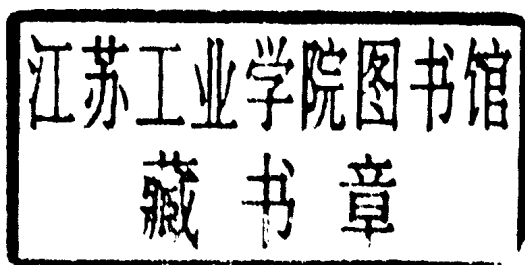


**Reaction Mechanisms of  
Inorganic and Organometallic  
Systems**

# **Reaction Mechanisms of Inorganic and Organometallic Systems**

ROBERT B. JORDAN



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# Preface

This book has evolved from the lecture notes of the author for a one-semester course given to senior undergraduates and graduate students over the past 20 years. There is more material than can be covered in depth in one semester, but the organization allows the lecturer to give less coverage to certain areas without jeopardizing an understanding of other areas. It is assumed that the students are familiar with elementary crystal field theory and its applications to electronic spectroscopy and energetics, and concepts of organometallic chemistry, such as the 18-electron rule,  $\pi$  bonding, and coordinative unsaturation. The terminology and developments of elementary kinetics are given in the first two chapters, where some background from a physical chemistry course would be useful, and a familiarity with simple differential and integral calculus is assumed.

The material generally has been updated to developments through 1990, with references to the original literature provided along with recent review articles. It is expected that students will obtain further information from these sources and gain a feeling for the excitement in the field and an ability to evaluate such work critically. Some sample problems covering the work in each chapter are given at the end of the book.

The issue of units continues to be a vexing one in this area. A major goal of this course has been to provide students with sufficient background that they can read and analyze current research papers. To do this and be able to compare results, the reader must be ever vigilant about the units used by different authors. There is now general agreement that the time unit for rate constants is  $s^{-1}$  and this has been adopted throughout. Energy units are a different matter. Since both joules and calories are in common usage, both units have been retained in the text, with the choice made on the basis of the units in the original work as much as possible. However, within individual sections the text attempts to use one energy unit. In spectroscopic areas the  $cm^{-1}$  is dominant, but spectra are often given in nanometers and the conversion between these units and calories and joules is given when it seems important to understanding the issue being covered. Bond lengths are given in angstroms, which are still commonly used in crystallography, and in picometers, which are used in theoretical calculations. The formulas for such calculations are given in the original or most common format and units

for the various quantities are always specified.

The author is indebted to all those whose research efforts have provided the core of material for this book. The author is pleased to acknowledge those who have provided the inspiration for this book: first, my parents, who contributed the early atmosphere and encouragement; second, Henry Taube, whose intellectual and experimental guidance ensured my continuing enthusiasm for mechanistic studies. Finally and foremost, Anna has been a vital force in the creation of this book through her understanding of the time commitment, her force of will to see the project completed, and her invaluable comments, criticisms, and assistance in producing the manuscript.

R. B. J.

*Edmonton, Alberta*  
*March 1991*

# Contents

## **1 Tools of the Trade, 1**

- 1.1 Basic Terminology, 1
- 1.2 Analysis of Rate Data, 2
- 1.3 Concentration Variables and First-Order Rates, 9
- 1.4 Complex Rate Laws, 10
- 1.5 Complex Kinetic Systems, 11
- 1.6 Temperature Dependence of Rate Constants, 13
- 1.7 Pressure Dependence of Rate Constants, 16
- 1.8 Ionic Strength Dependence of Rate Constants, 17
- 1.9 Diffusion-Controlled Rate Constants, 19

## **2 Rate Law and Mechanism, 23**

- 2.1 Steady-State Approximation, 23
- 2.2 Rapid Equilibrium Assumption, 25
- 2.3 Principle of Detailed Balancing, 27
- 2.4 Principle of Microscopic Reversibility, 27

