

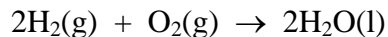


Lecture (6)

Chemical Kinetics – Reaction Orders

Introduction

Consider the reaction for the combustion of hydrogen gas:



At room temperature and pressure, ΔH° for this reaction is:

$$\begin{aligned} 2\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] - \{2\Delta H_f^\circ [\text{H}_2(\text{g})] + \Delta H_f^\circ [\text{O}_2(\text{g})]\} \\ = 2(-285.83 \text{ kJ/mol}) \\ = \underline{-571.66 \text{ kJ/mol}} \quad (\text{strongly exothermic}) \end{aligned}$$

\therefore The products are energetically favored. The reactants are entropically favored ($S_{\text{gas}} \gg S_{\text{liquid}}$). Will this reaction proceed spontaneously?

To answer this question, we must resort to 2nd law ideas, in particular, to the Gibbs free energy. At room temperature and pressure, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ for this reaction is:

$$\begin{aligned} 2\Delta G_f^\circ [\text{H}_2\text{O}(\text{l})] - \{2\Delta G_f^\circ [\text{H}_2(\text{g})] + \Delta G_f^\circ [\text{O}_2(\text{g})]\} \\ = 2(-237.13 \text{ kJ/mol}) \\ = \underline{-474.26 \text{ kJ/mol}} \end{aligned}$$

Since $\Delta G^\circ < 0$ for this process, thermodynamics predicts that this reaction will proceed spontaneously.

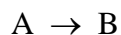
However, when $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ are mixed at ordinary room temperature and pressure, no observable quantity of $\text{H}_2\text{O}(\text{l})$ is formed, because the *rate of formation* of $\text{H}_2\text{O}(\text{l})$ is very slow.

Thermodynamics tells us nothing about reaction rates. Indeed, time as a variable does not enter into any thermodynamic equations. The realm of reaction rates is governed by the science of *chemical kinetics*.

Definitions



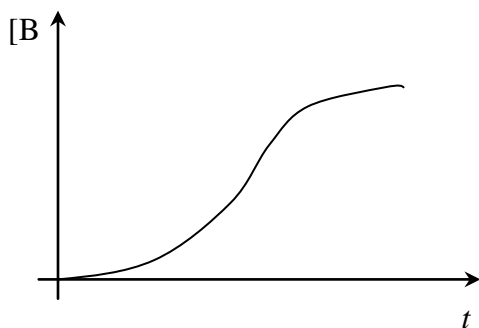
Consider the model reaction



and let $[A]$ and $[B]$ represent the concentrations of the reaction participants at any given time t during the course of the reaction. The easiest way to quantify how fast the reaction proceeds (the *rate* of the reaction) is to monitor the rate of formation of product, or equivalently, the rate of consumption of reactant. The rate of formation of product is given by

$$v_B = \frac{d[B]}{dt}$$

and a typical graph tracking the concentration of species B over time might look like this:



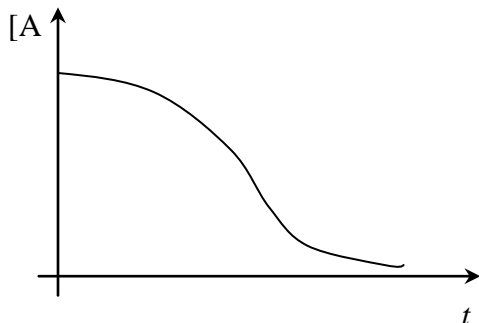
Since B is a product, $[B]$ always increases as the reaction proceeds, so $\frac{d[B]}{dt}$ is always positive, i.e., v_B is positive. Thus, the rate of the reaction $A \rightarrow B$ is

$$v_B = \frac{d[B]}{dt}$$

Analogously, the rate of consumption of reactant is given by

$$v_A = -\frac{d[A]}{dt}$$

and a graph showing how $[A]$ changes with time might look like this:



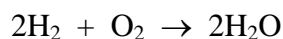


Since A is a reactant, [A] always decreases as the reaction proceeds, so $\frac{d[A]}{dt}$ is always negative, i.e., $v_A = -\frac{d[A]}{dt}$ is positive. Thus, the rate of the reaction $A \rightarrow B$ is also given by the formula

$$v_A = -\frac{d[A]}{dt}$$

Note that $v_A = v_B$, i.e., the rate of formation of B equals the rate of consumption of A.

