Analytical Chemistry

SECOND EDITION

DONALD J. PIETRZYK
CLYDE W. FRANK

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TYPICAL GRAVIMETRIC FACTORS

Repqrted as	Substance Weighed	Gravimetric Factor
Ag	AgCl	Ag/AgCl
Al	Al_2O_3	$2Al/Al_2O_3$
BaO	$BaSO_4$	$BaO/BaSO_4$
Ca	$CaSO_4$	$Ca/CaSO_4$
Cl_2	AgCl	$Cl_2/2AgCl$
Fe_3O_4	Fe_2O_3	$2Fe_3O_4/3Fe_2O_3$
K_2O	$KClO_4$	$K_2O/2KClO_4$
K_2O	K_2PtCl_6	K_2O/K_2PtCl_6
Mg	$Mg_2P_2O_7$	$2Mg/Mg_2P_2O_7$
P_2O_5	$Mg_2P_2O_7$	$P_2O_5/Mg_2P_2O_7$
SO_3	$BaSO_4$	$SO_3/BaSO_4$
V	V_2O_5	$2V/V_2O_5$
ZrO_2	ZrP_2O_7	ZrO_2/ZrP_2O_7

EQUATIONS

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$M \text{ (molarity)} = \frac{\text{moles of solute}}{\text{liter}} = \frac{\text{mmole of solute}}{\text{ml}}$$

$$\% \text{ A} = \frac{\text{ml}_B \times F_B \times \text{reaction ratio} \times \text{formula wt of A (mg/mmole)} \times 100}{\text{wt of sample (mg)}}$$

$$K_a = [H_3O^+][A^-]/[HA] \qquad K_b = [B^+][OH^-]/[BOH^-]$$

Henderson–Hasselbalch Equation

$$\text{pH} = pK_a + \log \frac{\text{Fraction neutralized}}{\text{Fraction unneutralized}}$$

$$\text{pH} = pK_w - pK_b + \log \frac{\text{Fraction unneutraliz}}{\text{Fraction neutralized}}$$

Nernst Equation

$$E = E^\circ_{ox,red} - \frac{0.0592}{n} \log \frac{[\text{red}]^b}{[\text{ox}]^a}$$

Beer's Law

$$A = \epsilon bc = \log \frac{1}{\% T/100} = 2 - \log \% T$$

Faraday's Law

$$w = \frac{i \times t \times \text{equiv wt}}{F}$$

FORMULA WEIGHTS

Element	Formula Weight	Element	Formula Weight
AgBr	187.78	$HgCl_2$	271.50
AgCl	143.35	HgO	216.59
AgCN	133.89	Hg_2Cl_2	472.08
$Ag_2Cr_2O_7$	413.73	KBr	119.01
Ag_2CrO_4	331.73	KCl	74.55
AgI	234.77	$KHC_8H_4O_4$(KHP)	204.23
$AgNO_3$	169.87	KI	166.01
Ag_3PO_4	418.58	KIO_3	214.00
AgSCN	165.95	KIO_4	230.00
Ag_2SO_4	311.80	$KMnO_4$	158.04
$Al(OH)_3$	78.00	KSCN	97.18
Al_2O_3	101.96	$K_2Cr_2O_7$	294.19
$AsCl_3$	181.27	$MgCl_2$	95.22
As_2O_3	197.84	$Mg(NH_4)PO_4$	137.32
As_2O_5	229.84	$NH_2CO_2NH_2$ (urea)	60.05
$BaCl_2$	208.25	$NH_2(C_4H_9O_3)$ (Tham)	121.14
$BaCl_2 \cdot 2H_2O$	244.27	NH_4Cl	53.49
$BaCO_3$	197.35	NH_4OH	35.05
$Ba(OH)_2$	171.35	NaBr	102.90
$BaSO_4$	233.40	$NaC_2H_3O_2$ (acetate)	82.04
Bi_2O_3	465.96	$Na(C_6H_5CO_2)$ benzoate	144.10
$CaCO_3$	100.09	NaCl	58.44
CaC_2O_4	128.10	NaF	41.99
$Ca(OH)_2$	74.10	$NaHCO_3$	84.01
$CaSO_4$	136.14	NaH_2PO_4	119.98
$Ca_3(PO_4)_2$	310.18	Na_2HPO_4	142.00
CdS	144.46	NaOH	40.00
CuS	95.60	Na_2CO_3	105.99
$CuSO_4 \cdot 5H_2O$	249.68	$Na_2C_2O_4$	134.00
$FeSO_4 \cdot 7H_2O$	182.02	$Na_2H_2Y \cdot 2H_2O$ (EDTA)	372.24
$HC_2H_3O_2$ (acetic acid)	60.05	$NaNO_2$	69.00
HCl	36.46	Na_2O	61.98
HNO_3	63.02	$Na_2S_2O_3$	158.10
HSO_3NH_2 (sulfamic acid)	97.09	$Ni(C_4H_8N_2O_2)_2$ (DMG)	288.94
$H_2C_2O_4$ (oxalic acid)	90.04	P_2O_5	141.94
$H_2C_2O_4 \cdot 2H_2O$	108.06	PbO_2	239.19
H_2O_2	34.02	PbI_2	461.00
H_2SO_3	82.08	$SnCl_2$	189.61
H_2SO_4	98.08	TlCl	239.82
H_3PO_4	98.00	$Zn_2P_2O_7$	304.68

