

Contents

Chapter 1 The Nature of Analytical Chemistry 1

- 1A The Role of Analytical Chemistry 2
- 1B Quantitative Analytical Methods 4
- 1C A Typical Quantitative Analysis 4
- 1D An Integral Role for Chemical Analysis:
Feedback Control Systems 9
- Feature 1-1** Deer Kill: A Case Study Illustrating the Use
of Analytical Chemistry to Solve a Problem
in Toxicology 10

PART I TOOLS OF ANALYTICAL CHEMISTRY 14

Chapter 2 Chemicals, Apparatus, and Unit Operations of Analytical Chemistry 15

- 2A Selecting and Handling Reagents
and Other Chemicals 16
- 2B Cleaning and Marking
of Laboratory Ware 17
- 2C Evaporating Liquids 18
- 2D Measuring Mass 18
- 2E Equipment and Manipulations
Associated with Weighing 25
- 2F Filtration and Ignition of Solids 28
- 2G Measuring Volume 34
- 2H Calibrating Volumetric Glassware 43
- 2I The Laboratory Notebook 45
- 2J Safety in the Laboratory 46

Chapter 3 Using Spreadsheets in Analytical Chemistry 48

- 3A Keeping Records and Making Calculations 49
- 3B More Complex Examples 52

Chapter 4 Calculations Used in Analytical Chemistry 62

- 4A Some Important Units of Measurement 62
- Feature 4-1** Unified Atomic Mass Units and the Mole 65
- Feature 4-2** The Factor-Label Approach
to Example 4-2 67
- 4B Solutions and Their Concentrations 67
- 4C Chemical Stoichiometry 75

Chapter 5 Errors in Chemical Analyses 82

- 5A Some Important Terms 84
- 5B Systematic Errors 87

Chapter 6 Random Errors in Chemical Analysis 93

- 6A The Nature of Random Errors 93
- Feature 6-1** Flipping Coins: A Student Activity to Illustrate a
Normal Distribution 97
- 6B Statistical Treatment of Random Errors 98
- Feature 6-2** Calculating the Areas under the Gaussian
Curve 101
- Feature 6-3** The Significance of the Number of Degrees of
Freedom 104
- Feature 6-4** Equation for Calculating the Pooled Standard
Deviation 107
- 6C Standard Deviation of Calculated Results 110
- 6D Reporting Computed Data 115

Chapter 7 Statistical Data Treatment and Evaluation 123

- 7A Confidence Intervals 124
- Feature 7-1** W. S. Gossett ("Student") 127
- 7B Statistical Aids to Hypothesis Testing 129
- 7C Analysis of Variance 140
- 7D Detection of Gross Errors 146

Chapter 8 Sampling, Standardization, and Calibration 153

- 8A Analytical Samples and Methods 153
- 8B Sampling 156
- 8C Automated Sample Handling 164
- 8D Standardization and Calibration 167
- Feature 8-1** Lab-on-a-Chip 168
- Feature 8-2** A Comparison Method for Aflatoxins 169
- Feature 8-3** Multivariate Calibration 180
- 8E Figures of Merit for Analytical Methods 186

PART II CHEMICAL EQUILIBRIA 196

Chapter 9 Aqueous Solutions and Chemical Equilibria 197

- 9A The Chemical Composition of Aqueous Solutions 197
- 9B Chemical Equilibrium 202
- Feature 9-1** Stepwise and Overall Formation Constants for
Complex Ions 205
- Feature 9-2** Why $[H_2O]$ Does Not Appear in Equilibrium-
Constant Expressions for Aqueous Solutions 206
- Feature 9-3** Relative Strengths of Conjugate Acid/Base Pairs 212
- Feature 9-4** The Method of Successive Approximations 217
- 9C Buffer Solutions 219

CONTENTS

- Feature 9-5 The Henderson-Hasselbalch Equation 221
Feature 9-6 Acid Rain and the Buffer Capacity of Lakes 227