For a slightly more complicated reaction, e.g.,



the rate of formation of $\text{H}_2\text{O} = 2 \times$ rate of consumption of O_2

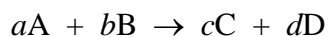
BUT

the rate of formation of $\text{H}_2\text{O} =$ rate of consumption of H_2 !

How do we define the rate of this reaction?

$$\text{reaction rate } v \equiv \frac{1}{2} \frac{d[\text{H}_2\text{O}]}{dt} = -\frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2]}{dt}$$

In general, then, for any chemical reaction



the reaction rate is defined as:

$$v = -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{c} \frac{d[\text{C}]}{dt} = \frac{1}{d} \frac{d[\text{D}]}{dt} \quad \dots (1)$$



Rate Laws

Often, one finds experimentally that the rate of a reaction is proportional to the concentrations of the reactant(s) raised to a power, e.g. for a reaction



it may be found that

$$\left. \begin{array}{l} v = k[A]^2 \\ v = k[A][B] \\ v = k \\ v = k[A][B]^2 \\ v = k[A]^{1/2}[B] \\ \dots \text{etc.} \end{array} \right\} \dots (2)$$

These equations describing the relation between the reaction rate and concentrations of the reactants are known as *rate laws* (or *rate equations* or *rate expressions*). The constant k in these expressions is called the *rate constant*, which is independent of reactant concentration, but is dependent on temperature. The power to which the concentration of a species is raised in a rate law is the *order* of the reaction with respect to that species. The sum of the orders of all the concentrations in the rate law is called the overall order of the reaction. For example, if a rate law for a reaction is found experimentally to be

$$v = k[A][B]^{3/4}[C]^{1/2}$$

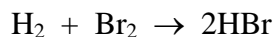
the reaction is said to be 1st order in $[A]$, $3/4$ order in $[B]$ and $1/2$ order in $[C]$.

Two fundamentally important facts must be kept in mind at this stage.

1. Equations (1) *define* the rate of a chemical reaction. The rate of any chemical reaction can be defined based on the balanced chemical equation for the reaction.
2. Equations (2) are *experimentally determined* equations describing the rate of a chemical reaction and its dependence on reactant concentrations. The order of the reaction with respect to any species has nothing to do with the stoichiometry of the reaction. *You cannot predict the rate law for a reaction from the balanced chemical equation for the reaction.*



An example will help clarify this distinction. Consider the simple reaction



It is a straightforward matter to define the reaction rate for this reaction based on the balanced equation just given:

$$v \equiv -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{Br}_2]}{dt} = \frac{1}{2} \frac{d[\text{HBr}]}{dt}$$

However, it took years of painstaking experimental measurements on this system for researchers to establish that the rate of this reaction is given by the rate law

$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$$

It would have been patently impossible, by merely looking at the chemical equation for this reaction, to have come up with this rate law for the reaction between H_2 and Br_2 . Note that as far as the order of this reaction is concerned, one can only say that it is first order in H_2 ; it is impossible to state the order of this reaction with respect to Br_2 , or the overall order of the reaction. Note also that the concentration of the product HBr appears in the rate law, and that there are two rate constants k and k' . These are not uncommon occurrences in the study of real reactions. We now turn our attention to reactions of specific order.

First Order Reactions

Consider the reaction



By definition, the rate of the reaction is:

$$v = -\frac{d[\text{A}]}{dt} = \frac{1}{2} \frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt}$$

Suppose we find *by experiment* that this reaction obeys the rate law:

$$v = k[\text{A}]$$

Thus, the reaction is first order in $[\text{A}]$. We can equate the two expressions for v , to find:

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]$$



This is a differential equation in the variables $[A]$ and t . Rearranging,

$$\frac{d[A]}{[A]} = -kdt$$

Integrating both sides of this equation,

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = - \int_0^t k dt$$

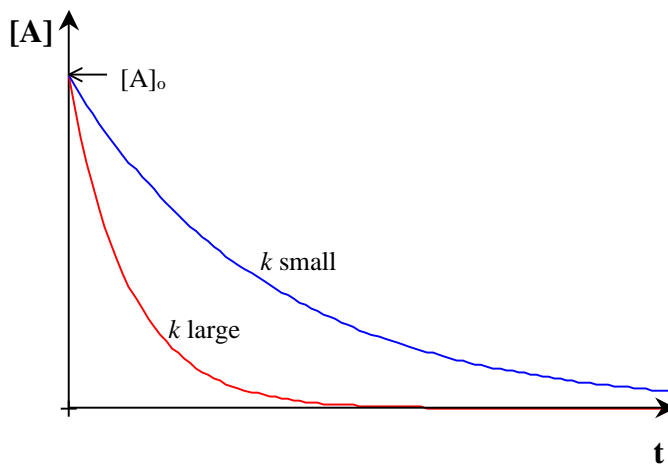
$$\Rightarrow \ln[A] - \ln[A]_0 = -k(t) \quad \dots (1)$$

