## Contents

Chapter 1 The Nature of Analytical Chemistry 1	Chapter 6 Random Errors in Chemical Analysis 93
1A The Role of Analytical Chemistry 2	6A The Nature of Random Errors 93
1B Quantitative Analytical Methods 4 1C A Typical Quantitative Analysis 4	Feature 6-1 Flipping Coins: A Student Activity to Illustrate a Normal Distribution 97
1D An Integral Role for Chemical Analysis:	6B Statistical Treatment of Random Errors 98
Feedback Control Systems 9	Feature 6-2 Calculating the Areas under the Gaussian
Feature 1-1 Deer Kill: A Case Study Illustrating the Use	Curve 101
of Analytical Chemistry to Solve a Problem in Toxicology 10	Freedom 104  Freedom 104
PART I TOOLS OF ANALYTICAL	Feature 6-4 Equation for Calculating the Pooled Standard Deviation 107
CHEMISTRY 14	6C Standard Deviation of Calculated Results 110
Chapter 2 Chemicals, Apparatus, and Unit Operations of Analytical Chemistry 15	6D Reporting Computed Data 115
2A Selecting and Handling Reagents	Chapter 7 Statistical Data Treatment and Evaluation 123
and Other Chemicals 16	7A Confidence Intervals 124
2B Cleaning and Marking	Feature 7-1 W. S. Gossett ("Student") 127
of Laboratory Ware 17	7B Statistical Aids to Hypothesis Testing 129
2C Evaporating Liquids 18	7C Analysis of Variance 140
2D Measuring Mass 18	7D Detection of Gross Errors 146
2E Equipment and Manipulations	and the sight state of the same and the same
Associated with Weighing 25	Chapter 8 Sampling, Standardization,
2F Filtration and Ignition of Solids 28	and Calibration 153
2G Measuring Volume 34	8A Analytical Samples and Methods 153
2H Calibrating Volumetric Glassware 43	8B Sampling 156
2I The Laboratory Notebook 45	8C Automated Sample Handling 164
2J Safety in the Laboratory 46	8D Standardization and Calibration 167
	Feature 8-1 Lab-on-a-Chip 168
Chapter 3 Using Spreadsheets in	Feature 8-2 A Comparison Method for Aflatoxins 169
Analytical Chemistry 48	Feature 8-3 Multivariate Calibration 180
3A Keeping Records and Making Calculations 49	8E Figures of Merit for Analytical Methods 186
3B More Complex Examples 52	
Chanton A. Calaulatiana I I ad	PART II CHEMICAL EQUILIBRIA 196
Chapter 4 Calculations Used	Chapter 9 Aqueous Solutions and Chemical
in Analytical Chemistry 62	Equilibria 197
4A Some Important Units of Measurement 62	9A The Chemical Composition of Aqueous Solutions 197
Feature 4-1 Unified Atomic Mass Units and the Mole 65	9B Chemical Equilibrium 202
Feature 4-2 The Factor-Label Approach	Feature 9-1 Stepwise and Overall Formation Constants for
to Example 4-2 67	Complex Ions 205
4B Solutions and Their Concentrations 67	Feature 9-2 Why [H <sub>2</sub> O] Does Not Appear in Equilibrium-
4C Chemical Stoichiometry 75	Constant Expressions for Aqueous Solutions 206
Chapter 5 Errors in Chemical Analyses 82	Feature 9-3 Relative Strengths of Conjugate Acid/Base Pairs 212
5A Some Important Terms 84	Feature 9-4 The Method of Successive Approximations 217
5B Systematic Errors 87	9C Buffer Solutions 219

