, 424 Bonding Biochemical Reagents, 424 Containing Biochemical Reagents, 425
- F. SEPARATION WITH BIOCHEMICAL REACTIONS, 426
  Separation on the Basis of Size, 426
  Separation on the Basis of Complexation Reactivity, 428
  Separation on the Basis of Mass and Density, 430
- G. IMMUNOASSAY, 434
  Direct Binding Reactions, 434
  Competitive Binding Reactions, 436
  Enzyme-Linked Immunosorbent Assay (ELISA), 438
  Enzyme Multiplied Immunoassay Technique
  (EMIT), 439

Applications of Immunoassay, 440

H. BIOCHEMICALLY BASED SENSORS, 441
Photon Emission Sensors, 441
Photon Absorption Sensors, 442

Electrode Potential Sensors, 443
Electrode Current Sensors, 444
PRACTICE QUESTIONS AND PROBLEMS, 446

### **Background Materials**

449

- A. STOICHIOMETRIC RATIOS IN CHEMICAL COMPOUNDS AND REACTIONS, 449 Molecular Formulas, 449 Reaction Stoichiometry, 449 Ionic Reactions, 450 Combining Quantities, 450
- Logarithms, 452
  Antilogarithms, 453
  "p" Units, 453
  Logarithmic Scales, 454
  Natural Logarithms, 454
  Operations with Exponents, 455
  Addition and Subtraction, 455
  Multiplication and Division, 455
  Operations with Logarithms, 455

B. Logarithms and Exponents, 452

C. ELECTRICAL QUANTITIES AND THEIR RELATIONSHIPS, 456
Electrical Conductors and Insulators, 456
Separation of Charge, 457
Electrical Current, 457
Electrical Capacitance, 458
Electrical Signals, 458

#### **Appendices**

461

- A. Tables of Activity Coefficients and  $a_x$ , 461
  - Calculated Values of Acitivity Coefficient Using the DHE, 461
  - 2. Table of Ion Size Parameters, **a**<sub>X</sub>, for Inorganic Ions, 462
  - 3. Table of Ion Size Parameters,  $\mathbf{a}_{X}$ , for Organic Ions, 462
- B.  $K_a^{\circ}$  Values for Weak Acids in Water, 463
- C. Table of Complex Formation  $(K_f^{\circ} \text{ and } K_f')$ Values, 468
- D.  $K_{sp}^{\circ}$  AND  $K_{sp}'$  VALUES FOR SOME PRECIPITATES, 472
- E. STANDARD REDUCTION POTENTIALS, 474
- F. INTERNATIONAL ATOMIC WEIGHTS, 476
- G. USEFUL CONSTANTS AND CONVERSIONS, 478 Prefixes for Units and their Multiplication Factors, 479
- H. TECHNIQUES DISCUSSED AND THEIR LOCATION, 480