

Fundamentals *of* Chemical Kinetics

基础化学动力学



S.R. LOGAN

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Fundamentals of Chemical Kinetics

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Preface

When teaching chemical kinetics to successive cohorts of undergraduates I have often wished that there existed an inexpensive textbook possessing all the conceivable virtues. It should, as far as possible, treat all aspects of kinetics, rather than leave important topics unmentioned. It should do justice to both experiment and theory, putting the role of each in context. It should explain concepts in ways that students might be expected to understand, aiming for the merits of lucidity and simplicity rather than for excessive erudition.

In December 1993, I was invited to prepare my own undergraduate text on kinetics. In doing this I have started at the beginning since I believe that many difficulties about kinetics are derived from an incomplete understanding of the basics. Technological advances have resulted in the widespread use of many kinetic techniques, not merely by physical chemists, but by organic (and not simply physical organic) chemists, inorganic chemists and biochemists. A growing proportion of the ever-expanding chemical literature contains some kinetic component. For all such workers, the fundamentals of the subject are vitally important. To avoid too large a compendium, in regard to various aspects I have had to make my selection. In so doing, my central aim has been to illustrate the principles involved.

Regarding terminology and units, I have tried to adhere to the best practices which are conventional in the current literature. One point of departure is that I have restricted the use of an arrow (" \rightarrow ") to elementary processes. This I have done because, to understand the kinetics of composite reactions, it is essential that individual reaction steps be clearly distinguished from the overall reaction. The IUPAC recommendation of two different kinds of arrows seems much too subtle a distinction, so overall reactions have been written as balanced equations using an equality sign, " $=$ ".

In writing this book I have had much assistance from friends in Coleraine and elsewhere. John Stewart, formerly of UU Jordanstown and Gertie Taggart, now at Athlone RTC, both plowed through the first draft and marked my errors and omissions. The reviewer enlisted by my publishers made helpful and penetrating observations. Gerry Shannon of Mathematics solved many equations for me. Elaine Urquhart and the Library staff have fetched lots of volumes from obscure corners and from elsewhere by Inter-

Library loan. Dick Jones of Kent and my Coleraine colleagues Norman Brown and Chris Knipe each gave me detailed comment on one draft chapter. Numerous other colleagues have helped me in regard to specific points and I thank them all. Despite all this assistance and my avowed intention to avoid perpetuating errors, I have no doubt that some have filtered through and for these I must accept responsibility.

The first part of my manuscript was typed in the departmental office by Carol Millar and the second part plus all the revisions by my wife Renée. Both had other things to do and to both I am deeply indebted. For the publishers, Kathy Hick and Chris Leeding were most co-operative.

S. R. Logan

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March 1995

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We are grateful to the following for permission to reproduce copyright material: the Royal Society and Lord Porter for Table 3.1; the Royal Society of Chemistry for Figure 12.8 and Table 8.1; the American Chemical Society for Figure 9.6; the American Institute of Physics and Professor Y. T. Lee for Figure 12.3.

To my wife, Renée, and our sons, Bruce and Alan

... and I have no doubt that you will find the book to be a valuable addition to your collection. I have no doubt that you will find the book to be a valuable addition to your collection. I have no doubt that you will find the book to be a valuable addition to your collection.

The first part of my manuscript was prepared in the Department of Chemistry at the University of California, San Diego, and the second part was prepared in the Department of Chemistry at the University of California, San Diego. I have no doubt that you will find the book to be a valuable addition to your collection.

We are grateful to the following for permission to reproduce the material: the Royal Society and Lord Kelvin for Table 1; the Royal Society of Chemistry for Tables 1-3 and Table 4; the American Chemical Society for Figure 2; the American Institute of Physics and Professor Y. I. Lee for Figure 11.

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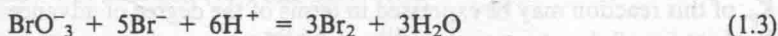
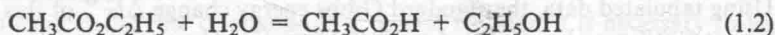
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1 The empirical framework of chemical kinetics

Among the various branches of physical chemistry, such as chemical thermodynamics or spectroscopy, chemical kinetics is unusual in that it interprets and reports experimental data in terms of essentially empirical parameters. In this opening chapter, the concepts which make up this empirical framework are introduced and explained. Their use in the treatment of data on the progress of chemical reactions is then illustrated in a series of selected examples.

1.1 Introduction

One of the basic notions in chemistry is that of a chemical reaction, in which one substance (or group of substances) is converted into another. For such a process, which involves a rearrangement of the bonding electrons of the constituent atoms, a balanced or stoichiometric equation may be written, as in the following examples:



Quantitative studies of chemical reactions tend to fall into one of two groups. There are those relating to the actual occurrence of the reaction, regardless of how quickly or how slowly it takes place. These may measure such quantities as the standard enthalpy change or the standard Gibbs energy change of the reaction. The latter may lead to a knowledge of the extent of reaction expected under specified conditions, for chemical equilibrium to be attained between the reacting substances, written on the left hand side of the equation and the product substances written on the right.

