

# Kinetics

The skills developed during the study of stoichiometry and thermodynamics help to assess the extent of a chemical reaction, a measure of amounts of matter and energy, respectively. How quickly the extent is achieved (rate) and the chemical trail followed (mechanism) are realized from a study of reaction kinetics. Kinetic analysis of a reaction can, for instance, allow for control of feedstock production, explosion prevention during an exothermic reaction, or catalyst development. Chemical kinetics is initially concerned with the measurement of reaction rate under changing conditions, including: temperature, reactant concentration, catalyst presence, and sterics. These measurements guide the development of an experimental **rate law**. By applying Arrhenius' **collision theory** and comparing the experimental rate law to theoretical rate laws, one can deduce a reaction **mechanism**. In this way chemists can detail reactions at the molecular and atomic levels by making macroscopic measurements.

## Objectives:

1. Discuss the basic principles of collision theory as they relate to the rate of a chemical reaction.
2. Calculate the rate of a chemical reaction using algebraic and graphical methods.
3. Predict reactant order using the initial rate method or the integrated rate law method.
4. Perform calculations of rate law and half-life ( $t_{1/2}$ ) for zeroth, first, and second order reactions.
5. Illustrate, calculate, and explain the energetics of a chemical reaction particularly with reference to temperature and catalysis.
6. Formulate a theoretical rate law from a proposed set of elementary steps (mechanism) and judge its reasonableness based on stoichiometry and an experimental rate law.

Unit Topics	Unit Learning Outcomes	Student Misconceptions & Challenges
Kinetics Introduction	<ul style="list-style-type: none"><li>• Define reaction rate in terms of concentration and time and discuss its use in understanding iron corrosion prevention, control of tropospheric O<sub>3</sub> concentrations, drug efficacy, or other process.</li><li>• List and discuss 4 factors which influence reaction rate.</li><li>• Discuss the factors which affect rate with respect to collisions of particles.</li><li>• Compare and contrast homogenous and heterogeneous reactions.</li></ul>	<ul style="list-style-type: none"><li>• Pressure and surface area are factors affecting rate that students suggest but do not associate with concentration.</li><li>• Temperature is thought to affect the frequency of collisions rather than the energy of all collisions (reactants and products).</li></ul>

<p>Reaction Rate- Macroscopic View</p>	<ul style="list-style-type: none"> <li>Evaluate average and instantaneous reaction rates using a graph of concentration vs. time from a rate experiment.</li> <li>Using a balanced chemical equation, write the differential reaction rate equation in terms of each reactant and product.</li> <li>Using a balanced chemical equation, calculate the reaction rate of any one reactant or product based on the reaction rate of another reactant or product.</li> <li>Calculate an <i>initial</i> reaction rate from a graph of concentration vs. time.</li> </ul>	<ul style="list-style-type: none"> <li>Stoichiometry associations are often confusing for students.</li> <li>The negative sign in the expression of rate for reactant concentration changing over time <math>(-\Delta[X]/\Delta t)</math> is incorrectly thought to imply a negative value of rate rather than positive (the negative of negative <math>\Delta[X]</math>).</li> </ul>
<p>Rate Laws-Macroscopic View</p>	<ul style="list-style-type: none"> <li>Explain the terms found in a rate law.</li> <li>Select, based on given data, either the initial rate method or integrated rate law to find an experimental rate law for a chemical reaction.</li> <li>Predict whether a reactant is 0<sup>th</sup>, 1<sup>st</sup> or 2<sup>nd</sup> order using the initial rate method.</li> <li>Predict whether a reactant is 0<sup>th</sup>, 1<sup>st</sup> or 2<sup>nd</sup> order using the integrated rate law equations. <ul style="list-style-type: none"> <li>0<sup>th</sup> <math>[A]_t = -kt + [A]_0</math></li> <li>1<sup>st</sup> <math>\ln[A]_t = -kt + \ln[A]_0</math></li> <li>2<sup>nd</sup> <math>\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}</math></li> </ul> </li> <li>Predict whether a reactant is 0<sup>th</sup>, 1<sup>st</sup>, or 2<sup>nd</sup> order using only graphical analysis of concentration and time data. <ul style="list-style-type: none"> <li>0<sup>th</sup> C vs. t</li> <li>1<sup>st</sup> lnC vs. t</li> <li>2<sup>nd</sup> 1/C vs. t</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>Reactant order and rate laws are thought to be determined by a balanced equation's coefficients.</li> <li>The initial attempt at solving an integrated rate law problem usually involves a student calculating differential rates from concentration and time data rather than applying the integrated rate laws.</li> <li>First order reactions are thought to be <i>always</i> decomposition reactions and involve no collisions between particles.</li> <li>Students think that <math>[A]_0</math> in an integrated rate law is not constant. It is treated as the concentration prior to the next time point rather than correctly being the concentration of the reactant at <math>t = 0</math>.</li> </ul>

