

## 5.8: Experimental Determination of Rate Laws

The determination of a rate law is a matter of finding an empirical equation that adequately describes reaction-rate data. We can distinguish two general approaches to this task. One approach is to measure reaction rate directly. That is, for  $A + B \rightarrow C$ , we measure the reaction rate in experiments where the concentrations,  $[A]$ ,  $[B]$ , and  $[C]$ , of reactants and products are known. The other is to measure a concentration at frequent time intervals as a batch reaction goes nearly to completion. We then seek a differential equation that is consistent with this concentration-*versus*-time data.

If the reaction is the only process that affects  $\Delta n_C$ , direct measurement of the reaction rate can be effected by measuring  $\Delta n_C$  over a short time interval,  $\Delta t$ , in which the concentrations,  $[A]$ ,  $[B]$ , and  $[C]$ , do not change appreciably. This is often difficult to implement experimentally, primarily because it is difficult to measure small values of  $\Delta n_C$  with the necessary accuracy at known values of  $[A]$ ,  $[B]$ , and  $[C]$ .

### Method of Initial Rates

The **method of initial rates** is an experimentally simple method in which the reaction rate is measured directly. Initial-rate measurements are extensively used in the study of enzyme-catalyzed reactions. Direct measurement of reaction rate can also be accomplished using a flow reactor. We discuss the method of initial rates, a particular kind of flow reactor known as a **CSTR**, and enzyme catalysis in Sections 5.10, 5.11, and 5.13, respectively.

The most common reaction-rate experiment is a batch reaction in which we mix the reactants as rapidly as possible and then monitor the concentration vs. time of one (or more) of the reactants or products as the reaction proceeds. We do the mixing so that the initially mixed reactants are at a known temperature, which can be maintained constant for the remainder of the experiment. The data from such an experiment are a set of concentrations and the times at which they are measured. To find the rate law corresponding to these concentration-*versus*-time data, we employ a trial-and-error procedure. We guess what the rate law is likely to be. We then obtain a general solution for this differential equation. This solution predicts the dependence of concentrations *versus* time as a function of one or more rate constants. If we can obtain a satisfactory fit of experimental concentration-*versus*-time data to the concentration-*versus*-time equation predicted by the rate law, we conclude that the rate law is a satisfactory representation of the experimental data.

For a reaction  $A \rightarrow C$  in a closed constant-volume system, we would want to test a first-order rate law rate law, which we can express in several alternative ways:

$$\frac{1}{V} \frac{d\xi}{dt} = -\frac{d[A]}{dt} = \frac{d[C]}{dt} = k[A]$$

Using the changing concentration of A to express the rate, separating variables, and integrating between the initial concentration  $[A] = [A]_0$  at  $t = 0$  and concentration  $[A]$  at time  $t$  gives

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

so that

$$\ln \frac{[A]}{[A]_0} = -kt$$

or

$$[A] = [A]_0 \exp(-kT)$$

Frequently it is convenient to introduce the extent of reaction or the concentration of a product as a parameter. In the present instance, if the initial concentration of  $C$  is zero,  $[C] = \xi/V = x$ . Then at any time,  $t$ , we have  $[A] = [A]_0 - x$ , and the first-order rate equation can be written as

$$\frac{dx}{dt} = k([A]_0 - x)$$

which we rearrange and integrate between the limits  $x(0) = 0$  and  $x(t) = x$  as

$$\int_0^x \frac{-dx}{[A]_0 - x} = -k \int_0^t dt$$

To give

$$\ln\left(\frac{[A]_0 - x}{[A]_0}\right) = -kt$$

It is easy to test whether concentration versus time data conform to the first-order decay model. If they do, a plot of  $\ln([A]_0 - x)$  or  $\ln[A]$ , versus time,  $t$ , is a straight line.

For a reaction  $2A \rightarrow C$ , we would want to test a rate law rate of the form

$$\frac{1}{V} \frac{d\xi}{dt} = -\frac{1}{2} \frac{d[A]}{dt} = \frac{d[C]}{dt} = k[A]^2$$

If the initial concentration of  $C$  is zero,  $[C] = \xi/V = x$ , and  $[A] = [A]_0 - 2x$  at any time  $t$ . The rate law can be written as

$$\frac{dx}{dt} = k([A]_0 - 2x)^2$$

and rearranged and integrated as

$$\int_0^x \frac{-dx}{([A]_0 - 2x)^2} = -k \int_0^t dt$$

to give

$$\frac{1}{[A]_0 - 2x} - \frac{1}{[A]_0} = 2kt$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = 2kt$$

If concentration-*versus*-time data conform to this second-order rate law, a plot of  $[A]^{-1}$  *versus* time is a straight line.

For a reaction  $A + B \rightarrow C$ , we would want to test a rate law of the form

$$\frac{1}{V} \frac{d\xi}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B]$$

If the initial concentration of  $C$  is again zero,  $[C] = \xi/V = x$ ,  $[A] = [A]_0 - x$  and  $[B] = [B]_0 - x$  at any time  $t$ . The rate law can be written as

$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)$$

If  $[A]_0 \neq [B]_0$ , this can be integrated (by partial fractions) to give

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0 ([B]_0 - x)}{[B]_0 ([A]_0 - x)} = kt$$

If experimental data conform to this equation, a plot of

$$\ln \frac{([B]_0 - x)}{([A]_0 - x)}$$

*versus* time is linear. In practice, this often has disadvantages, and experiments to study reactions like this typically exploit the technique of **flooding**.

Flooding is a widely used experimental technique that enables us to simplify a complex rate law in a way that makes it more convenient to test experimentally. In the case we are considering, we can often arrange to carry out the reaction with the initial concentration of  $B$  much greater than the initial concentration of  $A$ . Then the change that occurs in the concentration of  $B$  during

the reaction has much less effect on the reaction rate than the change that occurs in the concentration of  $A$ ; in the rate equation, it becomes a good approximation to let  $[B] = [B]_0$  at all times. (For a fuller consideration of this point, see problem 5.23.) The second-order rate equation simplifies to

$$\frac{d[A]}{dt} = -\frac{d[C]}{dt} = -k_{obs} [A]$$

where

$$k_{obs} = k[B]_0$$

Since the simplified rate equation is approximately first order, the *observed* rate constant,  $k_{obs}$ , is the slope of a plot of  $\ln[A]$  versus  $t$ .  $k_{obs}$  is called a **pseudo-first-order rate constant**.

Of course, one such experiment tests only whether the true rate law is first order in  $[A]$ . It tells nothing about the dependence on  $[B]$ . If we do several such experiments at different initial concentrations of  $B$ , the resulting set of  $k_{obs}$  values must be directly proportional to the corresponding  $[B]_0$  values. This can be tested graphically by plotting  $k_{obs}$  versus  $[B]_0$ . If the rate law is first order in  $[B]$ , the resulting plot is linear with an intercept of zero. The slope of this plot is the second-order rate constant,  $k$ .

Flooding works by simplifying the rate law that is observed in a given experiment. Similar simplification can be achieved by designing the experiment so that the initial concentrations of two or more reactants are proportional to their stoichiometric coefficients. For the reaction  $A + B \rightarrow C$  and the expected rate law

$$\frac{d[C]}{dt} = k[A][B]$$

we would initiate the experiment with equal concentration of reactants  $A$  and  $B$ . Letting  $[A]_0 = [B]_0 = \alpha$  and  $[C] = \xi/V = x$ , the concentrations of  $A$  and  $B$  at longer times become  $[A] = [B] = \alpha - x$ . The rate law becomes effectively second order.

$$\frac{dx}{dt} = k(\alpha - x)^2$$

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