

CHEMICAL AND BIOCHEMICAL KINETICS AND MACROKINETICS

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Summary

The analysis of chemically reacting systems is a foundation of the discipline of chemical engineering. Chemical engineers harness reactions to do their work in creating useful products from lower-value raw materials. Accordingly, the analysis of reacting systems is a key component in the chemical engineering toolkit. This chapter is an overview of chemical and biochemical kinetics in chemical engineering. The chapter begins with an overview of classification of chemical reactions and a definition of the reaction rate. Next, the analysis of chemical reactions is introduced with a specific focus on homogeneous chemistry. The mathematical analysis of chemical reactions concludes with an overview of heterogeneous systems. The remainder of the chapter then is devoted to methods for obtaining reaction rate coefficients. First, the analysis of experimental kinetic data is covered. The final section of the chapter discusses the prediction of reaction rates from theory.

1. Introduction

Chemical kinetics is the study of the rates of chemical reactions. Our chief task as chemical engineers is the efficient conversion of raw materials to useful products – and this is frequently accomplished through *chemical* means. Accordingly, it is imperative to build into our “engineering toolkit” a strong foundation in chemical kinetics. One of the earliest examples of the application of chemical kinetics to solve engineering problems can be to when humans began using fermentation to produce alcohol. During the 20th century the importance of chemical kinetics grew in tandem with the importance of crude oil refining in the production of fuels and plastics. More recently scientists and engineers have had tremendous success in harnessing the power of biochemical transformations for the production of fuels, pharmaceuticals and useful raw materials like plastics. Accordingly, the study of biochemical kinetics has become requisite learning in many chemical engineering curricula. This list is not meant to be exhaustive, but simply to illustrate the incredibly diverse range of problems for which a working knowledge of chemical and biochemical kinetics is necessary.

The field of *chemical reaction engineering* is intimately linked with the study of chemical kinetics. Chemical reaction engineering is the process in which individual reactions or a sequence of interconnected reactions, *i.e.* a reaction mechanism, is harnessed for useful purposes. Chemical reaction engineering requires intimate knowledge of the reactions taking place in a particular system so that advantageous reactions can be enhanced and deleterious reactions can be limited to the maximum extent possible. This process is shown schematically in Figure 1 in which the overall goal is to produce product D from reactant A. As shown in the Figure, byproducts are harmful to the overall production of D. A complete kinetic analysis of this system in conjunction with detailed material and energy balances will yield an optimum solution to this problem in which the production of D is maximized. The importance of chemical kinetics is further amplified when one considers that such an approach is quite general and may be applied to any field of study in which reacting systems are important.

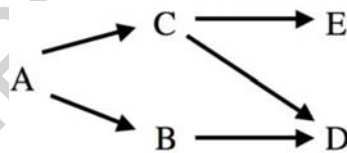


Figure 1. Schematic of Reaction Network

The remainder of the introduction will introduce an overview of how chemical reactions are classified. Finally, we introduce the concept of the chemical reaction rate and discuss the major factors that control the reaction rate.

1.1. Classification of Chemical Reactions

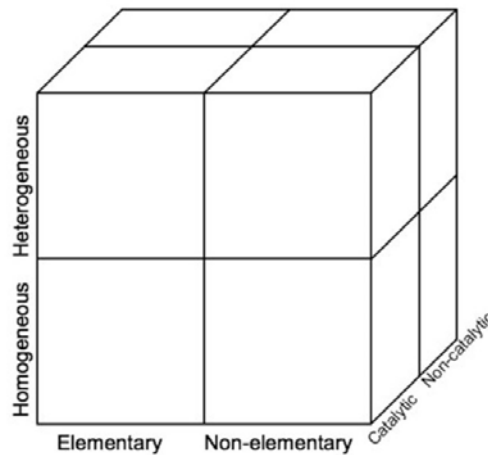
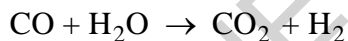


Figure 2. Categories for classifying chemical reactions

Chemical reactions can be classified in a number of different ways. Most methods for classifying a reaction are complementary. In fact, in many cases it is convenient and even necessary to use multiple classifications in order to fully understand a reaction. The major types of classifications for chemical reactions are shown in Figure 2. As shown in the Figure, the different classifications make up a three-dimensional space in which nearly all reactions can be usefully classified. A brief description of each classification follows.