Feature 9-5 The Henderson-Hasselbalch Equation 221	Chapter 15 Complex Acid/Base Systems 348
Feature 9-6 Acid Rain and the Buffer Capacity of Lakes 227	15A Mixtures of Strong and Weak Acids or Strong and Weak Bases 348
Chapter 10 Effect of Electrolytes on Chemical	15B Polyfunctional Acids and Bases 352
Equilibria 235	15C Buffer Solutions Involving Polyprotic Acids 354
10A The Effect of Electrolytes on Chemical Equilibria 235	15D Calculation of the pH of Solutions of NaHA 356
10B Activity Coefficients 239	15E Titration Curves for Polyfunctional Acids 360
Feature 10-1 Mean Activity Coefficients 242	Feature 15-1 The Dissociation of Sulfuric Acid 368
	15F Titration Curves for Polyfunctional Bases 369
Chapter 11 Solving Equilibrium Problems for Complex	· · · · · · · · · · · · · · · · · · ·
Systems 249	15G Titration Curves for Amphiprotic Species 371
11A Solving Multiple-Equilibrium Problems Using a Systematic Method 250	Feature 15-2 Acid/Base Behavior of Amino Acids 371 15H Composition of Polyprotic Acid Solutions as a Function
11B Calculating Solubilities by the Systematic Method 256	of pH 373
Feature 11-1 Algebraic Expressions Needed to Calculate the	Feature 15-3 A General Expression for Alpha Values 374
Solubility of CaC <sub>2</sub> O <sub>4</sub> in Water 262	Feature 15-4 Logarithmic Concentration Diagrams 375
11C Separation of Ions by Control of the Concentration of the Precipitating Agent 268	Chapter 16 Applications of Neutralization Titrations 381
Feature 11-2 Immunoassay: Equilibria in the Specific	16A Reagents for Neutralization Titrations 382
Determination of Drugs 272	16B Typical Applications of Neutralization Titrations 387
	Feature 16-1 Determining Total Serum Protein 388
PART III CLASSICAL METHODS OF ANALYSIS 279	Feature 16-2 Other Methods for Determining Organic Nitrogen 388
	Feature 16-3 Equivalent Masses of Acids and Bases 394
Chapter 12 Gravimetric Methods of Analysis 280	
12A Precipitation Gravimetry 280	Chapter 17 Complexation and Precipitation Reactions
Feature 12-1 Specific Surface Area of Colloids 287	and Titrations 400
12B Calculation of Results from Gravimetric Data 291	17A The Formation of Complexes 400
12C Applications of Gravimetric Methods 294	Feature 17-1 Calculation of Alpha Values for Metal Complexes 403
Chapter 13 Titrations in Analytical Chemistry 302	17B Titrations with Inorganic Complexing Agents 406
13A Some Terms Used in Volumetric Titrations 303	Feature 17-2 Determination of Hydrogen Cyanide in
13B Standard Solutions 305	Acrylonitrile Plant Streams 407
13C Volumetric Calculations 306	17C Organic Complexing Agents 413
Feature 13-1 Another Approach to Example 13-6(a) 311	17D Aminocarboxylic Acid Titrations 414
Feature 13-2 Rounding the Answer to Example 13-7 312	Feature 17-3 Species Present in a Solution of EDTA 415
13D Gravimetric Titrations 314	Feature 17-4 EDTA as a Preservative 418
13E Titration Curves 315	Feature 17-5 EDTA Titration Curves When a Complexing Agent
Feature 13-3 Calculating the NaOH Volumes Shown in the First	Is Present 428
Column of Table 13-1 317	Feature 17-6 Enhancing the Selectivity of EDTA Titrations with  Masking and Demasking Agents 435
Chapter 14 Principles of Neutralization Titrations 322	Feature 17-7 Test Kits for Water Hardness 436
14A Solutions and Indicators for Acid/Base Titrations 322	Total of the same to the same
14B Titration of Strong Acids and Bases 326	PART IV ELECTROCHEMICAL
Feature 14-1 Using the Charge-balance Equation to Construct	METHODS 441
Titration Curves 328	Chapter 18 Introduction to Electrochemistry 442
Feature 14-2 Significant Figures in Titration Curve	18A Characterizing Oxidation/Reduction Reactions 442
Calculations 331	Feature 18-1 Balancing Redox Equations 444
14C Titration Curves for Weak Acids 332	18B Electrochemical Cells 446
Feature 14-3 Determining Dissociation Constants of Weak Acids	Feature 18-2 The Daniell Gravity Cell 450
and Bases 334	18C Electrode Potentials 451
Feature 14-4 A Master Equation Approach to Weak Acid/Strong	Feature 18-3 Why We Cannot Measure Absolute Electrode
Base Titrations 336	Potentials 456
14D Titration Curves for Weak Bases 337	Feature 18-4 Sign Conventions in the Older Literature 464
Feature 14-5 Determining the pK Values for Amino Acids 339	Feature 18-5 Why Are There Two Electrode Potentials for Br <sub>2</sub> in
14E The Composition of Solutions During Acid/Base	Table 18-1? 466
Titrations 341	CONTRACT OF STATE

