Kinetic Aspects of Analytical Chemistry

Horacio A. Mottola

Department of Chemistry
Oklahoma State University

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS
New York / Chichester / Brisbane / Toronto / Singapore
## CONTENTS

### CHAPTER 1  AN OVERVIEW OF KINETICS IN ANALYTICAL CHEMISTRY  
1. Historical View of the Evolution of Kinetic-Based Methods of Determination  
2. Chemical Reactions and Physical Processes in Analytical Chemistry  
   1.1. Chemical Reactions  
   1.2. Physical Processes  
References

### CHAPTER 2  CATALYTIC METHODS: NONENZYMATIC METHODS  
1. Mathematical Basis of Catalytic Methods Based on Primary Catalytic Effects  
2. Practical Treatment of Data in Catalytic Determinations  
3. Chemical Reactions for Catalytic Determinations  
4. Limits of Detection, Sensitivity, Selectivity, and Optimization in Catalytic Determinations  
   1. Limits of Detection and Sensitivity  
   2. Selectivity and Specificity  
   3. Optimization of Catalytic Methods  
5. Some Applications of Nonenzymatic Catalytic Determinations  
   1. The Sandell-Kolthoff Reaction  
   2. Miscellaneous Applications of Catalyzed Reactions  
References

### CHAPTER 3  CATALYTIC METHODS: HOMOGENEOUS ENZYMATIC METHODS  
1. Enzymes as Catalysts  
2. Kinetics of Enzyme-Catalyzed Reactions  

ix
CHAPTER 6  RATE DETERMINATIONS USING
UNCATALYZED REACTIONS  111

6.1. Rate Considerations for the Determination of
a Single Species in Uncatalyzed Processes  111
   6.1.1. Pseudo-Zero-Order Conditions (Initial
          Rate Method)  111
   6.1.2. First-Order and Pseudo-First-Order
          Conditions  112

6.2. Special Cases for the Determination of a
Single Species in a Mixture by Use of an
Uncatalyzed Reaction  113

6.3. Selected Analytical Applications of Rates of
Uncatalyzed Reactions  115
   6.3.1. Determination of Inorganic Species  115
   6.3.2. Determination of Organic Species  115
References  120

CHAPTER 7  DIFFERENTIAL REACTION RATE METHODS  122

7.1. Methods Based on First-Order or Pseudo-
First-Order Kinetics (Region I of Figure 7.1)  124
   7.1.1. Logarithmic Extrapolation Method  124
   7.1.2. Single-Point Method  126
   7.1.3. Tangent Method  127
   7.1.4. Method of Proportional Equations  128

7.2. Methods Based on Second-Order Kinetics
(Regions III, IV, and V of Figure 7.1)  133
   7.2.1. Second-Order Logarithmic
          Extrapolation  133
   7.2.2. Second-Order Linear Extrapolation
          (Region IV), Second-Order Single-
          Point (Region IV), and Second-Order
          Graphical Differential (Tangents) and
          Integral (Regions III, IV, and V)
          Methods  134

7.3. Pseudo-First-Order Methods with Respect to
a Common Reagent (Region VII of Figure 7.1)  135
   7.3.1. Single-Point Method of Roberts and
          Regan  135
CONTENTS

7.3.2. Method of Proportional Equations 136
7.4. Pseudo-Zero-Order Methods (Regions I through VII of Figure 7.1) 136
  7.4.1. Single-Point Method 136
  7.4.2. Method of Proportional Equations 137
7.5. Critical Evaluation of Selected Differential Reaction Rate Methods 137
7.6. Application of Continuous-Flow Sample-Reagent(s) Processing in Implementing Differential Reaction Rate Procedures 137
7.7. Some Miscellaneous Approaches to Differential Determinations 140
References 146

CHAPTER 8 KINETIC METHODS BASED ON DETECTION OF LIGHT EMISSION: FLUORESCENCE, PHOSPHORESCENCE, CHEMILUMINESCE, AND BIOLUMINESCE 149

  8.1. Fluorescence and Phosphorescence 149
    8.1.1. Fluorescence 149
    8.1.2. Phosphorescence 153
  8.2. Chemiluminescence and Bioluminescence 158
      References 167

CHAPTER 9 INSTRUMENTATION 170

  9.1. Means of Mixing Reactants 171
    9.1.1. Mixing by Manual and Magnetic Stirring 171
    9.1.2. Stopped-Flow Mixing 172
    9.1.3. Continuous-Flow Mixing 178
    9.1.4. Mixing for Kinetic-Based Titrimetry and Stat Procedures 184
    9.1.5. Centrifugal Mixing 187
  9.2. Detection Approaches 189
    9.2.1. Absorptiometric Detection 189
    9.2.2. Detection by Means of Fluorescence,
CONTENTS

Chemiluminescence, and Bioluminescence 193
9.2.3. Electrochemical Detection 194
9.2.4. Other Methods 197
9.3. Ancillary Electronic Units 198
9.3.1. Circuit for Automatic Measurement of Slopes of Rate Curves 198
9.3.2. A Fixed-Time Digital Counting System 199
9.3.3. All-Electronic Reciprocal Time Computers 201
9.3.4. Systems for Differential Rate Measurements 201
9.3.5. Analog Systems for Catalytic End-Point Detection and Miscellaneous Switching Systems 203
9.4. Computers 207
References 207

CHAPTER 10 ERROR ANALYSIS IN KINETIC-BASED DETERMINATIONS 212

10.1. Minimization of Systematic and Random Fluctuations in Rate Coefficients 212
10.1.1. Single-Rate Measurement Approach 212
10.1.2. Two-Rate Measurement Approach 216
10.1.3. Multirate Measurements: Multipoint Linear Regression Treatment with Predictive Equilibrium Signal Values 218
10.1.4. Optimization of Irreversible, Coupled First-Order Reactions 222

10.2. Regression Computations in Differential Reaction Rate Methods 223
10.2.1. Least-Squares Regression 226
10.2.2. Nonlinear Regression 226

10.3. Comparative Error Studies 227

10.4. Kalman Filtering 230
References 233
CHAPTER 11 KINETIC COMPONENTS IN SEVERAL ANALYTICAL TECHNIQUES OR STEPS IN ANALYSIS

11.1. Diffusion in Analytical Chemistry 238
11.2. Kinetics in Chromatography 240
11.3. Kinetics in Electrochemical Processes 242
11.4. Kinetics in Absorption/Emission Spectroscopy 244
   11.4.1. Series Processes in Nonflame Atomic Absorption Spectroscopy 245
   11.4.2. Other Kinetic Considerations of Interest in Flameless Atomization 246
   11.4.3. Kinetics in Analytical Flame Spectroscopy 248
11.5. Kinetics in Continuous-Flow Sample–Reagent(s) Processing 248
   11.5.1. Kinetics in Air-Segmented Sample–Reagent(s) Processing Systems 249
   11.5.2. Kinetics in Single-Channel Unsegmented Sample–Reagent(s) Processing Systems 252
   11.5.3. Kinetics in Unsegmented Continuous-Flow Systems Using Mixing Chambers 254
11.6. Other Kinetic Aspects of Relevance in Analytical Chemistry 258
References 259

EPILOGUE 263

INDEX 265