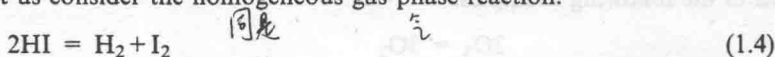
The second group of studies relates to the rapidity with which a chemical reaction occurs and, unlike the first group, it uses time as a variable. Also, it involves a clearly defined concept, called the *reaction rate*. Studies of the dependence of the rate on a range of factors can provide an empirical basis on which one might predict how rapidly the reaction will occur under hypothetical conditions.

In addition, they may provide relevant information about the detailed manner in which the chemical reaction takes place. In some instances they may demonstrate only that the reaction does not occur in a certain way. In others, they may suffice to show that the total chemical process represented in the stoichiometric equation comes about through a particular succession of events. Thus this second group of studies can potentially generate much information about a reaction that could never be discovered on the basis of even the most extended experiments of the first group.

The subject matter of this second group of studies is called *chemical kinetics*. The word "kinetics" (from the Greek, *kīnētikos* = moving) carries the connotation of movement or change. The term is used by chemists to denote not only studies of reaction rate and its dependence on the relevant parameters, but also an understanding of the factors which determine how quickly chemical reactions take place. Thus it encompasses experimental measurement as well as empirical and theoretical approaches to the interpretation of these measurements.

The inter-relationship of chemical thermodynamics and chemical kinetics is an issue of some interest and complexity. However, for chemical reactions that are readily amenable to kinetic study, the reactant and product species are usually all in the same homogeneous phase. Regardless of whether this is the gas phase or solution, thermodynamics tells us that only a certain extent of reaction is possible. For the system to progress beyond this extent of reaction would offend the Second Law of Thermodynamics. On the other hand, there are no laws stipulating how quickly this extent of reaction is approached. The reaction may well be so slow that this is unobservable.

Let us consider the homogeneous gas phase reaction:



Using tabulated data, the standard Gibbs energy change ΔG^\ominus of this reaction at 600 K may be estimated as $23.17 \text{ kJ mol}^{-1}$. The equilibrium constant, K_p , of this reaction may be expressed in terms of the degree of advancement, ξ , where $\xi = 0$ denotes no reaction and $\xi = 1$ represents complete conversion to the products. Thus we obtain the equation,

$$\Delta G^\ominus = -RT \ln \left\{ \frac{\xi^2}{4(1-\xi)^2} \right\} \quad (1.5)$$

which leads to

$$\frac{\xi}{2(1-\xi)} = \exp\left(\frac{-\Delta G^\ominus}{2RT}\right) = 0.0981 \quad (1.6)$$

and thus to $\xi = 0.164$. This means we can deduce that at 600 K, reaction (1.4) will proceed only about one-sixth of the way to completion.

It is pertinent to remember that a homogeneous chemical reaction approaching equilibrium is a dynamic system, with continual interconversion of reactants and products. A highly positive value of the Gibbs energy

change may well mean that only a very small degree of advancement of the reaction can be attained, but, no matter how small this is, this does not mean that the process of the forward reaction does not occur. Rather, the situation arises because at that minute value of ξ , the rates of the forward and the reverse reactions are equal.

In recent years, the respective roles of thermodynamics and kinetics may have been altered slightly. Where a chemical species is extremely reactive and inevitably undergoes reaction within a small fraction of a second, the usual means of measuring thermodynamic properties are not appropriate. In such a case, it *may* be possible to derive the standard Gibbs energy of formation of the unstable species by using kinetic data, and if the assumptions which require to be made are justified, then the value so obtained may be quite reliable. (A similar procedure is equally possible in the case of a stable species, but there is simply no need to resort to it.) This emphasises the complementary nature of these two areas of physical chemistry.

1.2 The rate equation

To express the rapidity of a chemical reaction in a quantitative manner requires a definition of the reaction rate. As this concept is normally used, it denotes the rate of change of concentration concomitant with reaction. Considering the hypothetical reaction,



taking place in a closed space, the instantaneous rate of this reaction is given by the rate of decrease of the concentration of A or by the rate of increase of the concentration of B.