## **3 Ligand Substitution Reactions, 29**

- 3.1 Operational Approach to Classification of Substitution Mechanisms, 29
- 3.2 Operational Tests for the Stoichiometric Mechanism, 30
- 3.3 Examples of Tests for a Dissociative Mechanism, 36
- 3.4 Operational Test of an Associative Mechanism, 40
- 3.5 Operational Tests for the Intimate Mechanism, 43
- 3.6 Some Special Effects, 57
- 3.7 Variation of Substitution Rates with Metal Ion, 65
- 3.8 Ligand Substitution on Labile Transition-Metal Ions, 74
- 3.9 Kinetics of Chelate Formation, 81

## **4 Stereochemical Change, 91**

- 4.1 Types of Ligand Rearrangements, 91
- 4.2 Optical and Geometrical Isomer Interconversion, 94
- 4.3 Stereochemical Change in Five-Coordinate Systems, 102
- 4.4 Fluxional Organometallic Compounds, 103

**5 Reaction Mechanisms of Organometallic Systems, 119**

- 5.1 Ligand Substitution Reactions, 119
- 5.2 Insertion Reactions, 130
- 5.3 Oxidative Addition Reactions, 136
- 5.4 Reactions of Alkenes, 142
- 5.5 Catalytic Hydrogenation of Alkenes, 146
- 5.6 Homogeneous Catalysis by Organometallic Compounds, 159

**6 Oxidation-Reduction Reactions, 167**

- 6.1 Classification of Reactions, 167
- 6.2 Outer-Sphere Electron-Transfer Theory, 170
- 6.3 Differentiation of Inner-Sphere and Outer-Sphere Mechanisms, 183
- 6.4 Bridging Ligand Effects in Inner-Sphere Reactions, 184
- 6.5 Intervalence Electron Transfer, 190
- 6.6 Electron Transfer in Metalloproteins, 194

**7 Inorganic Photochemistry, 198**

- 7.1 Basic Terminology, 198
- 7.2 Kinetic Factors Affecting Quantum Yields, 200
- 7.3 Photochemistry of Cobalt(III) Complexes, 201
- 7.4 Photochemistry of Rhodium(III) Complexes, 205
- 7.5 Photochemistry of Chromium(III) Complexes, 207
- 7.6 Ru(II) Polypyridine Complexes, 211
- 7.7 Organometallic Photochemistry, 211
- 7.8 Photochemical Generation of Reaction Intermediates, 219

**8 Bioinorganic Systems, 224**

- 8.1 Vitamin B<sub>12</sub>, 224
- 8.2 A Zinc(II) Enzyme: Carbonic Anhydrase, 233
- 8.3 Enzymic Reactions of Dioxygen, 239

**Problems, 255**

**Chemical Abbreviations, 267**

**Index, 269**

# 1

## Tools of the Trade

This chapter covers the basic terminology related to the types of studies that are commonly used to provide information about a reaction mechanism. More background material is available from physical chemistry texts.<sup>1,2</sup> Experimental techniques are not discussed in this book, but such information is available from the recent review by Wilkins<sup>3</sup> on rapid reaction methods and from the earlier book by Caldin.<sup>4</sup> The reader is also referred to the initial volumes of the series edited by Bamford and Tipper.<sup>5</sup>

### 1.1 BASIC TERMINOLOGY

As with most fields, the study of reaction kinetics has some terminology with which one must be familiar in order to understand advanced books and research papers in the area. The following is a summary of some of these basic terms and definitions. Many of these should be familiar from previous studies in introductory and physical chemistry, and further background can be obtained from textbooks devoted to the physical chemistry aspects of reaction kinetics.

#### Rate Law

The rate law is the experimentally determined dependence of the reaction rate on reagent concentrations. It has the following general form:

$$\text{Rate} = k [A]^m [B]^n \dots \quad (1.1)$$

where  $k$  is a proportionality constant called the rate constant. The exponents  $m$  and  $n$  are determined experimentally from the kinetic study. It should be noted that the exponents in the rate law have no necessary relationship to the stoichiometric coefficients in the balanced chemical reaction, and the rate law may even contain species that do not appear in the balanced reaction.

The rate law is an essential piece of mechanistic information because it contains the concentrations of species necessary to get from the reactant to the product by the lowest energy pathway. A fundamental requirement of an acceptable mechanism is that it must predict a rate law consistent with the experimental rate law.