$$\Rightarrow \ln[A] = -kt + \ln[A]_0 \quad \dots (2)$$

$$\Rightarrow \ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad \dots (3)$$

$$\Rightarrow [A] = [A]_0 e^{-kt} \quad \dots (4)$$

These four equations are different, equivalent forms of the *integrated rate law* for a first order reaction. This integrated rate law clearly states the time dependence of the concentration of reactant A, namely that $[A]$ decays exponentially with time. A plot of $[A]$ against time is shown below for a couple of different values of k . Note that the larger the value of k , the faster the reaction proceeds.



The *half-life*, $t_{1/2}$, of a reactant is the time required for its concentration to drop to half its initial value. In the above reaction, for example, it is the time required for the molarity of A to decrease from $[A]_0$ to $\frac{1}{2}[A]_0$. It should be noted that all radioactive decay processes follow first order kinetics.



The idea of a half-life can be expressed mathematically using equation (3):

$$\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -kt_{1/2}$$

$$\Rightarrow \frac{\ln\left(\frac{1}{2}\right)}{-k} = t_{1/2}$$

$$\Rightarrow \boxed{t_{1/2} = \frac{\ln 2}{k}} \quad (\ln 2 \approx 0.693)$$

For a first order reaction, therefore, the half-life is independent of the initial reactant concentration.

A less frequently used parameter called the *relaxation time* τ for a first order reaction is defined as:

$$\tau = \frac{1}{k}$$

Second Order Reactions

Consider the reaction



By definition, the rate of this reaction is:

$$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$$

Suppose we find by experiment that this reaction obeys the rate law:

$$v = k[A]^2$$

Thus, the reaction is second order in [A]. We can once again equate the two expressions for v , to find:

$$-\frac{d[A]}{dt} = k[A]^2$$



Rearranging this expression as before, we obtain

$$\frac{d[A]}{[A]^2} = -kdt$$

Both sides of this equation can be integrated:

$$\int_{[A]_0}^{[A]} \frac{1}{[A]^2} d[A] = - \int_0^t k dt$$

$$\Rightarrow -\frac{1}{[A]} - \left(-\frac{1}{[A]_0} \right) = -k(t)$$

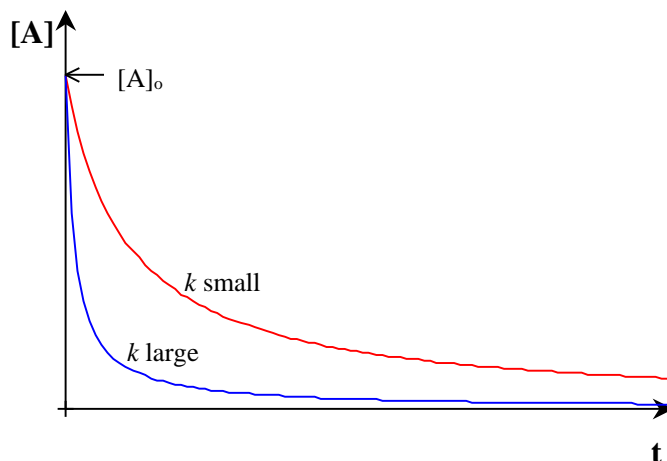
$$\Rightarrow \frac{1}{[A]} - \left(\frac{1}{[A]_0} \right) = kt$$

$$\Rightarrow \frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad \dots (5)$$

When analyzing a known second order reaction, one would plot $1/[A]$ against t , which would give the rate constant k as the slope. Solving explicitly for $[A]$, however, yields the formula

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

which gives the time dependence of the concentration of $[A]$. Note that it is roughly $1/t$ dependence. The plot of $[A]$ against time for this second order reaction shows a remarkable similarity to the analogous plot for first order kinetics:



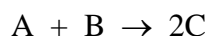


The half-life for this reaction is defined in the same way as in the first order case. Mathematically, we substitute the time and the concentration of A into equation (5) to get the following expression:

$$\begin{aligned}\frac{1}{\frac{1}{2}[A]_0} &= kt_{1/2} + \frac{1}{[A]_0} \\ \Rightarrow \frac{2}{[A]_0} &= kt_{1/2} + \frac{1}{[A]_0} \\ \Rightarrow \frac{1}{[A]_0} &= kt_{1/2} \\ \Rightarrow t_{1/2} &= \frac{1}{k[A]_0}\end{aligned}$$

Note that the half-life of a second order reaction depends on the initial concentration of reactant.