A fundamental classification for all reactions is whether the reaction is *elementary* or *non-elementary*. A good definition for an elementary reaction is that elementary reactions actually represent the chemical events that are occurring in a system. For example, the reaction:



is called the “water-gas shift reaction”. It is an important reaction in hydrocarbon production. In reality, this reaction proceeds through a number of intermediate steps, and while the overall reaction shown above represents the net chemical transformation, it does not show the actual chemical events that occur in the water-gas shift process. Thus, the reaction as shown above is a non-elementary reaction. It is important to know whether a reaction is elementary or non-elementary as this will determine how you approach, among other things, studying the reaction and estimating its rate using theoretical approaches.

The next major classification of chemical reactions refers to whether the reactions are mediated or not. Reactions that are *catalytic* occur in the presence of and are mediated by a *catalyst*. By definition a catalyst is anything that affects the rate of reaction without being consumed or destroyed in the process of the reaction. A catalyst can take any number of physical forms: enzymes are living catalysts, certain liquid acids function as catalyst, and many metals are known to be important catalysts.

A final important classification of reactions refers to the phase in which the reactions

take place. Reactions that are *homogeneous* are mono-phasic, and all the reactants exist in the same phase in which the reaction itself occurs. Homogeneous reactions can be catalyzed or uncatalyzed as well as elementary or non-elementary. Many common catalytic reactions are heterogeneous owing to the fact that industrial catalysts used in the production of chemicals are frequently metallic.

1.2. Definition of the Reaction Rate

In strict terms, the *rate* of a chemical reaction can be defined extensively. For any batch of reacting material there is a net rate of reaction that depends on the amount of material present. Strictly speaking, the rate of reaction is the time derivative of one of the amount of material undergoing reaction. In practice, however, it is far more common to define the reaction rate intensively based on some property of the reactor or catalyst. For example, in the reaction:



the rate of disappearance of compound A, *i.e.*, the rate of reaction is defined as:

$$r_A = -\frac{1}{V} \frac{dN_A}{dt} \left[\frac{\text{mol}}{\text{vol} * \text{time}} \right] \quad (1)$$

where N_A is the number of moles of reactant A and V is the volume of the reactor. As shown in Eq. (1), the reaction rate has units of mol/volume/time. Since component A is consumed in the above example, the time derivative dN_A/dt will be negative. By convention, the rate of reaction is always defined to be positive, hence the negative sign in Eq. (1). In most liquid-phase reactions the reactor volume is constant and it is more convenient to define the rate in terms of species concentrations:

$$r_A = -\frac{dC_A}{dt} \quad (2)$$

Depending on the type of reactor and the type of chemical reaction, it may be more convenient to define the reaction rate in terms of other quantities. In gas-phase reactions the partial-pressure of the reactants is often used in place of concentrations, in heterogeneous catalysis the rate is defined on a per-mass (of catalyst) basis, and in enzyme catalysis the rate can be defined in terms of the substrate concentration. Overall it is important to remember that the rate of reaction in a particular problem is best defined based on convenience. No matter how the rate is presented, the rate of change of moles of reactant is the same.

1.2.1. Factors Affecting the Reaction Rate

The definition of the reaction rate given above provides the mathematical relationship between the composition of the system and the velocity of a given reaction. The next step is to define a relationship between the velocity of the reaction and key system parameters, *i.e.*, temperature concentration, pressure. In general, most *rate expressions*

involve a term that depends on the concentration of one or more components and a term that depends on the temperature of the system. For example, in the reaction:



the rate of reaction could be defined as follows:

$$r_A = kC_A^2 \quad (3)$$

where the term k is known as the *rate coefficient* or the *rate constant*. The temperature dependence of the rate constant can often be defined using the familiar Arrhenius equation:

$$k = Ae^{-E_A/RT} \quad (4)$$

where A is called the *pre-exponential factor*, E_A is the activation energy, R is the ideal gas constant and T is the system temperature. Combining Eqs. (3) and (4) yields:

$$r_A = \left[Ae^{-E_A/RT} \right] C_A^2 \quad (5)$$

Equation (5) clearly shows how the temperature and concentration affect the reaction rate. For reactions that follow Arrhenius behavior, there is an exponential dependence on the temperature. On the contrary, there is, in general, a much more gentle dependence on the concentration of the species present.