Feature 14-6 Locating Titration End Points from

Chapter 19 Applications of Standard Electrode Potentials 473	Feature 23-1 Voltammetric Instruments Based on Operational Amplifiers 613
19A Calculating Potentials of Electrochemical Cells 473	23C Hydrodynamic Voltammetry 618
19B Determining Standard Potentials Experimentally 480	23D Polarography 633
Feature 19-1 Biological Redox Systems 482	23E Cyclic Voltammetry 635
19C Calculating Redox Equilibrium Constants 482	23F Pulse Voltammetry 639
Feature 19-2 A General Expression for Calculating Equilibrium	23G Applications of Voltammetry 642
Constants from Standard Potentials 487	23H Stripping Methods 643
19D Constructing Redox Titration Curves 488	23I Voltammetry with Microelectrodes 645
Feature 19-3 The Inverse Master Equation Approach for Redox	
Titration Curves 497	PART V SPECTROCHEMICAL ANALYSIS 649
Feature 19-4 Reaction Rates and Electrode Potentials 502	Chapter 24 Introduction to Spectrochemical
19E Oxidation/Reduction Indicators 502	Methods 650
19F Potentiometric End Points 505	24A Properties of Electromagnetic Radiation 651
Chapter 20 Applications of Ocidation (B. 1.	24B Interaction of Radiation and Matter 654
Chapter 20 Applications of Oxidation/Reduction Titrations 509	Feature 24-1 Spectroscopy and the Discovery of Elements 65
	24C Absorption of Radiation 658
20A Auxiliary Oxidizing and Reducing Reagents 509	Feature 24-2 Deriving Beer's Law 660
20B Applying Standard Reducing Agents 511	Feature 24-3 Why Is a Red Solution Red? 665
20C Applying Standard Oxidizing Agents 515	2D Emission of Electromagnetic Radiation 674
Feature 20-1 Determination of Chromium Species in Water Samples 517	01 251 6 0 110
Feature 20-2 Antioxidants 522	Chapter 25 Instruments for Optical Spectrometry 683
Theoretains 722	25A Instrument Components 683
Chapter 21 Potentiometry 535	Feature 25-1 Laser Sources: The Light Fantastic 687
21A General Principles 536	Feature 25-2 Origin of Equation 25-1 693
21B Reference Electrodes 537	Feature 25-3 Producing Ruled and Holographic Gratings 699
21C Liquid-Junction Potentials 539	Feature 25-4 Basis of Equation 25-2 698
21D Indicator Electrodes 540	Feature 25-5 Signals, Noise, and the Signal-to-Noise
Feature 21-1 An Easily Constructed Liquid-Membrane	Ratio 700
Ion-Selective Electrode 552  Feature 21-2 The Structure and Performance of Ion-Sensitive	Feature 25-6 Measuring Photocurrents with Operational Amplifiers 708
Field Effect Transistors 554	25B Ultraviolet/Visible Photometers and Spectrophotometers 710
Feature 21-3 Point-of-Care Testing: Blood Gases, and Blood	25C Infrared Spectrophotometers 713
Electrolytes with Portable Instrumentation 558	Feature 25-7 How Does a Fourier Transform Infrared
21E Instruments for Measuring Cell Potential 560	Spectrometer Work? 715
Feature 21-4 The Loading Error in Potential	
Measurements 560	Chapter 26 Molecular Absorption Spectrometry 722
Feature 21-5 Operational Amplifier Voltage Measurements 562	26A Ultraviolet and Visible Molecular Absorption
21F Direct Potentiometry 563	Spectroscopy 722
21G Potentiometric Titrations 569	26B Automated Photometric and Spectrophotometric
21H Potentiometric Determination of Equilibrium	Methods 744
Constants 573	26C Infrared Absorption Spectroscopy 746
Chapter 22 Bulk Electrolysis: Electrogravimetry and Coulometry 578	Feature 26-1 Producing Spectra with an FTIR Spectrometer 751
22A The Effect of Current on Cell Potential 579	Chapter 27 Molecular Fluorescence Spectroscopy 760
Feature 22-1 Overvoltage and the Lead/Acid Battery 586	27A Theory of Molecular Fluorescence 760
22B The Selectivity of Electrolytic Methods 586	27B Effect of Concentration on Fluorescence Intensity 764
	27C Fluorescence Instrumentation 765
22C Electrogravimetric Methods 588	27D Applications of Fluorescence Methods 766
22D Coulometric Methods 594 <b>Feature 22-2</b> Coulometric Titration of Chloride in	Feature 27-1 Use of Fluorescence Probes in Neurobiology:
Biological Fluids 603	Probing the Enlightened 767
Chapter 23 Voltammetry 610	27E Molecular Phosphorescence Spectroscopy 769 27F Chemiluminescence Methods 770
23A Excitation Signals in Voltammetry 611	2/1 Glichhummescence (vietnods //U

