

Chemical reaction kinetics

Chemical reaction kinetics, the branch of physical chemistry, provide a quantitative measurement of rates of reactions. Reaction kinetic studies provide insight into the dependence of these rates on variables, such as concentration, temperature, pressure, the presence of catalysts, or the physical state of the reactants. Since chemical reactions are dependent on the concentration of the reactant molecules and the conditions in which enable their collision, understanding the effect of variables on these interactions is critical to controlling the reaction for a successful outcome.

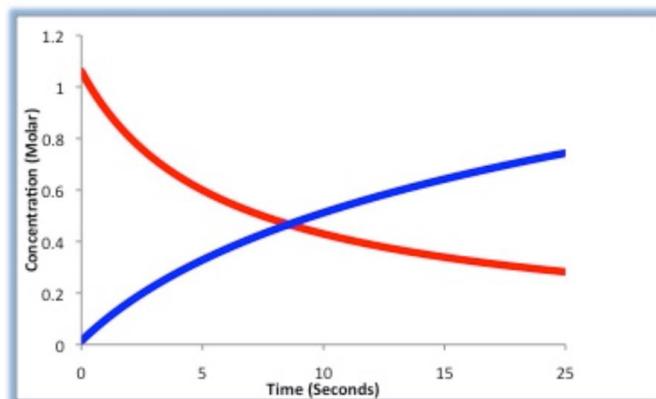
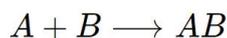
The Collision Model:

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory explains why different reactions occur at different rates, and suggests ways to change the rate of a reaction. Collision theory states that for a chemical reaction to occur, the reacting particles must collide with one another. The rate of the reaction depends on the frequency of collisions. The theory also tells us that reacting particles often collide without reacting. For collisions to be successful, reacting particles must (1) collide with (2) sufficient energy, and (3) with the proper orientation. Thus reaction rate should increase with an increase in the concentration of reactant molecules. In order for molecules to react they must collide. Therefore, the greater the number of collisions the faster the rate, as temperature increases, the molecules move faster and the collision frequency increases. Thus reaction rate should increase with an increase in temperature.

Reaction Rate

During the course of the reaction shown below, reactants A and B are consumed while the concentration of product AB increases. The reaction rate can be determined by measuring how fast the concentration of A or B decreases, or by how fast the concentration of AB increases. The following Figure 1 shows a hypothetical reaction profile in which the reactants (red) decrease in concentration as the products increase in concentration (blue).



For the stoichiometrically complicated Reaction:



$$\text{Rate} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Looking at Figure 1 above, we can see that the rate can be measured in terms of either reactant (A or B) or either product (C or D). Not all variables are needed to solve for the rate. Therefore, if you have the value for "A" as well as the value for "a" you can solve for the reaction rate.

You can also notice from Equation above that the change in reactants over the change in time must have a negative sign in front of them. The reason for this is because the reactants are decreasing as a function of time, the rate would come out to be negative (because it is the reverse rate). Therefore, putting a negative sign in front of the variable will allow for the solution to be a positive rate.

The Reaction Rate for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time. The speed of a chemical reaction may be defined as the change in concentration of a substance divided by the time interval during which this change is observed:

$$\text{rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$

For a reaction of the form $A + B \rightarrow C$, the rate can be expressed in terms of the change in concentration of any of its components:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = -\frac{\Delta[B]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[C]}{\Delta t}$$

in which $\Delta[A]$ is the difference between the concentration of A over the time interval t_2-t_1 :

$$\Delta[A] = [A]_2 - [A]_1$$

Consider now a reaction in which the coefficients are different:



It is clear that [B] decreases three times as rapidly as [A], so in order to avoid ambiguity when expressing the rate in terms of different components, it is customary to divide each change in concentration by the appropriate coefficient:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{3\Delta t} = \frac{\Delta[D]}{2\Delta t}$$

Example: For the oxidation of ammonia



it was found that the rate of formation of N_2 was $0.27 \text{ mol L}^{-1} \text{ s}^{-1}$.

- At what rate was water being formed?
- At what rate was ammonia being consumed?

Solution

a) From the equation stoichiometry, $\Delta[\text{H}_2\text{O}] = 6/2 \Delta[\text{N}_2]$, so the rate of formation of H_2O is

$$3 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.81 \text{ mol L}^{-1} \text{ s}^{-1}$$

b) 4 moles of NH_3 are consumed for every 2 moles of N_2 formed, so the rate of disappearance of ammonia is

$$2 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.54 \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate Laws and Rate Constants

A rate law is an expression which relates that rate of a reaction to the rate constant and the concentrations of the reactants. A rate constant, k , is a proportionality constant for a given reaction. The general rate law is usually expressed as:

$$\text{Rate} = k[\text{A}]^s[\text{B}]^t$$

As you can see from equation above, the reaction rate is dependent on the concentration of the reactants as well as the rate constant. However, there are also other factors that can influence the rate of reaction. These factors include temperature and catalysts. When you are able to write a rate law equation for a certain reaction, you can determine the Reaction Order based on the values of s and t .

Reaction Order

The reaction rate for a given reaction is a crucial tool that enables us to calculate the specific order of a reaction. The order of a reaction is important in that it enables us to classify specific chemical reactions easily and efficiently. Knowledge of the reaction order quickly allows us to understand numerous factors within the reaction including the rate law, units of the rate constant, half life, and much more. Reaction order can be calculated from the rate law by adding the exponential values of the reactants in the rate law.

$$\text{Rate} = k[\text{A}]^s[\text{B}]^t$$

$$\text{Reaction Order} = s + t$$

It is important to note that although the reaction order can be determined from the rate law, there is in general, **no relationship** between the reaction order and the stoichiometric coefficients in the chemical equation.

***NOTE:** The rate of reaction must be a non-negative value. It can be zero and does not need to be an integer.*

As shown in equation above, the complete reaction order is equal to the sum of " s " and " t ." But what does each of these variables mean? Each variable represents the order of the reaction with respect to the reactant it is placed on. In this certain situation, s is the order of the reaction with respect to $[\text{A}]$ and t is the order of the reaction with respect to $[\text{B}]$.

A list of the different reaction rate equations for zero-, first-, and second-order reactions can be seen in Table 1. This table also includes further equations that can be determined by this equation once the order of the reaction is known (Half life, integrated rate law, etc.)

Table (1): The table below displays numerous values and equations utilized when observing chemical kinetics for numerous reactions types.

	Zero-Order	First-Order	Second-Order
Rate Law	$Rate = k$	$Rate = k[A]$	$Rate = k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = -kt + \frac{1}{[A]_0}$
Units of Rate Constant (k):	$\text{molL}^{-1}\text{s}^{-1}$	s^{-1}	$\text{Lmol}^{-1}\text{s}^{-1}$
Linear Plot to Determine (k):	[A] versus time	$\ln[A]$ versus time	$\frac{1}{[A]}$ versus time
Relationship of Rate Constant to the Slope of Straight Line:	$slope = -k$	$slope = -k$	$slope = k$
Half-life:	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$