For a given reacting system, the rate equation(s) of the form of Eq. (2) can be written down once the entire *reaction mechanism* is known. The reaction mechanism is the set of governing chemical reactions relevant in a system. This could be just a single reaction, as we have considered in this section, or it could be a complex, inter-connected network of reactions consisting of hundreds of species and thousands of reactions. However, in order to be useful the rate equations need to be related to system composition, temperature, pressure, catalyst mass, etc. as shown in Eqs. (3-5). In general, this elucidation of rate equations is accomplished through the analysis of experimental data or the use of theory and computer simulation. The next two sections of this chapter are devoted to the various types of reactions (and their corresponding rate equations) that chemical engineers typically encounter. The final two sections of this chapter deal with the analysis of kinetic data and the prediction of reaction rates from theory.

2. Analysis of Common Reactions

As chemical engineers there are a number of reactions that are frequently encountered. For example, in analyzing the reaction $A \rightarrow B + C$, we posed the rate expression shown in Eq. (2). The concentration term in equation two is raised to the power of two and accordingly we can say that Eq. (2) is a *second order* rate equation. The *order* of a rate equation is the sum of all the powers of all concentration dependent terms. For a large

number of reactions, the *law of mass action* applies. The law of mass action states that the rate of reaction is proportional to the product of the concentrations of the reactants. In essence, this means that the rate law can be derived from an examination of the stoichiometry. For example, consider the generic reaction, $\alpha A + \beta B + \gamma C \rightarrow \delta D + \varepsilon E$, which we assume can be treated using mass action kinetics. The corresponding rate equation for this reaction (and all reactions for which mass action kinetics are applied) is simple:

$$r_A = kC_A^\alpha C_B^\beta C_C^\gamma \quad (6)$$

It is important to remember that elementary reactions obey the law of mass action, but all reactions that demonstrate mass action kinetics are not elementary. Non-elementary reactions can have very complicated rate expressions that are not obvious simply from examining the stoichiometry of the reaction. Elementary reactions are almost always first or second order, and occasionally third order. Since elementary reactions actually represent the chemical events that occur, a third order elementary reaction can only happen in the event of a simultaneous tri-molecular collision – an event that is statistically much less probable compared with other collision events.

2.1 Zero, First and Second Order Reactions

For low-order reactions that obey mass action kinetics (both elementary and non-elementary), it is helpful to be familiar with the relationship between the reaction rate and the concentration of the reactant(s). Table 1 gives the rate equations for the reaction $A \rightarrow B$ for the cases when the reaction is zero, first or second order. The relationship between the concentration of species A and the overall rate of reaction for these three cases is shown in Figure 3. The x-axis of the Figure is plotted in reverse in order to show how the reaction proceeds from start to finish. The initial concentration of species A is shown in the figure as C_{A0} and the final concentration is C_{Af} . In the case of the zero-order reaction, there is no dependence on the concentration, and the reaction rate is constant for the entire range of concentrations shown. Overall the Figure shows that the higher the order of reaction, the faster the reaction rate, and, thus, the faster the depletion of reactants.