### Order of the Rate Law

The order of the rate law is the sum of the exponents in the rate law. For example, if  $m = 1$  and  $n = -2$  in Eq. (1.1), the rate law has an overall order of  $-1$ . However, except in the simplest cases, it is best to describe the order with respect to individual reagents; in this example, first order in  $[A]$  and inverse second order in  $[B]$ .

### Rate Constant

The rate constant ( $k$ ) is the proportionality constant that relates the rate to the reagent concentrations (or activities or pressures, for example), as shown in Eq. (1.1). The units of  $k$  depend on the rate law and must give the right-hand side of Eq. (1.1) the same units as the left-hand side.

### Half-time

The half-time ( $t_{1/2}$ ) is the time required for a reactant concentration to change by half of its total change. This term is used to convey a qualitative idea of the time scale and has a quantitative relationship to the rate constant in simple cases. In complex systems, the half-time may be different for different reagents and one should specify the reagent to which the  $t_{1/2}$  refers.

### Lifetime

For a particular species, the lifetime ( $\tau$ ) is the concentration of that species divided by its rate of disappearance. This term is commonly used in so-called lifetime methods, such as nmr, and in relaxation methods, such as temperature-jump.

## 1.2 ANALYSIS OF RATE DATA

In general, a kinetic study begins with the collection of data of concentration versus time of a reactant or product. As will be seen later, this can also be accomplished by determining the time dependence of some variable that is proportional to concentration, such as absorbance or nmr peak intensity. The next step is to fit the concentration-time data to some model that will allow one to determine the rate constant if the data fits the model.

The following section develops some integrated rate laws for the models most commonly encountered in inorganic kinetics. This is essentially a mathematical problem; given a particular rate law as a differential equation, the equation must be reduced to one concentration variable and then integrated. The integration can be done by standard methods or by reference to integration tables. Many more complex examples are given in advanced textbooks on kinetics.

### 1.2.a Zero-Order Reaction

A zero-order reaction is rare for inorganic reactions in solution but is

included for completeness. For the general reaction



the zero-order rate law is given by

$$\frac{d[B]}{dt} = k \quad (1.3)$$

and integration over the limits  $[B] = [B]_0$  to  $[B]$  and  $t = 0$  to  $t$  yields

$$[B] - [B]_0 = kt \quad (1.4)$$

This predicts that a plot of  $[B]$  or  $[B] - [B]_0$  versus  $t$  should be linear with a slope of  $k$ .

### 1.2.b First-Order System Coming to Equilibrium

Normally, the simple first-order system would be described at this point but, since it can be generated as a special case of the equilibrium situation, we will start with the more complex system described by Eq. (1.5):



The rate of disappearance of A equals the rate of appearance of B and

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1 [A] - k_{-1} [B] \quad (1.6)$$

The problem is to convert this equation to a form with only one concentration variable, either  $[A]$  or  $[B]$ , and then integrate the equation to obtain the *integrated rate law*. The choice of the variable to retain will depend on what has actually been measured experimentally. The elimination of one concentration is done by considering the reaction stoichiometry and the initial conditions. The most general conditions are that both A and B are present initially at concentrations  $[A]_0$  and  $[B]_0$ , respectively. If the concentrations are defined as  $[A]$  and  $[B]$  at any time and as  $[A]_e$  and  $[B]_e$  at equilibrium, then from mass balance

$$[A]_0 + [B]_0 = [A] + [B] = [A]_e + [B]_e \quad (1.7)$$

therefore

$$[A] = [A]_0 + [B]_0 - [B] \quad \text{and} \quad [A]_0 = [A]_e + [B]_e - [B]_0 \quad (1.8)$$

so that

$$[A] = [A]_e + [B]_e - [B]_0 + [B]_0 - [B] = [A]_e + [B]_e - [B] \quad (1.9)$$

Now one can substitute for  $[A]$  from Eq. (1.9) into Eq. (1.6) to obtain

$$\frac{d[B]}{dt} = k_1 ([A]_e + [B]_e) - (k_1 + k_{-1}) [B] \quad (1.10)$$

Note that the initial concentrations have been eliminated.