23B Voltammetric Instrumentation 612

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	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
30A Rates of Chemical Reactions 820	35C Accuracy in the Analysis of Complex Materials 967
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 36 Preparing Samples for Analysis 970 36A Preparing Laboratory Samples 970 36B Moisture in Samples 972 36C Determining Water in Samples 975
Chapter 31 Introduction to Analytical Separations 847	Chapter 37 Decomposing and Dissolving the
31A Separation by Precipitation 848	Sample 976
31B Separation of Species by Distillation 852	37A Sources of Error in Decomposition and
31C Separation by Extraction 852	Dissolution 977
Feature 31-1 Derivation of Equation 31-3 854	37B Decomposing Samples with Inorganic Acids in Open Vessels 977
31D Separating Ions by Ion Exchange 857	37C Microwave Decompositions 979
Feature 31-2 Home Water Softeners 860	37D Combustion Methods for Decomposing Organic
31E Chromatographic Separations 861	Samples 982
Feature 31-3 What Is the Source of the Terms Plate and Plate Height? 871	37E Decomposing Inorganic Materials with Fluxes 984
Feature 31-4 Derivation of Equation 31-24 872	Chapter 38 Selected Methods of Analysis 986
Chapter 32 Gas Chromatography 887	38A An Introductory Experiment 987
32A Instruments for Gas-Liquid Chromatography 888	38B Gravimetric Methods of Analysis 996
32B Gas Chromatographic Columns and Stationary Phases 897	38C Neutralization Titrations 1000 38D Precipitation Titrations 1009
32C Applications of Gas-Liquid Chromatography 901	38E Complex-Formation Titrations with EDTA 1012
Feature 32-1 Use of GC/MS to Identify a Drug Metabolite	38F Titrations with Potassium Permanganate 1015
in Blood 903	38G Titrations with Iodine 1021
32D Gas-Solid Chromatography 909	38H Titrations with Sodium Thiosulfate 1023
Chapter 33 High-Performance Liquid	38I Titrations with Potassium Bromate 1026
Chromatography 912	38J Potentiometric Methods 1028
33A Instrumentation 913	38K Electrogravimetric Methods 1032
Feature 33-1 LC/MS and LC/MS/MS 920	38L Coulometric Titrations 1034
33B Partition Chromatography 921	38M Voltammetry 1036
33C Adsorption Chromatography 924	38N Methods Based on the Absorption of Radiation 1038
33D Ion Chromatography 925	380 Molecular Fluorescence 1042
33E Size-Exclusion Chromatography 927	38P Atomic Spectroscopy 1043 38Q Application of Ion-Exchange Resins 1046
Feature 33-2 Buckyballs: The Chromatographic Separation of Fullerenes 929	38R Gas-Liquid Chromatography 1048
33F Affinity Chromatography 931 33G Chiral Chromatography 931	257. One Exquite Ontolliniography 10-10

33H Comparison of High-Performance Liquid Chromatography and Gas Chromatography 932

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