Chapter 10 Effect of Electrolytes on Chemical Equilibria 235

- 10A The Effect of Electrolytes on Chemical Equilibria 235
10B Activity Coefficients 239
Feature 10-1 Mean Activity Coefficients 242

Chapter 11 Solving Equilibrium Problems for Complex Systems 249

- 11A Solving Multiple-Equilibrium Problems Using a Systematic Method 250
11B Calculating Solubilities by the Systematic Method 256
Feature 11-1 Algebraic Expressions Needed to Calculate the Solubility of CaC_2O_4 in Water 262
11C Separation of Ions by Control of the Concentration of the Precipitating Agent 268
Feature 11-2 Immunoassay: Equilibria in the Specific Determination of Drugs 272

PART III CLASSICAL METHODS OF ANALYSIS 279

Chapter 12 Gravimetric Methods of Analysis 280

- 12A Precipitation Gravimetry 280
Feature 12-1 Specific Surface Area of Colloids 287
12B Calculation of Results from Gravimetric Data 291
12C Applications of Gravimetric Methods 294

Chapter 13 Titrations in Analytical Chemistry 302

- 13A Some Terms Used in Volumetric Titrations 303
13B Standard Solutions 305
13C Volumetric Calculations 306
Feature 13-1 Another Approach to Example 13-6(a) 311
Feature 13-2 Rounding the Answer to Example 13-7 312
13D Gravimetric Titrations 314
13E Titration Curves 315
Feature 13-3 Calculating the NaOH Volumes Shown in the First Column of Table 13-1 317

Chapter 14 Principles of Neutralization Titrations 322

- 14A Solutions and Indicators for Acid/Base Titrations 322
14B Titration of Strong Acids and Bases 326
Feature 14-1 Using the Charge-balance Equation to Construct Titration Curves 328
Feature 14-2 Significant Figures in Titration Curve Calculations 331
14C Titration Curves for Weak Acids 332
Feature 14-3 Determining Dissociation Constants of Weak Acids and Bases 334
Feature 14-4 A Master Equation Approach to Weak Acid/Strong Base Titrations 336
14D Titration Curves for Weak Bases 337
Feature 14-5 Determining the pK Values for Amino Acids 339
14E The Composition of Solutions During Acid/Base Titrations 341
Feature 14-6 Locating Titration End Points from pH Measurements 342

Chapter 15 Complex Acid/Base Systems 348

- 15A Mixtures of Strong and Weak Acids or Strong and Weak Bases 348
15B Polyfunctional Acids and Bases 352
15C Buffer Solutions Involving Polyprotic Acids 354
15D Calculation of the pH of Solutions of NaHA 356
15E Titration Curves for Polyfunctional Acids 360
Feature 15-1 The Dissociation of Sulfuric Acid 368
15F Titration Curves for Polyfunctional Bases 369
15G Titration Curves for Amphoteric Species 371
Feature 15-2 Acid/Base Behavior of Amino Acids 371
15H Composition of Polyprotic Acid Solutions as a Function of pH 373
Feature 15-3 A General Expression for Alpha Values 374
Feature 15-4 Logarithmic Concentration Diagrams 375

Chapter 16 Applications of Neutralization Titrations 381

- 16A Reagents for Neutralization Titrations 382
16B Typical Applications of Neutralization Titrations 387
Feature 16-1 Determining Total Serum Protein 388
Feature 16-2 Other Methods for Determining Organic Nitrogen 388
Feature 16-3 Equivalent Masses of Acids and Bases 394

