CONTENTS

Chapter 1 The Nature of Analytical Chemistry 2 1A The Role of Analytical Chemistry 3 1B Quantitative Analytical Methods 4 1C A Typical Quantitative Analysis 5	Chapter 5 Errors in Chemical Analyses 90 5A Some Important Terms 92 5B Systematic Errors 95
1D An Integral Role for Chemical Analysis: Feedback Control Systems 10 Feature 1-1 Deer Kill: A Case Study Illustrating the Use of Analytical Chemistry to Solve a Problem in Toxicology 12	Chapter 6 Random Errors in Chemical Analysis 105 6A The Nature of Random Errors 105 Feature 6-1 Flipping Coins: A Student Activity to Illustrate a Normal Distribution 109 6B Statistical Treatment of Random Error 110 Feature 6-2 Calculating the Areas under the Gaussian
PART I Tools of Analytical Chemistry 17 A Conversation with Richard N. Zare 18	Feature 6-3 The Significance of the Number of Degrees of Freedom 116
Chapter 2 Chemicals, Apparatus, and Unit Operations of Analytical Chemistry 20 2A Selecting and Handling Reagents and Other	Feature 6-4 Equation for Calculating the Pooled Standard Deviation 124 6C Standard Deviation of Calculated Results 127 6D Reporting Computed Data 133
Chemicals 21 2B Cleaning and Marking of Laboratory Ware 22 2C Evaporating Liquids 23 2D Measuring Mass 23 2E Equipment and Manipulations Associated with Weighing 30 2F Filtration and Ignition of Solids 33	Chapter 7 Statistical Data Treatment and Evaluation 142 7A Confidence Intervals 143 Feature 7-1 Breath Alcohol Analyzers 148 7B Statistical Aids to Hypothesis Testing 149 7C Analysis of Variance 160
2G Measuring Volume 39 2H Calibrating Volumetric Glassware 48 2l The Laboratory Notebook 51 2J Safety in the Laboratory 52	7D Detection of Gross Errors 167 Chapter 8 Sampling, Standardization, and Calibration 175 8A Analytical Samples and Methods 175
Chapter 3 Using Spreadsheets in Analytical Chemistry 54 3A Keeping Records and Making Calculations: Spreadsheet Exercise 1 55	8B Sampling and Sample Handling 178 Feature 8-1 Lab-on-a-Chip 191 8C Standardization and Calibration 192 Feature 8-2 A Comparison Method for Aflatoxins 192
3B Calculating Molar Masses Using Excel: Spreadsheet Exercise 2 60	Feature 8-3 Multivariate Calibration 208 8D Figures of Merit for Analytical Methods 214
Chapter 4 Calculations Used in Analytical Chemistry 71	PART II Chemical Equilibria 225
4A Some Important Units of Measurement 71 Feature 4-1 Atomic Mass Units and the Mole 73	A Conversation with Sylvia Daunert 226
4B Solutions and Their Concentrations 764C Chemical Stoichiometry 83	Chapter 9 Aqueous Solutions and Chemical Equilibria 228