Since the preceding equation contains only one concentration variable,  $[B]$ , it can be integrated directly. However, it is convenient in the end to eliminate  $[A]_e$  by noting that, at equilibrium, the rate in the forward direction must be equal to the rate in the reverse direction:

$$k_1 [A]_e = k_{-1} [B]_e \quad (1.11)$$

and substitution for  $k_1[A]_e$  into Eq. (1.10) gives

$$\begin{aligned} \frac{d[B]}{dt} &= k_{-1} [B]_e + k_1 [B]_e - (k_1 + k_{-1}) [B] \\ &= (k_1 + k_{-1}) ([B]_e - [B]) \end{aligned} \quad (1.12)$$

This equation can be rearranged and integrated over the limits  $[B] = [B]_0$  to  $[B]$  and  $t = 0$  to  $t$  to obtain

$$\ln([B]_e - [B]) - \ln([B]_e - [B]_0) = -(k_1 + k_{-1}) t \quad (1.13)$$

Therefore, a plot of  $\ln([B]_e - [B])$  versus  $t$  should be linear with a slope of  $-(k_1 + k_{-1})$ . Note that the kinetic study yields the sum of the forward and reverse rate constants. If the equilibrium constant ( $K$ ) is known, then  $k_1$  and  $k_{-1}$  can be calculated since  $K = k_1/k_{-1}$ .

A very important practical advantage of the first-order system is that *the analysis can be done without any need to know the initial concentrations*. This means that the collection of concentration-time data can be started at any time arbitrarily defined as  $t = 0$ .

At the reaction half-time,  $t = t_{1/2}$ ,  $[B] = 1/2([B]_e - [B]_0) + [B]_0$ , and substitution into Eq. (1.13) gives

$$t_{1/2} = \frac{\ln 2}{k_1 + k_{-1}} = \frac{0.693}{k_1 + k_{-1}} \quad (1.14)$$

Therefore, the half-time is independent of the initial concentrations.

### 1.2.c First-Order Irreversible System

Strictly speaking, there is no such thing as an irreversible reaction. It is just a system in which the rate constant in the forward direction is much larger than that in the reverse direction. Since  $K = k_1/k_{-1}$ , this corresponds to having a very large equilibrium constant for the reaction, so that Eq. (1.5) simplifies to



The kinetic analysis of the irreversible system is a special case of the reversible system just described in which  $k_1 \gg k_{-1}$ . Then  $[B]_e$  is replaced by  $[B]_\infty$ , the final concentration of B at "infinite time." In addition, mass balance requires that

$$[B]_\infty = [A]_0 + [B]_0 \quad (1.16)$$

so that substitution into Eq. (1.13), noting that  $(k_1 + k_{-1}) = k_1$  because  $k_1 \gg k_{-1}$ , gives

$$\ln([B]_\infty - [B]) - \ln([B]_\infty - [B]_0) = -k_1 t \quad (1.17)$$

A plot of  $\ln([B]_\infty - [B])$  versus  $t$  should be linear with a slope of  $-k_1$ .

At the reaction half-time,  $[B] = 1/2([B]_\infty - [B]_0) + [B]_0$ , and substitution into Eq. (1.17) gives

$$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1} \quad (1.18)$$

A more familiar form of the integrated rate law in terms of A can be obtained by substitution from Eq. (1.16) into Eq. (1.17) and noting that

$$[B] = [B]_0 + [A]_0 - [A] \quad (1.19)$$

to give

$$-\ln[A] + \ln[A]_0 = k_1 t \quad (1.20)$$

or

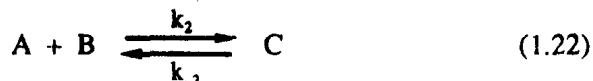
$$[A] = [A]_0 e^{-k_1 t} \quad (1.21)$$

The same form is obtained by directly integrating  $-d[A]/dt = k_1[A]$ .

The first-order irreversible solution has the same mathematical form as the reversible case and the same advantages with regard to initial conditions.