Chapter 17 Complexation and Precipitation Reactions and Titrations 400

- 17A The Formation of Complexes 400
Feature 17-1 Calculation of Alpha Values for Metal Complexes 403
17B Titrations with Inorganic Complexing Agents 406
Feature 17-2 Determination of Hydrogen Cyanide in Acrylonitrile Plant Streams 407
17C Organic Complexing Agents 413
17D Aminocarboxylic Acid Titrations 414
Feature 17-3 Species Present in a Solution of EDTA 415
Feature 17-4 EDTA as a Preservative 418
Feature 17-5 EDTA Titration Curves When a Complexing Agent Is Present 428
Feature 17-6 Enhancing the Selectivity of EDTA Titrations with Masking and Demasking Agents 435
Feature 17-7 Test Kits for Water Hardness 436

PART IV ELECTROCHEMICAL METHODS 441

Chapter 18 Introduction to Electrochemistry 442

- 18A Characterizing Oxidation/Reduction Reactions 442
Feature 18-1 Balancing Redox Equations 444
18B Electrochemical Cells 446
Feature 18-2 The Daniell Gravity Cell 450
18C Electrode Potentials 451
Feature 18-3 Why We Cannot Measure Absolute Electrode Potentials 456
Feature 18-4 Sign Conventions in the Older Literature 464
Feature 18-5 Why Are There Two Electrode Potentials for Br_2 in Table 18-1? 466

Chapter 19 Applications of Standard Electrode Potentials 473

- 19A Calculating Potentials of Electrochemical Cells 473
- 19B Determining Standard Potentials Experimentally 480

Feature 19-1 Biological Redox Systems 482

- 19C Calculating Redox Equilibrium Constants 482

Feature 19-2 A General Expression for Calculating Equilibrium Constants from Standard Potentials 487

- 19D Constructing Redox Titration Curves 488

Feature 19-3 The Inverse Master Equation Approach for Redox Titration Curves 497

Feature 19-4 Reaction Rates and Electrode Potentials 502

- 19E Oxidation/Reduction Indicators 502

- 19F Potentiometric End Points 505

Chapter 20 Applications of Oxidation/Reduction Titrations 509

- 20A Auxiliary Oxidizing and Reducing Reagents 509

- 20B Applying Standard Reducing Agents 511

- 20C Applying Standard Oxidizing Agents 515

Feature 20-1 Determination of Chromium Species in Water Samples 517

Feature 20-2 Antioxidants 522

Chapter 21 Potentiometry 535

- 21A General Principles 536

- 21B Reference Electrodes 537

- 21C Liquid-Junction Potentials 539

- 21D Indicator Electrodes 540

Feature 21-1 An Easily Constructed Liquid-Membrane Ion-Selective Electrode 552

Feature 21-2 The Structure and Performance of Ion-Sensitive Field Effect Transistors 554

Feature 21-3 Point-of-Care Testing: Blood Gases, and Blood Electrolytes with Portable Instrumentation 558