ATOMIC WEIGHTS
Based on Carbon-12

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	
Aluminum	Al	13	26.9815
Americium	Am	95	
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	
Barium	Ba	56	137.34
Berkelium	Bk	97	
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.980
Boron	B	5	10.811
Bromine	Br	35	79.909
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	
Carbon	C	6	12.01115
Cerium	Ce	58	140.12
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.54
Curium	Cm	96	
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	
Fluorine	F	9	18.9984
Francium	Fr	87	
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.967
Hafnium	Hf	72	178.49
Helium	He	2	4.0026
Holmium	Ho	67	164.930
Hydrogen	H	1	1.00797
Indium	In	49	114.82
Iodine	I	53	126.9044
Iridium	Ir	77	192.2
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9381
Mendelevium	Md	101	
Mercury	Hg	80	200.59

Element	Symbol	Atomic Number	Atomic Weight
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.183
Neptunium	Np	93	
Nickel	Ni	28	58.71
Niobium	Nb	41	92.906
Nitrogen	N	7	14.0067
Nobelium	No	102	
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	
Polonium	Po	84	
Potassium	K	19	39.102
Praseodymium	Pr	59	140.907
Promethium	Pm	61	
Protactinium	Pa	91	
Radium	Ra	88	
Radon	Rn	86	
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.905
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.35
Scandium	Sc	21	44.956
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.870
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.064
Tantalum	Ta	73	180.948
Technetium	Tc	43	
Tellurium	Te	52	127.60
Terbium	Tb	65	158.924
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yitrium	Y	39	88.905
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

Preface

This text is designed for introductory courses in analytical chemistry, especially those shorter courses servicing chemistry majors and life and health science majors.

Before undertaking this revision, we discussed the role of analytical chemistry with advisers from the various academic disciplines whose students traditionally require exposure to analytical courses. Two major objectives arose from these discussions: first, students should become acquainted with the fundamental principles encountered in modern chemical and instrumental methods of analysis, and second, students need to master the basic quantitative skills and techniques required to perform careful measurements in the laboratory. These are essentially the same goals one strives for in a course for chemistry majors.

Within the pages of this text, we attempt to present information that will accommodate both the chemistry major and students majoring in other disciplines without sacrificing the fundamentals of analytical chemistry. This was accomplished by using examples from related disciplines to illustrate the fundamental principles. In addition, most experiments involve procedures identical to those that would be used for real samples. We have not utilized real samples in the experiments, since students at this level need to know if they have obtained the correct answer. This is accomplished best by using well-characterized unknowns.

The text begins with a core of six chapters containing concepts basic to all of analytical chemistry. Five major areas are then emphasized. These include neutralization, potentiometry, spectroscopy, chromatography, and electrolysis methods. Each of these are subdivided into units. The first unit provides the fundamentals specific to that area, while the following units build by presenting additional concepts, applications, calculations, instrumentation, and chemical reactions specific to that particular area.

In neutralization, concepts relating to solutions of strong acids and bases, weak acids and bases, their salts, and buffer solutions are stressed. Final expressions are written when appropriate in a Henderson–Hasselbalch form. All approximations are clearly defined and discussed, while concepts necessary for exact calculations are introduced in chapters dealing with complexes in analytical chemistry.

Oxidation–reduction reactions and instrumental measurements of these reactions via cell potential determinations are discussed in several chapters. Accompanying this section is a broad development of the fundamental concepts and the utility of ion-selective electrodes.

In spectroscopy, atomic and molecular absorption, emission, and luminescence techniques are discussed. The first chapter of this unit provides the fundamental concepts, while subsequent chapters contain specific details for each technique including a discussion of the key components of the required instrumentation. Many practical examples are cited. For example, a comparison is made for the various ways of applying Beer's Law.

Separations are introduced in a series of six chapters with an emphasis on chromatography. The first of these chapters provides a brief survey of separation techniques and introduces the concepts common to all of chromatography. Subsequent chapters describe sheet and column methods, gas chromatography, ion-exchange chromatography, and solvent extraction. All the fundamentals are provided while stressing operational features for each technique.