To express the rate of change in a precise manner, it is necessary to use calculus. For reaction (1.7) one may write:

$$\text{Rate of reaction} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} \quad (1.8)$$

In many instances a more careful definition of reaction rate is necessary, as is readily illustrated. For reaction (1.3), taking place in homogeneous aqueous solution, the rates of decrease of concentration of bromate and bromide ions are unequal and neither is equal to the rate of increase of the concentration of Br_2 . The convention is that into each rate of change expressions we put, as a quotient, the corresponding stoichiometric coefficient in the balanced chemical equation, where the latter is written in the simplest manner that avoids fractions among these coefficients. Thus, for reaction (1.3), we have:

$$\text{Rate of reaction} = -\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = -\frac{1}{6} \frac{d[\text{H}^+]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt} \quad (1.9)$$

It is prudent to add that, in regard to reaction rate, we are speaking of the change of concentration *due to reaction*. Concentrations may, of course, be altered in other ways, for example by adding more of a substance or by diluting the reaction mixture with solvent. While the definition in equation (1.8) is ideal for a closed system, it needs to be used carefully if the change in concentration of a reactant contains contributions that do not arise from its reaction in the process under study.

For a reaction far from equilibrium, at constant temperature, the rate usually depends on the concentration of each reactant species, in the sense that the rate of reaction is proportional to the concentration raised to a certain power. Expressing it generally, we have the following definition. For the reaction represented by the stoichiometric equation,



if the rate of reaction, $-\frac{1}{\alpha} \frac{d[A]}{dt}$, is proportional to $[A]^p[B]^q[C]^r$, then

p = order of reaction with respect to A,

q = order of reaction with respect to B,

r = order of reaction with respect to C,

and $n = p + q + r$ = the overall reaction order.

Two points implicit in this statement may merit special attention. Firstly, the rate of a chemical reaction is usually a function of the concentration of each *reactant*, but it is unusual for it to be influenced by the concentration of a reaction *product*. Secondly, the reaction orders, p , q and r , are not to be confused with the stoichiometric coefficients, α , β and γ , in the sense that the former group are neither required nor expected to be identical to the latter group.

To turn a proportionality into an equation merely requires the insertion of a constant of proportionality. By putting in such a constant we obtain the equation:

$$\text{Reaction rate} = \frac{1}{\alpha} \frac{d[A]}{dt} = k_n [A]^p [B]^q [C]^r \quad (1.11)$$

This constant k_n is an n th order rate constant*, since n is the overall order of the reaction. The magnitude of k_n may be seen as a measure of the rapidity of the reaction. To consider the simplest situation, if the concentrations of A, B and C were all equal to unity then the reaction rate would be *numerically* equal to k_n : this illustrates the role of a rate constant as a criterion of the reaction rate under specified conditions.

The dimensions and units of the rate constant merit particular attention. Referring to equation (1.11), the left hand side has the dimensions of

* In 1887, Arrhenius argued that the constant of proportionality should be called the "specific reaction rate". Whatever the merits of his argument, his view did not prevail. Among practising kineticists and in the major journals of physical chemistry, the term "rate constant" has virtually universal acceptance, and so it is employed in this book.

Table 1.1 The dependence on the reaction order of the units of a rate constant and of the function of concentration that equates to kt .

Order of reaction	Units of the rate constant	Function of concentration equal to kt
0: zeroth order	$\text{mol dm}^{-3} \text{s}^{-1}$	x
1: first order	s^{-1}	$\ln\{a/(a-x)\}$
2: second order	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\frac{x}{a(a-x)}$
3: third order	$\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	$\frac{a^2 - (a-x)^2}{2a^2(a-x)^2}$

concentration \times (time)⁻¹. Since the right hand side must have the same dimensions and the product, $[A]^p[B]^q[C]^r$, has dimensions, (concentration)ⁿ, it follows that the dimensions of the n th order rate constant k_n are (concentration)⁽¹⁻ⁿ⁾ \times (time)⁻¹.

Although reaction order is defined as above, in a purely empirical manner, it is not unusual to find that it is a positive integer. If $n = 1$, the reaction is said to be *first* order; if $n = 2$, it is *second* order and if $n = 0$, it is *zeroth* order. The resulting units of the rate constant for these and other cases are shown in Table 1.1, where the unit of concentration employed is mol dm^{-3} which is that normally used for kinetic studies in solution.

1.3 Integrated rate equations

On the above basis, for any chemical reaction one can conceive of a rate equation analogous to equation (1.11). Since the left hand side of such an expression will necessarily involve the first derivative of concentration with respect to time, it follows that integration is essential to obtain an expression which inter-relates reactant concentration and time.

For simplicity, let us initially consider a first order reaction. Suppose the chemical reaction denoted by the equation



is kinetically first order. Also, suppose the initial concentration of A at $t = 0$ is equal to a : it is convenient to introduce the variable x to denote the change in concentration as reaction proceeds. So at time t after the reaction has commenced, the concentration of A has fallen to $(a-x)$ and that of L has risen to x . We then have, corresponding to equation (1.11) the relation:

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a-x) \quad (1.12)$$