9A The Chemical Compositions of Aqueous Solutions 228	13C Volumetric Calculations 341	
9B Chemical Equilibrium 233	Feature 13-1 Another Approach to Example 13-6(a) 346	
Feature 9-1 Stepwise and Overall Formation Constants	Feature 13-2 Rounding the Answer to	
for Complex Ions 236	Example 13-7 347	
Feature 9-2 Why [H ₂ 0] Does Not Appear in Equilibrium-	13D Gravimetric Titrimetry 349	
Constant Expressions for Aqueous	13E Titration Curves in Titrimetric Methods 350	
Solutions 237	13F Precipitation Titrimetry 353	
Feature 9-3 Relative Strengths of Conjugate Acid/Base Pairs 244	Feature 13-3 Calculating the Concentration of Indicator Solutions 361	
Feature 9-4 The Method of Successive		
Approximations 248	Chapter 14 Principles of Neutralization Titrations 368	
9C Buffer Solutions 251	14A Solutions and Indicators for Acid/Base	
Feature 9-5 The Henderson-Hasselbalch Equation 252	Titrations 368	
Feature 9-6 Acid Rain and the Buffer Capacity of	14B Titration of Strong Acids and Strong Bases 372	
Lakes 259	Feature 14-1 Using the Charge-Balance Equation to Construct Titration Curves 375	
Chapter 10 Effect of Electrolytes on Chemical Equilibria 267	Feature 14-2 How Many Significant Figures Should We Retain in Titration Curve	
10A The Effect of Electrolytes on Chemical	Calculations? 378	
Equilibria 267	14C Titration Curves for Weak Acids 378	
10B Activity Coefficients 271	Feature 14-3 Determining Dissociation Constants for Weak Acids and Bases 381	
Feature 10-1 Mean Activity Coefficients 274	14D Titration Curves for Weak Bases 383	
GI . 44 G	Feature 14-4 Determining the pK Values for Amino	
Chapter 11 Solving Equilibrium Calculations for Complex Systems 281	Acids 385	
11A Solving Multiple-Equilibrium Problems by a Systematic Method 282	14E The Composition of Solutions During Acid/Base Titrations 387	
11B Calculating Solubilities by the Systematic Method 287	Feature 14-5 Locating Titration End Points from pH Measurements 388	
Feature 11-1 Algebraic Expressions Needed to		
Calculate the Solubility of CaC ₂ O ₄ in Water 294	Chapter 15 Titration Curves for Complex Acid/Base Systems 395	
11C Separation of Ions by Control of the Concentration of the Precipitating Agent 300	15A Mixtures of Strong and Weak Acids or Strong and Weak Bases 398	
Feature 11-2 Immunoassay: Equilibria in the Specific	15B Polyfunctional Acids and Bases 399	
Determination of Drugs 304	15C Buffer Solutions Involving Polyprotic Acids 401	
	15D Calculation of the pH of Solutions of NaHA 403	
PART III Classical Methods of Analysis 311	15E Titration Curves for Polyfunctional Acids 407 Feature 15-1 The Dissociation of Sulfuric Acid 415	
A Conversation with Larry R. Faulkner 312	15F Titration Curves for Polyfunctional Bases 416	
Ti Conversation with Larry at Luminer 512	15G Titration Curves for Amphiprotic Species 417	
Chapter 12 Gravimetric Methods of Analysis 314	Feature 15-2 Acid/Base Behavior of Amino Acids 418	
12A Precipitation Gravimetry 315	15H The Composition of Solutions of a Polyprotic Acid	
Feature 12-1 Specific Surface Area of Colloids 322	as a Function of pH 419	
12B Calculation of Results from Gravimetric Data 326	Feature 15-3 A General Expression for Alpha	
12C Applications of Gravimetric Methods 329	Values 420	
126 Applications of Gravillicule Methods 323	Feature 15-4 Logarithmic Concentration Diagrams 422	
Chapter 13 Titrimetric Methods; Precipitation		
Titrimetry 337	Chapter 16 Applications of Neutralization	
13A Some Terms Used in Volumeric Titrimetry 338	Titrations 428	
13B Standard Solutions 340	16A Reagents for Neutralization Titrations 429	