**1.2.d Second-Order System Coming to Equilibrium**

This system can be described by



and the rate of formation of C is given by

$$\frac{d[C]}{dt} = k_2 [A] [B] - k_{-2} [C] \quad (1.23)$$

To simplify the development, one can assume that there is no C present initially and that the stoichiometry is 1 : 1 : 1, so that mass balance gives initially

$$[A] = [A]_0 - [C] \quad \text{and} \quad [B] = [B]_0 - [C] \quad (1.24)$$

and at equilibrium

$$[A]_e = [A]_0 - [C]_e \quad \text{and} \quad [B]_e = [B]_0 - [C]_e \quad (1.25)$$

If the stoichiometry is other than 1 : 1 : 1, then appropriate stoichiometry coefficients must be used in the mass balance conditions and in Eq. (1.23).

Substitution of the initial conditions into Eq. (1.23) gives an equation that can be integrated because [C] is the only concentration variable. However, it proves convenient to eliminate  $k_{-2}$  from the equation before integrating by noting that the forward and reverse rates are equal at equilibrium:

$$k_2 ([A]_0 - [C]_e) ([B]_0 - [C]_e) = k_{-2} [C]_e \quad (1.26)$$

so that

$$k_{-2} = \frac{k_2 ([A]_0 - [C]_e) ([B]_0 - [C]_e)}{[C]_e} \quad (1.27)$$

and substitution into Eq. (1.23) yields

$$\frac{d[C]}{dt} = k_2 \frac{([C]_e - [C]) ([A]_0 [B]_0 - [C]_e [C])}{[C]_e} \quad (1.28)$$

This equation can be rearranged and integrated over the limits  $[C] = 0$  to  $[C]$  and  $t = 0$  to  $t$  to give the following solution:

$$\ln\left(\frac{[A]_0[B]_0 - [C]_e[C]}{[C]_e([C]_e - [C])}\right) + \ln\left(\frac{[C]_e^2}{[A]_0[B]_0}\right) = \left(\frac{([A]_0[B]_0 - [C]_e^2)k_2}{[C]_e}\right)t \quad (1.29)$$

A plot of the first term on the left-hand side of Eq. (1.29) versus  $t$  should be linear with a slope related to  $k_2$ , as indicated by the right-hand side of Eq. (1.29). It is apparent that *one must know the initial concentrations,  $[A]_0$  and  $[B]_0$ , and the final concentration,  $[C]_e$ , in order to do the analysis and to determine the value of  $k_2$  from the slope.* These requirements make this an unpopular and uncommon situation for experimental studies.

### 1.2.e Second-Order Irreversible System

This system can be obtained as a special case of the reversible system by simple consideration of the stoichiometry conditions. If  $[A]_0 < [B]_0$  and the reaction in Eq. (1.22) goes essentially to completion, then  $[C]_e = [A]_0$ , and substitution of this condition into Eq. (1.29) gives

$$\ln\left(\frac{[B]_0 - [C]}{[A]_0 - [C]}\right) + \ln\left(\frac{[A]_0}{[B]_0}\right) = ([B]_0 - [A]_0)k_2t \quad (1.30)$$

In this case, the initial concentrations of both reactants are required in order to plot the first term on the left versus  $t$  and to determine  $k_2$  from the slope. These conditions are not as restrictive as those for the reversible second-order system, but they are still worse than those for the first-order system.

At the half-time for this second-order reaction,  $[C] = [A]_0/2$ , and substitution into Eq. (1.30) shows that

$$t_{1/2} = \frac{1}{([B]_0 - [A]_0)k_2} \ln\left(\frac{2[B]_0 - [A]_0}{[B]_0}\right) \quad (1.31)$$

### 1.2.f Pseudo-First-Order Reaction Conditions

The pseudo-first-order reaction condition is very widely used, but it is seldom mentioned in textbooks. Although many reactions have second-order or more complex rate laws, the experimental kineticist wishes to optimize experiments by taking advantage of the first-order rate law since it imposes the fewest restrictions on the conditions required to determine a reliable rate constant. The trick is to use the pseudo-first-order condition.

The *pseudo-first-order condition* is that the concentration of the reactant whose concentration is monitored is much smaller ( $<10$  times) than that of all the other reactants, so that the concentrations of all the latter remain essentially constant during the reaction. Under this condition, the rate law usually simplifies to a first-order form and one gains the advantage of not needing to know the initial concentration of the deficient reagent.

