

5.2: Reaction Rates and Rate Laws

Chemical reactions occur under a wide variety of circumstances: Many chemicals are manufactured by passing a homogeneous mixture of gaseous reactants through a bed of solid catalyst pellets. Corrosion of metals is a reaction between the solid metal and oxygen from the air, often catalyzed by other common chemical species like water or chloride ion. An enormous number of biological reactions occur within the cells of living organisms. In the laboratory, we typically initiate a reaction by mixing the reactants, often with a solvent, in a temperature-controlled vessel.

Chemical reactions can be carried out in **batch reactors** and in a wide variety of **flow reactors**. A batch reactor is simply a container, in which we initiate the reaction by mixing the reactants with one another (and any additional ingredients), and in which the reaction occurs and the products remain—until we get around to removing them. A reaction carried out under these conditions is called a **batch reaction**. If any of the reactants are gases, a batch reactor must be sealed to prevent their escape. Otherwise, we may leave the reactor open to the atmosphere as the reaction occurs.

Flow reactor have been designed to achieve a variety of objectives. Nevertheless, they have a number of characteristics in common. A flow reactor is a container, into which reactants and other ingredients are injected. The products are recovered by withdrawing portions of the reaction mixture from one or more locations within the reactor. The rates at which materials are injected or withdrawn are usually constant. In the simplest case, the reactants are mixed at one end of a long tube. The reacting mixture flows through the tube. If the tube is long enough, the mixture emerging from the other end contains the equilibrium concentrations of reactants and products. In such a **tubular reactor**, it is usually a good approximation to assume that the material injected during one short time interval does not mix with the material injected during the next time interval as they pass through the tube. We view the contents of the reactor as a series of fluid “plugs” that traverse the reactor independently of one another and call this behavior **plug flow**.

In [Section 5.11](#), we discuss another simple flow stirred tank, called a **continuous stirred-tank reactor** (CSTR) or a **capacity-flow reactor**. A CSTR consists of a single constant-volume vessel into which reactants are continuously injected and from which reaction mixture is continuously withdrawn. The contents of this container are constantly stirred. In our discussion, we assume that the reactor is completely filled with a homogeneous liquid solution. We express the rate of reaction within the CSTR in moles per liter of reactor volume per second, $\text{mol L}^{-1}\text{s}^{-1}$.

When we talk about the rate of a particular reaction, we intend to specify the amount of chemical change that occurs in unit time because of that reaction. It is usually advantageous to specify the amount of chemical change in units of moles. We can specify the amount of chemical change by specifying the number of moles of a reactant that are consumed, or the number of moles of a product that are produced, per second, by that reaction. If we do so, the amount of chemical change depends on the stoichiometric coefficient of the reactant or product that we choose. Moreover, the rate is proportional to the size of the system. Since the properties of reaction rates that are of interest to us are usually independent of the size of the system, we find it convenient to express reaction rates as moles per second per unit system size, so that the most convenient units are usually concentration per second.

For reactors containing heterogeneous catalysts, we typically express the reaction rate in moles per unit volume of catalyst bed per second. For corrosion of a metal surface, we often express the rate in moles per unit area per second. For biological reactions, we might express the reaction rate in moles per gram of biological tissue per second. For reactions in liquid solutions, we typically express the rate in moles per liter of reaction mixture per second, $\text{mol L}^{-1}\text{s}^{-1}$ or $\underline{M} \text{ s}^{-1}$.

Evidently, we need to express the rate of a reaction in a way that accounts for the stoichiometry of the reaction and is independent of the size of the system. Moreover, we must distinguish the effect of the reaction on the number of moles of a reagent present from the effects of other processes, because competing reactions and mechanical processes can affect the amount of a substance that is present.