Rate Laws-Macroscopic View	<ul style="list-style-type: none"> <li>Identify the overall reaction order and individual reactant orders based on the rate law.</li> <li>Use a rate law to predict how a reaction rate varies with changing concentrations.</li> <li>Use the integrated rate equations to predict how a reaction rate varies with changing time.</li> </ul>	
Half-life	<ul style="list-style-type: none"> <li>Calculate the half-life for a zeroth, first, and second order reaction by approximation using only concentration and time data, and more accurately using the integrated rate law equations.</li> <li>Convert <math>t_{1/2}</math> to <math>k</math> for a zeroth, first, and second order reaction.</li> </ul>	
Temperature, Energy, Steric and Catalytic Effects from a Collision Theory Perspective	<ul style="list-style-type: none"> <li>Describe how temperature changes affect reaction rate.</li> <li>Describe how sterics affect the reaction rate.</li> <li>Using Boltzmann distributions explain how increasing temperature increases the fraction of particles with <math>\overline{E}_k \geq E_a</math>.</li> <li>Explain the Arrhenius equation, its ramifications, and each of its terms. Be able solve Arrhenius equation problems.</li> <li>Draw a reaction coordinate diagram (RCD), and label all kinetic and thermodynamic features.</li> <li>Discuss the concept of the transition state (TS) and compare and contrast the roles of an activated complex and an intermediate.</li> <li>Discuss homogeneous (enzymes, chlorine radicals) and heterogeneous catalysts (catalytic converter, chlorine radicals).</li> <li>Sketch on a RCD the effect of adding a catalyst to a reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Temperature is thought to affect the magnitude of the activation energy when it does not.</li> <li>Temperature is thought to affect the frequency of collisions rather than the energy of all collisions (reactants and products).</li> <li>Increasing temperature is thought to decrease the activation energy.</li> <li>The Arrhenius equation is only used for single step reactions. More correctly it can be applied to single step and multistep reactions.</li> </ul>

<p>Reaction Mechanism and Rate Laws- Microscopic View</p>	<ul style="list-style-type: none"> <li>• Define reaction mechanism and elementary steps (reactions).</li> <li>• Apply collision theory to a set of elementary steps to evaluate each step's overall order and rate law.</li> <li>• Identify rate-determining steps, catalysts, and intermediates when shown a series of elementary steps.</li> <li>• Identify and write a reaction's theoretical rate law when the slowest step is first and the slowest step is second yet preceded by a fast equilibrium (pre-equilibrium).</li> <li>• Evaluate a mechanism based on the stoichiometry of the overall reaction equation and comparison of an experimental rate law with a derived theoretical rate law</li> <li>• Apply steady state analysis to derive a general rate law subject to conditions.</li> <li>• Demonstrate saturation kinetics using Michaelis-Menten analysis.</li> </ul>	<ul style="list-style-type: none"> <li>• Students may get the sense that the mechanism is proof of how a reaction occurs. Multiple mechanisms must always be proposed as no direct proof is typically possible.</li> <li>• Experimental data that supports a mechanism is often thought to be proof of that mechanism.</li> <li>• When a student creates a mechanism often electronegativity is used to develop less probable electron transfer elementary steps compared to simpler combination or decomposition steps.</li> </ul>