Electrochemical techniques are introduced but not covered in depth. However, the principles discussed are sufficient to provide a background for understanding electrolysis, coulometry, and polarography.

Complementing these five areas are chapters devoted to the discussion of precipitation and complexes in analytical chemistry. Principles and applications and the relationship of these reactions to the other areas are stressed.

The remaining portion of the book is devoted to the laboratory. In one chapter, the basic laboratory operations are discussed with an emphasis on safety. This is followed by a series of experiments that are designed to reinforce the concepts developed in the chapters.

Many changes have been made in this second edition. Readily apparent ones are the omission of the chapter on radiochemistry and a restructuring of the chapter order. The first was done as a compromise due to the space needed for the many additions, while the second was based on user response. It should be emphasized that after the core of introductory chapters the presentation of the other areas is independent enough to allow instructors to assign chapters according to their own course outline.

Other changes in the second edition deal with improvements in the presentation, addition of new concepts or expansion of previously discussed concepts, and the inclusion of many new examples and problems. In the core of introductory chapters, Chapters 1 to 6, discussion of the problems of method

development and of obtaining standards and suitable samples has been broadened. Particularly noteworthy is that the chapter on Statistical Handling of Analytical Data has been broadened and introduces the concept of propagation of error.

In the chapters dealing with precipitation, neutralization, and oxidation–reduction in analytical chemistry (Chapters 7 to 12), several new examples have been introduced which illustrate typical calculations. Precipitation titrations (Chapter 14) has been separated from the chapter on precipitation methods (Chapter 7) and follows the chapter on ion-selective electrodes. Thus, its development is tied with cell potential measurements. The ion-selective electrode chapter has been broadened to contain more applications, including a discussion of gas-permeable membranes.

Additions in the chapter on spectroscopy include more practical examples and discussion of the instrumental requirements for measurement of atomic emission and related techniques. In chromatography, emphasis has been increased on the discussion of the chromatographic peak and how it is used in qualitative and quantitative determinations. Also, chromatographic detection techniques have been broadened. More examples have been introduced in the chapters on electrochemistry.

Throughout the presentation we have illustrated principles by often referring to biological, clinical, pharmaceutical, environmental, and industrial problems. Not only do they illustrate practical analytical chemistry but they also illustrate the mathematical steps, approximations, etc. encountered in analytical chemistry. Many new practical problems are also included at the end of each chapter.

We would like to thank the many students and colleagues at The University of Iowa for their timely advice, help in proofreading, and constructive criticism. Particularly valuable to us have been the many comments from students and faculty who used the first edition.

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Contents

Preface xvii

CHAPTER ONE
Introduction to Analytical Chemistry 1

To the Student 1
Analytical Chemistry 1
Analytical Chemistry in Allied Areas 2
The Analytical Chemist and the Analyst 8

CHAPTER TWO
Development of an Analytical Method 10

The Analytical Problem 10
Choosing an Analytical Method 11
Types of Analytical Methods 12
Methods of Analysis 14
Literature in Analytical Chemistry 17

CHAPTER THREE
Stoichiometry 20

Introduction 20
Units 22
Concentration 22
Calculations 29
Standards 40
Questions 45
Problems 46

CHAPTER FOUR
Statistical Treatment of Analytical Data 48

Introduction 48
Definitions 49
Elimination of Data 53
Propagation of Errors 58
Questions 61
Problems 61

CHAPTER FIVE
Preliminary Operations in Quantitative Analysis 63

Introduction 63
Sampling 63
Drying 69
Weighing 70
Dissolving 70
Questions 74

CHAPTER SIX
Introduction to Chemical Reactions in Analytical Chemistry 76

Scope 76
Completeness of Reaction 76
Equilibrium Concept 77
Reaction Rates 79
Equilibrium Constant 80
Application of the Equilibrium Concept 83
Equilibrium Condition: Fundamental Definition 86
Summary 88
Questions 88

CHAPTER SEVEN
Precipitation Methods 90

Introduction 90
Gravimetry 90
Formation of a Precipitate 94
Properties of Precipitates 96
Coprecipitation 97
Types of Precipitating Reagents 100
Solubility 106
Solubility Product 108
Typical Gravimetric Examples 116
Homogeneous Precipitation 120
Calculations 124

Questions 126
Problems 127

CHAPTER EIGHT
Neutralization in Analytical Chemistry 131

Introduction 131
Acid–Base Theories 131
Acid and Base Strength 133
Leveling Effect 134
pH 135
pH Scale 136
pH of Acid and Base Solutions 138
Buffers 147
Neutralization as a Volumetric Method 154
Polyfunctional Acids and Bases 165
Titration of Salts 172
Differential Titration 177
Primary Standards 180
End-Point Detection 181
Summary of Acid–Base Titration Curves 186
Applications 186
Calculations 191
Questions 193
Problems 195