16B Typical Applications of NeutralizationTitrations 435	19D Constructing Redox Titration Curves 538 Feature 19-3 The Inverse Master Equation Approach
Feature 16-1 Determining Total Serum Protein 435	for Redox Titration Curves 547
Feature 16-2 Other Methods for Determining Organic Nitrogen 436	Feature 19-4 Reaction Rates and Electrode Potentials 552
Feature 16-3 Equivalent Weights of Acids and	19E Oxidation/Reduction Indicators 552
Bases 442	19F Potentiometric End Points 555
Chapter 17 Complexation Reactions and Titrations 449	Chapter 20 Applications of Oxidation/Reduction
17A The Formation of Complexes 449	Titrations 560
Feature 17-1 Calculation of Alpha Values for Metal Complexes 452	20A Auxiliary Oxidizing and Reducing Reagents 560 20B Applying Standard Reducing Agents 562
17B Titrations with Inorganic Complexing Agents 455	20C Applying Standard Oxidizing Agents 566
Feature 17-2 Determination of Hydrogen Cyanide in Acrylonitrile Plant Streams 456	Feature 20-1 Determination of Chromium Species in Water Samples 568
17C Organic Complexing Agents 457	Feature 20-2 Antioxidants 573
17D Aminocarboxylic Acid Titrations 458	Todali o E o E , iliao iliani a si o
Feature 17-3 Species Present in a Solution of EDTA 459	Chapter 21 Potentiometry 588
Feature 17-4 EDTA as a Preservative 462	21A General Principles 589
Feature 17-5 EDTA Titration Curves When a Complex-	21B Reference Electrodes 590
ing Agent Is Present 473	21C Liquid-Junction Potentials 592
Feature 17-6 How Masking and Demasking Agents Can	21D Indicator Electrodes 593
Be Used to Enhance the Selectivity of EDTA Titrations 480	Feature 21-1 An Easily Constructed Liquid-Membrane Ion-Selective Electrode 606
Feature 17-7 Test Kits for Water Hardness 482	Feature 21-2 The Structure and Performance of Ion- Selective Field Effect Transistors 608
PART IV Electrochemical Methods 487 A Conversation with Allen J. Bard 488	Feature 21-3 Point-of-Care Testing: Blood Gases and Blood Electrolytes with Portable Instrumentation 612
Conversation with Anen J. Bart. 400	21E Instruments for Measuring Cell Potential 614
Chapter 18 Introduction to Electrochemistry 490	Feature 21-4 The Loading Error in Potential
18A Characterizing Oxidation/Reduction Reactions 490	Measurements 614
Feature 18-1 Balancing Redox Equations 492	Feature 21-5 Operational Amplifier Voltage
18B Electrochemical Cells 494	Measurements 615
Feature 18-2 The Daniell Gravity Cell 498	21F Direct Potentiometry 616
18C Electrode Potentials 499	21G Potentiometric Titrations 623
Feature 18-3 Why We Cannot Measure Absolute Electrode Potentials 504	21H Potentiometric Determination of Equilibrium Constants 627
Feature 18-4 Sign Conventions in the Older Literature 513	Chapter 22 Bulk Electrolysis: Electrogravimetry and
Feature 18-5 Why Are There Two Electrode Potentials	Coulometry 633
for Br ₂ in Table 18-1? 515	22A The Effect of Current on Cell Potential 634
	Feature 22-1 Overvoltage and the Lead/Acid
Chapter 19 Applications of Standard Electrode Potentials 523	Battery 641 22B The Selectivity of Electrolytic Methods 641
19A Calculating Potentials of Electrochemical Cells 523	22C Electrogravimetric Methods 643
19B Determining Standard Potentials Experimentally 530	22D Coulometric Methods 649 Feature 22-2 Coulometric Titration of Chloride in
19C Calculating Redox Equilibrium Constants 532	Biological Fluids 658
Feature 19-1 Biological Redox Systems 532	Cl. 4 22 1/1
Feature 19-2 A General Expression for Calculating	Chapter 23 Voltammetry 665
Equilibrium Constants from Standard	23A Excitation Signals 666
Potentials 537	23B Linear Sweep Voltammetry 667

23C Pulse Polarographic and Voltammetric Methods 689	27C Fluorescence Instruments 830
	27D Applications of Fluorescence Methods 831
Feature 23-1 Voltammetric Instruments Based on Operational Amplifiers 668	Feature 27-1 Use of Fluorescence Probes in Neurobiology Probing the Enlightened Mind 832
23D Cyclic Voltammetry 694	27E Molecular Phosphorescence Spectroscopy 834
Feature 23-2 Modified Electrodes 697	27F Chemiluminescence Methods 835
23E Stripping Methods 699 23F Voltammetry with Microelectrodes 703	Chapter 28 Atomic Spectroscopy 839
231 Volcammen y with wind ociectiones 703	28A Origins of Atomic Spectra 840
PART V Spectrochemical Methods 707	28B Production of Atoms and Ions 843 28C Atomic Emission Spectrometry 854
A Conversation with Gary M. Hieftje 708	28D Atomic Absorption Spectrometry 858
Chapter 24 Introduction to Spectrochemical	Feature 28-I Determining Mercury by Cold-Vapor Atomic Absorption Spectroscopy 865
Methods 710	28E Atomic Fluorescence Spectrometry 868
24A Properties of Electromagnetic Radiation 711	28F Atomic Mass Spectrometry 868
24B Interaction of Radiation and Matter 714	
Feature 24-1 Spectroscopy and the Discovery of	
Elements 717	PART VI Kinetics and Separations 875
24C Radiation Absorption 718 Feature 24-2 Deriving Beer's Law 720	
Feature 24-2 Deriving Beer's Law 720 Feature 24-3 Why Is a Red Solution Red? 725	A Conversation with Isiah M. Warner 876
24D Emission of Electromagnetic Radiation 734	Charter 20 Vissis Made to SAssissis 070
2 10 Emission of Electromagnetic reduction 754	Chapter 29 Kinetic Methods of Analysis 878
Chapter 25 Instruments for Optical Spectrometry 744	29A Rates of Chemical Reactions 879
25A Instrument Components 744	Feature 29-1 Enzymes 886
Feature 25-1 Laser Sources: The Light Fantastic 748	29B Determining Reaction Rates 892
Feature 25-2 Derivation of Equation 25-1 754	Feature 29-2 Fast Reactions and Stopped-Flow Mixing 892
Feature 25-3 Ruling Gratings 756	29C Applications of Kinetic Methods 900
Feature 25-4 Deriving Equation 25-2 759	Feature 29-3 The Enzymatic Determination of Urea 90
Feature 25-5 Signals, Noise, and the Signal-to-Noise	
Ratio 761	Chapter 30 Introduction to Analytical
Feature 25-6 Measuring Photocurrents with Operational Amplifiers 769	Separations 906
25B Ultraviolet-Visible Photometers and	30A Separation by Precipitation 907
Spectrophotometers 771	30B Separation of Species by Distillation 911
25C Infrared Spectrophotometers	30C Separation by Extraction 911
Feature 25-7 How Does a Fourier Transform Infrared	Feature 30-1 Derivation of Equation 30-3 913
Spectrometer Work? 776	30D Separating lons by Ion Exchange 916
GI	Feature 30-2 Home Water Softeners 919
Chapter 26 Molecular Absorption Spectrometry 784	30E Chromatographic Separations 920
26A Ultraviolet and Visible Molecular Absorption Spectroscopy 784	Feature 30-3 What is the Source of the Terms Plate and Plate Height? 930
26B Automated Photometric and Spectrophotometric Methods 807	Chapter 31 Gas Chromatography 947
26C Infrared Absorption Spectroscopy 811	31A Instruments for Gas-Liquid Chromatography 948
Feature 26-1 Using The Fourier Transform To Produce Infrared Spectra 818	31B Gas Chromatography Columns and Stationary Phases 958
To take to the state of the sta	31C Applications of Gas-Liquid Chromatography 963
Chapter 27 Molecular Fluorescence Spectroscopy 825	Feature 31-1 Use of GC/MS to identify a Drug
27A Theory of Molecular Fluorescence 825	Metabolite in Blood 965
27B Effect of Concentration On Fluorescence Intensity 829	Feature 31-2 High-Speed Gas Chromatography 969 31D Gas-Solid Chromatography 970