- 21E Instruments for Measuring Cell Potential 560

Feature 21-4 The Loading Error in Potential Measurements 560

Feature 21-5 Operational Amplifier Voltage Measurements 562

- 21F Direct Potentiometry 563

- 21G Potentiometric Titrations 569

- 21H Potentiometric Determination of Equilibrium Constants 573

Chapter 22 Bulk Electrolysis: Electrogravimetry and Coulometry 578

- 22A The Effect of Current on Cell Potential 579

Feature 22-1 Overvoltage and the Lead/Acid Battery 586

- 22B The Selectivity of Electrolytic Methods 586

- 22C Electrogravimetric Methods 588

- 22D Coulometric Methods 594

Feature 22-2 Coulometric Titration of Chloride in Biological Fluids 603

Chapter 23 Voltammetry 610

- 23A Excitation Signals in Voltammetry 611

- 23B Voltammetric Instrumentation 612

Feature 23-1 Voltammetric Instruments Based on Operational Amplifiers 613

- 23C Hydrodynamic Voltammetry 618

- 23D Polarography 633

- 23E Cyclic Voltammetry 635

- 23F Pulse Voltammetry 639

- 23G Applications of Voltammetry 642

- 23H Stripping Methods 643

- 23I Voltammetry with Microelectrodes 645

PART V SPECTROCHEMICAL ANALYSIS 649

Chapter 24 Introduction to Spectrochemical Methods 650

- 24A Properties of Electromagnetic Radiation 651

- 24B Interaction of Radiation and Matter 654

Feature 24-1 Spectroscopy and the Discovery of Elements 657

- 24C Absorption of Radiation 658

Feature 24-2 Deriving Beer's Law 660

Feature 24-3 Why Is a Red Solution Red? 665

- 2D Emission of Electromagnetic Radiation 674

Chapter 25 Instruments for Optical Spectrometry 683

- 25A Instrument Components 683

Feature 25-1 Laser Sources: The Light Fantastic 687

Feature 25-2 Origin of Equation 25-1 693

Feature 25-3 Producing Ruled and Holographic Gratings 695

Feature 25-4 Basis of Equation 25-2 698

Feature 25-5 Signals, Noise, and the Signal-to-Noise Ratio 700

Feature 25-6 Measuring Photocurrents with Operational Amplifiers 708

- 25B Ultraviolet/Visible Photometers and Spectrophotometers 710

- 25C Infrared Spectrophotometers 713

Feature 25-7 How Does a Fourier Transform Infrared Spectrometer Work? 715

Chapter 26 Molecular Absorption Spectrometry 722

- 26A Ultraviolet and Visible Molecular Absorption Spectroscopy 722

- 26B Automated Photometric and Spectrophotometric Methods 744

- 26C Infrared Absorption Spectroscopy 746

Feature 26-1 Producing Spectra with an FTIR Spectrometer 751

Chapter 27 Molecular Fluorescence Spectroscopy 760

- 27A Theory of Molecular Fluorescence 760

- 27B Effect of Concentration on Fluorescence Intensity 764

- 27C Fluorescence Instrumentation 765

- 27D Applications of Fluorescence Methods 766

Feature 27-1 Use of Fluorescence Probes in Neurobiology: Probing the Enlightened 767

- 27E Molecular Phosphorescence Spectroscopy 769

- 27F Chemiluminescence Methods 770

Chapter 28 Atomic Spectroscopy 773

- 28A Origins of Atomic Spectra 774
- 28B Production of Atoms and Ions 776
- 28C Atomic Emission Spectrometry 786
- 28D Atomic Absorption Spectrometry 790
- Feature 28-1** Determining Mercury by Cold-Vapor Atomic Absorption Spectroscopy 797
- 28E Atomic Fluorescence Spectrometry 799

Chapter 29 Mass Spectrometry 802

- 29A Principles of Mass Spectrometry 802
- 29B Mass Spectrometers 804
- 29C Atomic Mass Spectrometry 808
- 29D Molecular Mass Spectrometry 811

PART VI KINETICS AND SEPARATIONS 818

Chapter 30 Kinetic Methods of Analysis 819

- 30A Rates of Chemical Reactions 820
- Feature 30-1** Enzymes 827
- 30B Determining Reaction Rates 833
- Feature 30-2** Fast Reactions and Stopped-Flow Mixing 833
- 30C Applications of Kinetic Methods 840
- Feature 30-3** The Enzymatic Determination of Urea 842

Chapter 31 Introduction to Analytical Separations 847

- 31A Separation by Precipitation 848
- 31B Separation of Species by Distillation 852
- 31C Separation by Extraction 852
- Feature 31-1** Derivation of Equation 31-3 854
- 31D Separating Ions by Ion Exchange 857
- Feature 31-2** Home Water Softeners 860
- 31E Chromatographic Separations 861
- Feature 31-3** What Is the Source of the Terms *Plate* and *Plate Height*? 871
- Feature 31-4** Derivation of Equation 31-24 872