Now suppose that the reaction we have studied,



was found experimentally to have the rate law

$$v = k[A][B]$$

This is also a second order reaction (overall; first order in each reactant). Now, proceeding as before, we equate the defined rate to the experimentally determined rate:

$$-\frac{d[A]}{dt} = k[A][B] \quad \dots (6)$$

The above differential equation has three variables ([A], [B] and t), and cannot be solved as stated. Instead, we introduce a new variable x , where

$$x \equiv [A]_0 - [A]$$

The quantity x can be recognized as the amount of A consumed. Note that we could just as well have defined x as $[B]_0 - [B]$, since A and B are consumed at the same rate in this reaction.



Our differential equation (6) now becomes

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

Now we need to rewrite $[A]$ in terms of x , in order to get a differential equation solely in terms of x and t :

$$[A] = [A]_0 - x \quad \dots (7)$$

Differentiating both sides of (7) with respect to t , we obtain

$$\frac{d[A]}{dt} = -\frac{dx}{dt}$$

since $[A]_0$ is a constant which does not depend on t . Equivalently, we could write,

$$-\frac{d[A]}{dt} = \frac{dx}{dt}$$

We now write our differential equation (6) entirely in terms of the two variables x and t :

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

Rearranging,

$$\frac{1}{([A]_0 - x)([B]_0 - x)} dx = k dt$$

Integrating both sides ($x = 0$ at $t = 0$),

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)} dx = \int_0^t k dt$$

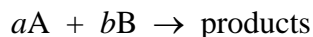
This works out to:

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

The above integrated rate law is valid for the reaction $A + B \rightarrow 2C$, with rate expression $v = k[A][B]$. Notice that the equation blows up when $[A]_0 = [B]_0$. For this reaction, the quantity $\ln([B]/[A])$ can be plotted against t to obtain the value of k from the slope.



Generalizing, for any reaction



obeying the rate law

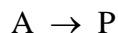
$$v = k[A][B]$$

the integrated rate law is:

$$\frac{1}{a[B]_0 - b[A]_0} \ln \left(\frac{[A]_0[B]}{[B]_0[A]} \right) = kt$$

Zeroth Order Reactions

Consider the reaction



By definition, the rate of this reaction is given by the formulas

$$v \equiv -\frac{d[A]}{dt} = \frac{d[P]}{dt}$$

Suppose we find by experiment that this reaction obeys the rate law

$$v = k$$

That is, the rate of this reaction has no dependence on the reactant concentration, or the reaction rate is zero order with respect to the reactant. Zero order kinetics only show up in heterogeneous reactions. Now, we can equate the two expressions for v to obtain

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

$$\Rightarrow d[A] = -kdt$$

Integrating both sides,

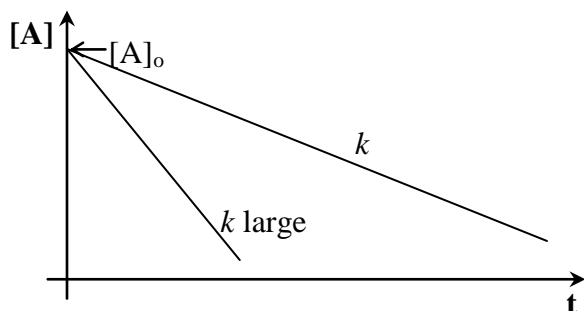
$$\int_{[A]_0}^{[A]} d[A] = -\int_0^t kdt$$



$$\Rightarrow [A] - [A]_o = -k(t)$$

$$\Rightarrow [A] = -kt + [A]_o \quad \dots (8)$$

A plot of $[A]$ against t in this case will yield a straight line with slope $-k$:



The half-life of a zeroth order reaction is obtained from equation (8):

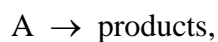
$$\frac{[A]_o}{2} - [A]_o = -kt_{1/2}$$

$$\Rightarrow \frac{[A]_o}{2} = kt_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{[A]_o}{2k}$$

Reactions of General Order

In general, for a reaction



for which, by definition

$$v \equiv -\frac{d[A]}{dt}$$

and which follows the experimentally determined rate law

$$v = k[A]^n \quad (n \neq 1)$$



the integrated rate law is:

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$$

The half-life in this general case is given by the formula:

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

No reactions are known with order $n > 3$.