In the preceding irreversible second-order example, if it is assumed that the conditions have been set so that  $[B]_0 \gg [A]_0$ , then  $[B]_0 \gg [C]$ . In addition, the concentration of B will remain constant at  $[B]_0$ , and the final concentration of C is  $[C]_\infty = [A]_0$  if the reaction is irreversible and has 1 : 1 stoichiometry. Substitution of these conditions into Eq. (1.30) gives

$$\ln \left( \frac{[C]_\infty}{[C]_\infty - [C]} \right) = [B]_0 k_2 t \quad (1.32)$$

This equation predicts that a plot of  $\ln([C]_\infty - [C])$  versus  $t$  should be linear with a slope of  $-k_2[B]_0$ . This is identical in form to the first-order rate law except that  $k_1$  is replaced by  $k_2[B]_0$ . The latter constant is often called the observed or experimental rate constant ( $k_{\text{obsd}}$  or  $k_{\text{exp}}$ ). Since  $[B]_0$  is known, it is possible to calculate  $k_2$ .

In a more general case, if the rate of disappearance of reactant A is given by

$$-\frac{d[A]}{dt} = k [X]^x [Y]^y [Z]^z [A] \quad (1.33)$$

and the conditions are such that  $[X]_0, [Y]_0, [Z]_0 \gg [A]$ , then

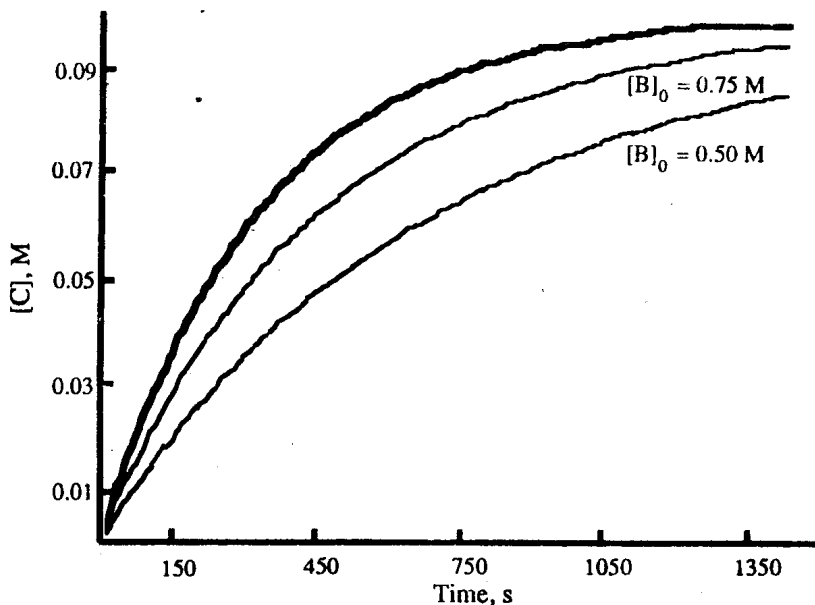
$$-\frac{d[A]}{dt} = k [X]_0^x [Y]_0^y [Z]_0^z [A] = k_{\text{exp}} [A] \quad (1.34)$$

and the rate law has the first-order form.

### 1.2.g Comparison of First-Order and Second-Order Conditions

It is helpful to compare the time dependence of the formation of C for the first- and second-order conditions for the case where the rate constant is the same and the initial concentrations are changed.

In Figure 1.1,  $[A]_0 = 0.10 \text{ M}$  and  $k_2 = 3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . The heavy line shows a pseudo-first-order dependence of  $[C]$  when  $[B]_0 = 10 \times [A]_0 = 1.0 \text{ M}$ , so that  $k = [B]_0 k_2 = 3 \times 10^{-3} \text{ s}^{-1}$ . Under second-order conditions, such as  $[B]_0 = 5 \times [A]_0 = 0.50 \text{ M}$ , the time dependence of  $[C]$  follows a second-order rate law and  $[C]$  increases more slowly than in the pseudo-first-order case. As  $[B]_0$  increases to  $0.75 \text{ M}$ , the second-order curve becomes more similar to the first-order curve, and when  $[B]_0 = 10 \times [A]_0$ , the two curves are nearly indistinguishable. The system is now approaching a pseudo-first-order condition; this is the rationale for the general rule that pseudo-first-order conditions require at least a 10-fold excess of the reagents whose concentrations are to remain constant.