CHAPTER NINE
Nonaqueous Acid–Base Titrations 199

Scope 199
Solvents 199
Equilibria in a Nonaqueous Solvent 201
Choosing a Solvent 202
Titrants 206
End-Point Detection 207
Applications 208
Indirect Acid–Base Methods 209
Calculations 211
Questions 213
Problems 214

CHAPTER TEN
Oxidation–Reduction Equilibria 216

Definitions 216
Electrochemical Cells 218

Cell Calculations 223
Nernst Equation 226
Equilibrium Constant 230
Measurement of Potential 232
Reference-Indicator Electrodes 235
Biological Systems 239
Questions 241
Problems 242

CHAPTER ELEVEN
Oxidation–Reduction Titrations 245

Introduction 245
Titration Curve 245
Differential Titrations 255
End-Point Detection 257
Questions 262
Problems 263

CHAPTER TWELVE
Oxidizing and Reducing Agents as Titrants in Analytical Chemistry 265

Introduction 265
Oxidizing Titrants 266
Reducing Titrants 274
Adjustment of Oxidation State 278
Calculations 282
Questions 287
Problems 288

CHAPTER THIRTEEN
Ion-Selective Electrodes 291

Introduction 291
Electrodes for Hydronium Ion 292
Non-Half-Cell Ion-Selective Electrodes 297
Glass Membrane Electrode 298
Solid State and Precipitate Electrodes 303
Liquid–Liquid Electrode 307
Gas- and Enzyme-Sensing Electrodes 310
Calibration 312
Applications 314
Measurements with a pH Meter 316

Questions 317
Problems 318

CHAPTER FOURTEEN
Precipitation Titrations 320

Introduction 320
Titration Requirements 320
Titration Curve 321
Calculations 333
Questions 334
Problems 335

CHAPTER FIFTEEN
Complexes in Analytical Chemistry: Complexometric Titrations 337

Introduction 337
Classification of Ligands 342
Stability 342
Kinetics 343
Advantages and Practical Aspects of Coordination Compounds 344
Complexometric Titrations 350
Titrants 351
End-Point Detection 359
Applications 367
Questions 368
Problems 369

CHAPTER SIXTEEN
Introduction to Multiple Equilibrium Systems 371

Introduction 371
Effect of Experimental Variables in EDTA Titrations 371
Calculation of a Titration Curve 383
Other Examples 386
Questions 387
Problems 388

CHAPTER SEVENTEEN
Fundamental Principles of Optical Spectroscopy 389

Introduction 389
Beer's Law: Law of Photometry 395

Instrumentation 400
Questions 408
Problems 408

CHAPTER EIGHTEEN
Qualitative Analysis: Ultraviolet, Visible, and Infrared 410

Introduction 410
Electronic Spectra: Organic Compounds 411
Inorganic Spectra 415
Vibrational Spectra–Qualitative Identification 417
Questions 422
Problems 423

CHAPTER NINETEEN
Quantitative Analysis in Absorption Spectroscopy 425

Introduction 425
Quantitative Analysis: Ultraviolet–Visible 426
Analysis of Organic Compounds 431
Inorganic Analysis 433
Multicomponent Analysis 438
Automation in Spectrophotometric Analysis 441
Quantitative Infrared 442
Photometric Titrations 444
Questions 446
Problems 446

CHAPTER TWENTY
Spectroscopy of Atoms 450

Introduction 450
Atomic Emission 450
Atomic Absorption 459
Atomic Fluorescence 462
Questions 463
Problems 463

CHAPTER TWENTY-ONE
Luminescence 466

Fluorescence 466
Phosphorescence 471
Chemiluminescence 472
Light Scattering 473

Questions 474
Problems 475

CHAPTER TWENTY-TWO
Separations: Introduction to Chromatography 476

Scope 476
Classification of Separation Methods 477
Chromatography 478
General Concepts 485
Some Fundamental Concepts 492
Summary 498
Questions 498

CHAPTER TWENTY-THREE
Column Methods 500

Introduction 500
Columns 500
Adsorption or Partition 503
Adsorption 505
Partition 507
Bonded Phases 510
Detection of Column Effluent 510
Liquid Chromatography Apparatus 513
High-Performance Liquid Chromatography 514
Questions 516

CHAPTER TWENTY-FOUR
Gas Chromatography 517

Introduction 517
The Chromatogram and Its Interpretation 517
Instrumentation 518
Factors Affecting Separation 527
Qualitative Analysis 528
Quantitative Analysis 529
Applications 531
Questions 537
Problems 538

CHAPTER TWENTY-FIVE
Sheet Methods 540

Introduction 540
Paper Chromatography 541