Chapter 32 High-Performance Liquid Chromatography 973
31A Instrumentation 974
Feature 32-1 Liquid Chromatography (LC)/Mass
Spectrometry (MS) and LC/MS/NS 980
32B High-Performance Partition Chromatography 982
32C High-Performance Adsorption Chromatography 986
32D Ion-Exchange Chromatography 986
32E Size-Exclusion Chromatography 988
Feature 32-2 Buckyballs: The Chromatographic Separation of Fullerenes 989
32F Affinity Chromatography 991
32G Chiral Chromatography 991
32H Comparison of High-Performance Liquid Chromatography and Gas Chromatography 992
Chapter 33 Miscellaneous Separation Methods 996
33A Supercritical-Fluid Chromatography 996
33B Planar Chromatography 1000
33C Capillary Electrophoresis 1003
Feature 33-1 Capillary Array Electrophoresis in DNA Sequencing 1010
33D Capillary Electrochromatography 1011
33E Field-Flow Fractionation 1013
PART VII Practical Aspects of Chemical Analysis 1021
A Conversation with Julie Leary 1022
Chapter 34 Analysis of Real Samples 1024
34A Real Samples 1024
34B Choice of Analytical Method 1026
34C Accuracy in the Analysis of Complex Materials 1031
Chapter 35 Preparing Samples for Analysis 1034
35A Preparing Laboratory Samples 1034
35B Moisture in Samples 1036
35C Determining Water in Samples 1039
Chapter 36 Decomposing and Dissolving the Sample 1041
36A Sources of Error in Decomposition and Dissolution 1042
36B Decomposing Samples With Inorganic Acids in Open Vessels 1042
36C Microwave Decompositions 1044
36D Combustion Methods for Decomposing Organic Samples 1047
36E Decomposition of Inorganic Materials by

Fluxes 1049

Chapter 37 Selected Methods of Analysis This chapter is only available as an Adobe Acrobat® PDF file on the Analytical Chemistry CD-ROM enclosed in this book or on our Web site at http://chemistry.brookscole.com/skoogfac/. 37A An Introductory Experiment 37B Gravimetric Methods of Analysis 37C Neutralization Titrations 37D Precipitation Titrations 37E Complex-Formation Titrations with EDTA 37F Titrations with Potassium Permanganate 37G Titrations with lodine 37H Titrations with Sodium Thiosulfate 371 Titrations with Potassium Bromate 37J Potentiometric Methods 37K Electrogravimetric Methods 37L Coulometric Titrations 37M Voltammetry 37N Methods Based on the Absorption of Radiation 370 Molecular Fluorescence 37P Atomic Spectroscopy 37Q Application of Ion Exchange Resins 37R Gas-Liquid Chromatography

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