CONTENTS

-11)

	Preface	xi
	How to use the workbooks, exercises, and problems	xvii
Chapter 1	Generalities about the rates of chemical reactions	1
	Introduction	1
	Chemical kinetics: what is it?	1
	The rate of a chemical reaction	4
	How to define the rate of a reaction	4
	The extent of reaction	4
	The evolution of the extent of reaction	6
	The reaction rate	6
	Mass conservation in a chemical reaction	8
	Example: rate of decomposition of uranyl nitrate	9
	The general scheme of kinetics	11
	Let us add some theory: a phenomenological	
	approach	13
	Testing the equation and determining	
	the rate constant	14

Supplement 1.2. A summary of interpretified to know about

v

	Supplement 1.1 Concentration	16
	Supplement 1.2 A summary of what you need to know about	
	differential equations	18
	A differential equation has an infinite number	
	of solutions	19
	The initial condition	20
	How to solve differential equations: a practical guide	21
	Systems of differential equations	21
Chapter 2	Irreversible first-order reactions	23
	Introduction	23
	What is an irreversible first-order reaction?	23
	Unimolecular irreversible reactions	23
	The rate equation	24
	Not all unimolecular reactions have a first-order rate	24
	Solution of the rate equation	25
	The extent of reaction	25
	Solving the rate equation to calculate $\eta(t)$	27
	The concentrations	27
	Test whether Eq. 2.10 fits the data and determine the	
	constant $k(T, p)$	28
	A crude fitting method	28
	The least-squares method for fitting the data	30
Chapter 3	The temperature dependence of the rate	
Chemical broeper	constant: the Arrhenius formula	33
	Introduction	33
	The Arrhenius formula	34
	How to determine the parameters in the Arrhenius formula	35
	How to determine k_0 , E , and n	35
	How to determine the constants in the Arrhenius	26
	A graphic method for using the Amberius formula	26
	A graphic method for using the Arthenius formula	30
	formula	37
	Jornau	01

	The determination of k_0 and E by least-squares fitting	38
	The activation energy	40
	Determination of the Arrhenius parameters: a more realistic	
	example	40
	Fitting the data to determine k_0 and E	41
	How do we use these results?	45
	The decay rate	47
	Where do these equations come from?	47
	Why the rate law is $dA/dt = -kA$?	48
	Why the Arrhenius law?	48
Chapter 4	Irreversible second-order reactions	51
	Introduction	51
	The rate equation for an irreversible, bimolecular reaction	52
	The rate equation for the reaction $A + B \rightarrow C + D$	52
	The rate equation for the reaction $2A \rightarrow C + D$	53
	The rate equation for the reaction $A + B \rightarrow C + D$ in	
	terms of the extent of reaction	53
	The dependence of $\eta(t)$ on time	54
	The evolution of the concentrations	55
	How to use these kinetic equations in practice	57
	An example: the problem and the data	57
	An example: setting up the equations	58
	An example: numerical analysis of the kinetics	59
	What controls the decay time	61
	How to analyze kinetic data for second-order reactions	63
	An example of analysis	64
	Method I. Calculating k for each data point	66
	Method II. Using a least-squares fitting	66
Chapter 5	Reversible first-order reactions	69
	Introduction	69
	The rate equation and its solution	72
	The rate equation for concentration	72
	The evolution of the concentrations	74

	The change of the extent of reaction and concentration:	
	an example	74
	Understanding the numerical results in the example	76
	The connection to thermodynamic equilibrium	78
	Equilibrium concentration by taking the long time limit	
	in the kinetic theory	78
	Data analysis: an example	80
	The conversion of 4-hydroxybutanoic acid to its lactone	80
	The equations used in analysis	81
	A method of analysis	84
Chapter 6	Reversible second-order reactions	87
	Introduction	87
	The rate equations	88
	The equilibrium conditions	89
	Mass conservation	90
	The rate equations in terms of the extent of reaction	91
	A general equation for the rate of change of $\eta(t)$	92
	The solution of the general rate equation for $\eta(t)$	94
	The solution provided by Mathematica	95
	Solving the differential equation for $\eta(t)$ by using	
	the methods learned in calculus	96
	Calculate $\eta(t)$ for the four types of reaction	97
	The use of these equations	98
	Analysis of the reaction $2HI \rightleftharpoons H_2 + I_2$	100
	A summary of the equations needed for analysis	102
	Using the equilibrium information	103
	Fitting the data to find k_b	105
	How to use the results of this analysis	106
Chapter 7	Coupled reactions	109
	Introduction	109
	First-order irreversible parallel reactions	111
	The rate equations	111
	Independent variables: the extents of the reactions	111

	The change of concentration: mass conservation	112
	The rate equations in terms of η_1 and η_2	113
	Solving the rate equations for $\eta_1(t)$ and $\eta_2(t)$	114
	First-order irreversible consecutive reactions	116
	The rate equations	116
	Mass conservation	117
	The rate equations for η_1 and η_2	118
	Solving the rate equations to obtain $\eta_1(t)$ and $\eta_2(t)$	118
	The evolution of the concentrations	119
	The analysis of the results	120
	The steady-state approximation	122
	Why this is called the steady-state approximation	124
	Testing how well the approximation works	125
Chapter 8	An example of a complex reaction:	
Starson in the	chain reactions	129
	Introduction	129
	The correct rate equation	130
	The reaction mechanism: chain reactions	130
	Another chain reaction: nuclear reactors and	
	nuclear bombs	132
	The rate equations for the reactions involved in the	
	mechanism	134
	The rate of change of [HBr]	134
	The rate of change of [Br]	135
	The net rate of change for HBr	136
	Using the five rate equations	137
	The temperature dependence	138
Chapter 9	Enzyme kinetics	141
	Introduction	141
	The Michaelis-Menten mechanism: exact numerical	
	solution	143
	The rate equations	143
	The extents of reaction	145

ix

Mass conservation	145
The rate equations for $\eta_1(t)$ and $\eta_2(t)$	146
The solution of the rate equations	147
The Michaelis–Menten mechanism: the steady-state	
approximation	149
The differential equation for $R(t)$	151
The differential equation for the evolution of $P(t)$	152
Practical use of the steady-state approximation to determine	
K_m and $k_2 E(0)$	152
The evolution of the concentrations in the steady-state	
approximation	155
The evolution of $R(t)$	155
The evolution of $P(t)$ in the steady-state approximation	156
The concentration of the complex and of the enzyme	
in the steady-state approximation	156
The Michaelis-Menten mechanism: how good is the	
steady-state approximation?	156

Further reading	161
Index	163