**Figure 1.1.** The time dependence of  $[C]$  for first-order (—) and various second-order (---) conditions with  $[A]_0 = 0.10$  M.

### 1.3 CONCENTRATION VARIABLES AND FIRST-ORDER RATES

The rate laws have been developed in terms of concentrations, but in many cases it is not practical or possible to determine actual molar concentrations as a function of time. However, it is easy to measure some property that is known to be directly proportional to molar concentration, such as absorbance, nmr or ir integrated peak intensity, conductance, or refractive index. In such cases, the first-order system can still be analyzed to determine the rate constant.

The following development assumes an irreversible system but can easily be expanded to the more general reversible case. The system and integrated rate law are given by Eqs. (1.15) and (1.21), respectively. If the property being observed is called  $I$  and the proportionality constant with concentration is  $\epsilon$ , then initially

$$I_0 = \epsilon_A [A]_0 \quad (1.35)$$

at the end

$$I_\infty = \epsilon_B [B]_\infty = \epsilon_B [A]_0 \quad (1.36)$$



at any time

$$\begin{aligned} I &= \epsilon_A [A] + \epsilon_B [B] = \epsilon_A [A] + \epsilon_B ([A]_0 - [A]) \\ &= (\epsilon_A - \epsilon_B) [A] + I_\infty \end{aligned} \quad (1.37)$$

Substitution for  $[A]$  and  $[A]_0$  in terms of  $I$  and  $I_\infty$  into Eq. (1.21) gives

$$\frac{(I - I_\infty)}{(\epsilon_A - \epsilon_B)} = \frac{I_\infty}{\epsilon_B} e^{-k_1 t} \quad (1.38)$$

so that

$$\ln(I - I_\infty) = \ln\left(\frac{(\epsilon_A - \epsilon_B) I_\infty}{\epsilon_B}\right) - k_1 t \quad (1.39)$$

Therefore, a plot of  $\ln(I - I_\infty)$  versus  $t$  should be linear with a slope of  $-k_1$ .

It is not necessary to know the concentration of  $A$  or any values of  $\epsilon$  in order to determine the rate constant, but one does need  $I_\infty$ . Sometimes it is impossible to measure  $I_\infty$  because of secondary reactions, or inconvenient because the reaction is slow. Such systems can be analyzed by nonlinear least-squares fitting of the data over as much of the reaction as possible, or in a more classical way by the Guggenheim method described in more detail by Moore and Pearson<sup>1</sup> (p. 71), Mangelsdorf,<sup>6</sup> and Espenson<sup>7</sup> (p. 25).

#### 1.4 COMPLEX RATE LAWS

It is not unusual for a rate law to be more complex than the simple zero-, first-, or second-order cases we have considered. In general, the rate law has the following form:

$$\frac{d[A]}{dt} = f([X], [Y], [Z]) [A] = k_{\text{exp}} [A] \quad (1.40)$$

where  $f([X], [Y], [Z])$  is a function of the concentrations of  $X$ ,  $Y$ , and  $Z$ .

In inorganic systems, some common forms of  $k_{\text{exp}}$  are

$$\begin{aligned} k_{\text{exp}} &= k' [X] & k_{\text{exp}} &= k' + k'' [X] \\ k_{\text{exp}} &= \frac{k' [X]}{k'' + [Y]} & k_{\text{exp}} &= \frac{k' [Y] + k''}{k''' + [Z]} \end{aligned} \quad (1.41)$$

The dependence of  $k_{\text{exp}}$  on  $[X]$ ,  $[Y]$ , and  $[Z]$  is determined from a series of kinetic experiments under pseudo-first-order conditions, keeping  $[Y]$  and  $[Z]$