Chapter 32 Gas Chromatography 887

- 32A Instruments for Gas-Liquid Chromatography 888
- 32B Gas Chromatographic Columns and Stationary Phases 897
- 32C Applications of Gas-Liquid Chromatography 901
- Feature 32-1** Use of GC/MS to Identify a Drug Metabolite in Blood 903
- 32D Gas-Solid Chromatography 909

Chapter 33 High-Performance Liquid Chromatography 912

- 33A Instrumentation 913
- Feature 33-1** LC/MS and LC/MS/MS 920
- 33B Partition Chromatography 921
- 33C Adsorption Chromatography 924
- 33D Ion Chromatography 925
- 33E Size-Exclusion Chromatography 927
- Feature 33-2** Buckyballs: The Chromatographic Separation of Fullerenes 929
- 33F Affinity Chromatography 931
- 33G Chiral Chromatography 931
- 33H Comparison of High-Performance Liquid Chromatography and Gas Chromatography 932

Chapter 34 Miscellaneous Separation Methods 935

- 34A Supercritical Fluid Separations 935
- 34B Planar Chromatography 940
- 34C Capillary Electrophoresis 942
- Feature 34-1** Capillary Array Electrophoresis in DNA Sequencing 949
- 34D Capillary Electrochromatography 949
- 34E Field-Flow Fractionation 952

PART VII PRACTICAL ASPECTS OF CHEMICAL ANALYSIS 959

The following chapters are available as Adobe Acrobat® PDF files at www.cengage.com/chemistry/skoog/fac9.

Chapter 35 The Analysis of Real Samples 960

- 35A Real Samples 960
- 35B Choice of Analytical Method 962
- 35C Accuracy in the Analysis of Complex Materials 967

Chapter 36 Preparing Samples for Analysis 970

- 36A Preparing Laboratory Samples 970
- 36B Moisture in Samples 972
- 36C Determining Water in Samples 975

Chapter 37 Decomposing and Dissolving the Sample 976

- 37A Sources of Error in Decomposition and Dissolution 977
- 37B Decomposing Samples with Inorganic Acids in Open Vessels 977
- 37C Microwave Decompositions 979
- 37D Combustion Methods for Decomposing Organic Samples 982
- 37E Decomposing Inorganic Materials with Fluxes 984

Chapter 38 Selected Methods of Analysis 986

- 38A An Introductory Experiment 987
- 38B Gravimetric Methods of Analysis 996
- 38C Neutralization Titrations 1000
- 38D Precipitation Titrations 1009
- 38E Complex-Formation Titrations with EDTA 1012
- 38F Titrations with Potassium Permanganate 1015
- 38G Titrations with Iodine 1021
- 38H Titrations with Sodium Thiosulfate 1023
- 38I Titrations with Potassium Bromate 1026
- 38J Potentiometric Methods 1028
- 38K Electrogravimetric Methods 1032
- 38L Coulometric Titrations 1034
- 38M Voltammetry 1036
- 38N Methods Based on the Absorption of Radiation 1038
- 38O Molecular Fluorescence 1042
- 38P Atomic Spectroscopy 1043
- 38Q Application of Ion-Exchange Resins 1046
- 38R Gas-Liquid Chromatography 1048

CONTENTS

Glossary G-1

APPENDIX 1 The Literature of Analytical Chemistry A-1

APPENDIX 2 Solubility Product Constants at 25°C A-6

APPENDIX 3 Acid Dissociation Constants at 25°C A-8

APPENDIX 4 Formation Constants at 25°C A-10


APPENDIX 5 Standard and Formal Electrode Potentials A-12

APPENDIX 6 Use of Exponential Numbers and Logarithms A-15

APPENDIX 7 Volumetric Calculations Using Normality and Equivalent Weight A-19

APPENDIX 8 Compounds Recommended for the Preparation of Standard Solutions of Some Common Elements A-27

APPENDIX 9 Derivation of Error Propagation Equations A-29

 *Answers to Selected Questions and Problems* A-34

Index I-1