To develop the basic idea underlying our definition of reaction rate, let us consider a chemical substance, A , that undergoes a single reaction in a closed system whose volume is V . For a gas-phase reaction, this volume can vary with time, so that $V = V(t)$. (The volume of any open system can vary with time.) Since the system is closed, the reaction is the only process that can change the amount of A that is present. Let Δn_A be the increase in the number of moles of A in a short interval, Δt , that includes time t . Let the average rate at which the number of moles of A increases in this interval be $\bar{r}(A) = \Delta n_A / \Delta t$. The corresponding instantaneous rate is

$$r(A) = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta n_A}{\Delta t} \right) \\ = \frac{dn_A}{dt}$$

To express this information per unit volume, we can define the instantaneous rate of reaction of A , at time t , as

$$R(A) = \frac{1}{V(t)} \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta n_A}{\Delta t} \right) \\ = \frac{1}{V(t)} \frac{dn_A}{dt}$$

Experimental studies of reaction rate are typically done in constant-volume closed systems under conditions in which only one reaction occurs. Most of the discussion in this chapter is directed toward reactions in which these conditions are satisfied, and the system comprises a single homogeneous phase. In the typical case, we mix reactants with a liquid solvent in a reactor and immerse the reactor in a constant-temperature bath. Under these conditions, the rate at which a particular substance reacts is equal to the rate at which its concentration changes. Writing $[A]$ to designate the molarity, mol L^{-1} , of A , we have

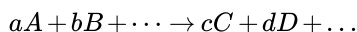
$$R(A) = \frac{1}{V} \frac{dn_A}{dt} \\ = \frac{d(n_A/V)}{dt} \\ = \frac{d[A]}{dt}$$

If we express a reaction rate as a rate of concentration change, it is essential that both conditions be satisfied. If both n_A and V vary with time, we have

$$\frac{d[A]}{dt} = \frac{d(n_A/V)}{dt} \\ = \frac{1}{V} \frac{dn_A}{dt} - \frac{n_A}{V^2} \frac{dV}{dt}$$

The instantaneous rate at which substance A undergoes a particular reaction is equal to $V^{-1} (dn_A/dt)$ only if the reaction is the sole process that changes n_A ; the contribution to $d[A]/dt$ made by $(n_A V^{-2}) dV/dt$ vanishes only if the volume is constant.

If a single reaction is the only process that occurs in a particular system, the rate at which the number of moles of any reactant or product changes is a measure of the rate of the reaction. However, these rates depend on the stoichiometric coefficients and the size of the system. For a reaction of specified stoichiometry, we can use the **extent of reaction**, ξ to define a unique reaction rate, R . The amounts of reactants and products present at any time are fixed by the initial conditions and the stoichiometry of the reaction. Let us write n_A to denote the number of moles of reagent A present at an arbitrary time and n_A^o to denote the number of moles of A present at the time ($t = 0$) that the reaction is initiated. We define the extent of reaction as the change in the number of moles of a product divided by the product's stoichiometric coefficient or as the change in the number of moles of a reactant divided by the negative of the reactant's stoichiometric coefficient. For the stoichiometry



we have

$$\xi = \frac{n_A - n_A^o}{-a} = \frac{n_B - n_B^o}{-b} = \dots \\ = \frac{n_C - n_C^o}{c} = \frac{n_D - n_D^o}{d} = \dots$$

If A is the limiting reagent, ξ varies from zero, when the reaction is initiated with $n_A = n_A^o$, to n_A^o/a , when $n_A = 0$. At any time, t , we have

$$\begin{aligned}\frac{d\xi}{dt} &= -\frac{1}{a} \frac{dn_A}{dt} = -\frac{1}{b} \frac{dn_B}{dt} = \dots \\ &= \frac{1}{c} \frac{dn_C}{dt} = \frac{1}{d} \frac{dn_D}{dt} = \dots\end{aligned}$$

and we can define a unique **reaction rate** as

$$\begin{aligned}R &= \frac{1}{V(t)} \frac{d\xi}{dt} \\ &= -\frac{1}{aV(t)} \frac{dn_A}{dt} \\ &= -\frac{1}{bV(t)} \frac{dn_B}{dt} = \dots \\ &= \frac{1}{cV(t)} \frac{dn_C}{dt} \\ &= \frac{1}{dV(t)} \frac{dn_D}{dt} = \dots\end{aligned}$$