Reaction order	Rate equation
0	$r_A = k$
1	$r_A = kC_A$
2	$r_A = kC_A^2$

Table 1. Rate equations for zero, first and second order reactions

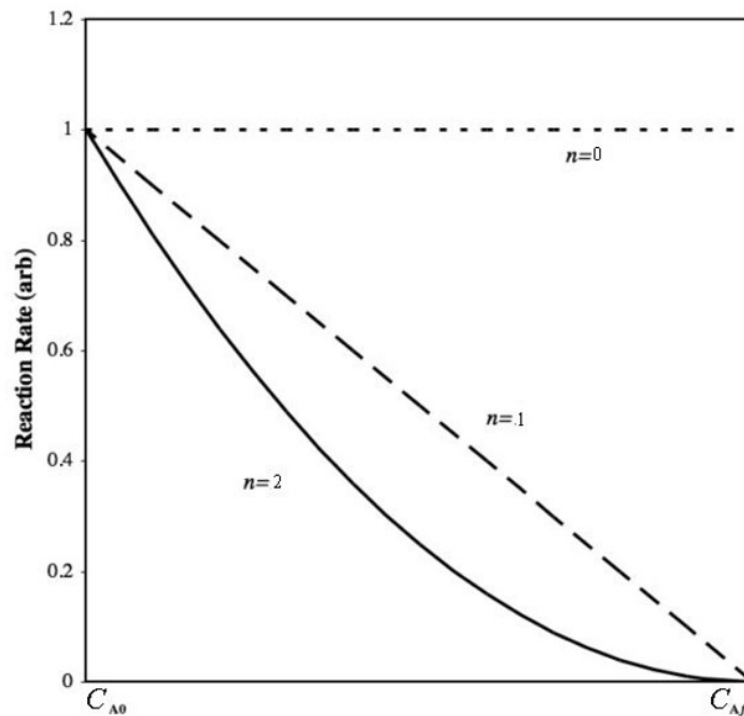


Figure 3. Relationship between reaction order, reaction rate and concentration. The rate relationship is $r = kC_A^n$

In order to elucidate the actual time evolution of the concentration of all species in a reacting system, information about the physical configuration of the reactor must also be included. This is the study of *chemical reaction engineering* and *chemical reactor design*. Both of these subjects are separate chapters in this theme of the EOLSS.

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Bibliography

- Cramer C.J. (2004). *Essentials of Computational Chemistry: Theories and Models*. New York: Wiley.
- Fogler H.S. (2005). *Elements of Chemical Reaction Engineering*. Upper Saddle River, New Jersey: Prentice Hall. [Excellent undergraduate-level textbook for reaction engineering]
- Leach A.R. (2001). *Molecular Modeling: Principles and Applications*. Harlow: Prentice Hall. [This book offers a modern overview of molecular modeling. Including the use of quantum chemical techniques.]
- Levenspiel O. (1999). *Chemical Reaction Engineering*. New York: John Wiley and Sons. [This is a broad overview of chemical kinetics and reactor design. The book is an excellent reference for the analysis of

heterogeneous and catalytic systems]

Masel R.I. (2002). *Chemical Kinetics and Catalysis*. New York: Wiley. [This book offers very a broad overview of kinetics and catalysis.]

Moore J.W. and Pearson R.G. (1981). *Kinetics and Mechanism*. New York: John Wiley and Sons. [This book is an outstanding reference for chemical kinetics. The overview of various reaction rate theories is excellent]

Rawlings O. and Ekerdt J.B. (2007). *Chemical Reactor Analysis and Design Fundamentals*. Madison, Wisconsin: Nob Hill Publishing. [This is a graduate-level text which has a nice overview of chemical kinetics and reactor design]

Sandler S.I. (1999). *Chemical and Engineering Thermodynamics*. New York: Wiley. [This book is recommended for its discussion of thermodynamic equilibrium in chemical reactions and clear discussion on the equilibrium constant.]

Biographical Sketch

Jim Pfaendtner was born in Detroit, MI, USA. He obtained his B.S. in Chemical Engineering (2001) from the Georgia Institute of Technology and his PhD in Chemical Engineering (2007) from Northwestern University under the supervision of Professor Linda J. Broadbelt. In 2009 Jim joined the faculty of The University of Washington as an Assistant Professor of Chemical Engineering. He subsequently was a research associate at the Center for Biophysical Modeling and Simulation (University of Utah, USA) under the supervision of Distinguished Professor Gregory A. Voth. In 2007 he became a National Science Foundation International Research Postdoctoral Fellow (NSF-IRFP) and has since worked in collaboration with Professor Dr. Michele Parrinello and Professor Voth. His research focus features multiscale modeling of biomolecular systems with an emphasis on reaction coordinate elucidation, free-energy calculations, and coarse-grained modeling.