CONTENTS

_	. .				
1.	Introduction				
2.	Mea	surement of Reaction Rates	6		
	I.	Introduction	6		
	II.	Slow Reactions.	7		
		A. Change in Temperature	8		
		B. Change in Concentration	9		
		C. Change in Solvent or Ionic Strength	10		
	III.	Fast Reactions	10		
	111,	A Mixing Mothoda			
		A. Mixing Methods B. Sneuer and Residie Methods	12		
		B. Sprung and Periodic Methods.	13		
		C. Continuous Steady-State Methods	20		
		References	20		
3.	Kine	tic Methods for Catalyzed Reactions	22		
	I.	Introduction	22		
	II.	Definition of a Catalyst	23		
	III.	General Catalyst Mechanism	24		
		A. Equilibrium Case	24		
		B. Steady-State Case.	25		
	IV.	Methods for Determining the Catalyst Concentration	25 25		
		A. Initial Reaction Rate Method of Analysis	25 27		
		B. Integration Method	27 30		
	v.	Sensitivity of the Catalyzed Reactions	30 31		
	VI.	Applications of Catalyzed Reactions for Analysis	32		
		A. Homogeneous Catalyzed Solution Reactions			
		B. Heterogeneous Catalyzed Electrode Reactions	32		
		References	56		
			60		
4.	Kine	tic Methods for Uncatalyzed Reactions	67		
	I.	Introduction	67		
	II.	Methods for the Quantitative Determination of a Single Species	67		
		A. Some Analytical Applications	69		
	III.	Methods for the Determination of a Single Species in a Mixture	79		
		A. Criteria for Neglecting Reactions of Slower Reacting Com-			
		ponents			
		B. Criteria for Neglecting Reactions of Faster Reacting Com-			
		ponents			
	IV.	Methods for the Determination of Both Species in a Mixture: $k_A/$			
		$k_{\rm B}$ Is Very Large	75		
		A. Change of Reaction Temperature	75		
		B. Changing Concentration of Reagent or Solvent	40		

CONTENTS

		C. Addition of a Catalyst	76
		References	77
5.		ic Methods for the <i>in situ</i> Simultaneous Determination of Closely	
	Relat	ed Mixtures	78
	I.	Introduction	78
	II.	Analytical Differential Reaction Rate Methods	80.
		A. First-Order or Pseudo-First-Order with Respect to Reactants	~~
		$\{\text{Region I, } [R]_0 \gg ([A]_0 + [B]_0) \} \dots$	80
		B. Second Order (Regions III, IV, and V)	92
		C. Pseudo-First-Order with Respect to the Reagent {Region VII,	
		$ [R]_0 \ll ([A]_0 + [B]_0) \}. $ D. Pseudo-Zero-Order Methods {Regions I through VII, [R]_0 \ll	
		1). Fieldo-Zero-Order Methods (Regions I through VII, [1]) ($([A]_0 + [B]_0)$ through $[R]_0 \gg ([A]_0 + [B]_0)$	137
		$([A]_0 + [D]_0) \text{ introdyn} [A]_0 \gg ([A]_0 + [D]_0) \dots \dots$	140
			110
6.		iderations for the Determination of Organic Mixtures Based on	
		rential Reaction Rates	142
	I.	Reaction Mechanisms	142
		A. Transition State	144
	II.	Correlation of Reaction Rate with Structure	145 145
		A. Aromatic Side-Chain Reactions (The Hammett Equation)B. Resonance Effects on Aromatic Side-Chain Reactions	143
		C. Nucleophilic and Electrophilic Substitution on Aromatic Rings	140
		D. Reactions of Aliphatic Compounds	149
		E. Steric Effects	150
		F. Neighboring Group Participation	152
		G. Effects of Conformation	153
		H. Overall Considerations	155
		I. Other Effects	155
	III.	Applications of Differential Kinetics to Simultaneous Determina-	
		tions of Two Components in a Mixture	156
		A. Established Applications	157
		B. A Perspective of Possible Applications for Differential Reac-	
		tion Rate Analysis	162
		References	183
7	Eval	luation and Comparison of Differential Rate Methods Employed for	
'		Simultaneous Determination of Closely Related Compounds (with	
		the assistance of Louis J. Papa)	187
	. I.	Evaluation of Differential Kinetic Methods	187
		A. The Graphical Extrapolation Method	188
		B. The Method of Proportional Equations	201
		C. First Order and Pseudo-First-Order Methods Where [Reac-	
		$tants] \ll [Reagents]$	215
	II.	Comparison of General First-Order Methods	226
	,	References	230

CONTENTS

8.	Anal	ytical Reactions from the Kinetic Viewpoint	232
	I.	Introduction	232
		A. Fast Solution Reactions.	233
		B. Inorganic Oxidation-Reduction Reactions	236
		C. The Marcus Theory	237
	II.	Reducing Agents	239
		A. Reagents Capable of Reducing Water	239
		B. Reagents Stable in Water	262
	III.	Oxidizing Agents	275
		A. Reagents Capable of Oxidizing Water	275
		B. Analytical Oxidizing Agents	291
	IV.	Some Analytical Implications	308
		References	312
Au	thor]	Index	319
Sul	bject	Index	331

xi