The relationship between the instantaneous rate at which reactant A undergoes this reaction, $R(A)$, and the reaction rate, R , is

$$R(A) = \frac{1}{V(t)} \frac{dn_A}{dt} = -\frac{a}{V(t)} \frac{d\xi}{dt} = -aR$$

If the volume is constant, we have

$$\begin{aligned}\frac{\xi}{V} &= \frac{[A] - [A]_0}{-a} = \frac{[B] - [B]_0}{-b} = \dots \\ &= \frac{[C] - [C]_0}{c} = \frac{[D] - [D]_0}{d} = \dots\end{aligned}$$

and the reaction rate is

$$\begin{aligned}R &= \frac{1}{V} \frac{d\xi}{dt} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \dots \\ &= \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = \dots\end{aligned}$$

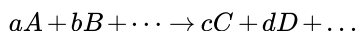
The name “extent of reaction” is sometimes given to the fraction of the stoichiometrically possible reaction that has occurred. To distinguish this meaning, we call it the **fractional conversion**, χ . When A is the stoichiometrically limiting reactant, the fractional conversion is

$$\chi = -\frac{n_A - n_A^o}{n_A^o}$$

The extent of reaction, ξ , and the fractional conversion, χ , are related as $\chi = \frac{a\xi}{n_A^o}$

We have $0 \leq \xi \leq n_A^o/a$ and $0 \leq \chi \leq 1$.

The rate of a reaction usually depends on the concentrations of some or all of the substances involved. The dependence of reaction rate on concentrations is the rate law. It must be determined by experiment. For reaction



the observed rate law is often of the form

$$\begin{aligned}R &= \frac{1}{V} \frac{d\xi}{dt} \\ &= k[A]^m[B]^n \dots [C]^p[D]^q\end{aligned}$$

where m, n, \dots, p, q, \dots are small positive or negative integers or (less often) simple fractions.

We use a conventional terminology to characterize rate laws like this one. We talk about the **order in a chemical species** and the **order of the reaction**. To characterize the rate law above, we say that the reaction is “ m^{th} order in compound A ,” “ n^{th} order in compound B ,” “ p^{th} order in compound C ,” and “ q^{th} order in compound D .” We also say that the reaction is “ $(m + n + \dots + p + q + \dots)^{\text{th}}$ order overall.” Here k is an experimentally determined parameter that we call the **rate constant** or **rate coefficient**.

It frequently happens that we are interested in an overall chemical change whose stoichiometric mechanism involves two or more elementary reactions. In this case, an exact rate model includes a differential equation for each elementary reaction. Nevertheless, it is often possible to approximate the rate of the overall chemical change by a single differential equation, which may be a relatively complex function of the concentrations of the species present in the reaction mixture. For the reaction above, the experimental observation might be

$$R = \frac{1}{V} \frac{d\xi}{dt} \\ = \frac{k_1 [A] [B]}{k_2 [C] + k_3 [D]}$$

In such cases, we continue to call the differential equation the rate law. The concept of an overall order is no longer defined. The constants (k_1 , k_2 , and k_3) may or may not be rate constants for elementary reactions that are part of the overall process. Nevertheless, it is common to call any empirical constant that appears in a rate law a rate constant. In a complex rate law, the constants can often be presented in more than one way. In the example above, we can divide numerator and denominator by, say, k_3 , to obtain a representation in which the constant coefficients have different values, one of which is unity.

Most of the rest of this chapter is devoted to understanding the relationship between an observed overall reaction rate and the rates of the elementary processes that contribute to it. Our principal objective is to understand chemical equilibrium rates in terms of competing forward and reverse reactions. At equilibrium, chemical reactions may be occurring rapidly; however, no concentration changes can be observed because each reagent is produced by one set of reactions at the same rate as it is consumed by another set. For the most part, we focus on reactions that occur in closed constant-volume systems.

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