Pure solids will not react with one another unless surface area is increased by grinding the solids

\[ \text{Rate} = \frac{\Delta [x]}{\Delta t} \]  
(put a negative sign if the change in concentration is for the reactant since it's being used up)

If \( aA + bB \rightarrow cC + dD \), then \( \text{Rate} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t} \)

\[ \text{Rate} = k[A][B] \] where the overall reaction rate is the sum of the exponents (individual orders can be 0, fractional, or negative)

The rate constant is generally consistent and can be found as an average with 2 significant digits

For overall orders 0, 1, 2, and 3, the units for \( k \) are \( M s^{-1}, s^{-1}, M^{-1}s^{-1}, \) and \( M^{-2}s^{-1} \) respectively

Example of how to solve for rate orders: \( \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k([A]_2)^x}{k([A]_1)^x} \)

**Important:** The order for a rate can be figured out if not given by analyzing the units of \( k \)

### 14.4 – Change of Concentration with Time

The rate constant when the equation is plotted as a straight line is equivalent to the slope of the line \( (y = mx + b) \)

**Zero Order:** \( [A]_t = [A]_0 - kt \)  
(typically observed with catalysts, enzymes and solids)

\([A]_t \text{ vs. } t\) will produce a straight line

**First Order:** \( \ln[A]_t = \ln[A]_0 - kt \)  
or \( \frac{[A]_t}{[A]_0} = e^{-kt} \)  
or \( [A]_t = [A]_0 e^{-kt} \)

\( \ln[A]_t \text{ vs. } t \) will produce a straight line

\([A]_t \text{ vs. } t\) will produce an exponential decay

The middle equation is useful for concentration fractions

**For gases**, pressure can be used instead of concentration

**Second Order:** \( \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \)

\( \frac{1}{[A]_t} \text{ vs. } t \) will produce a straight line

To test these without plotting: \( \frac{\Delta [A]}{\Delta t} \) should be constant for zero order, \( \frac{\Delta \ln[A]}{\Delta t} \) for 1st order, and \( \frac{\Delta \left( \frac{1}{[A]} \right)}{\Delta t} \) for 2nd order
Andrew Rosen

Half-Life for First Order (all radioactive processes): \[ \ln 2 = \frac{t_1}{2} \]

Half-Life for Second Order: \[ \frac{1}{k[A]_0} = \frac{t_1}{2} \]

14.5 – Temperature and Rate

As temperature increases, so does rate (k is temperature dependent)

The arrangement of atoms in the transition state (activated complex at the top of a reaction energy profile) is unstable

As temperature increases, the Maxwell-Boltzmann Distribution of kinetic energies broadens and flattens (more with KE)

Fraction of molecules with energy above the activation energy is \( f = e^{-\frac{E_a}{RT}} \) (R is 8.314 here)

Arrhenius Equation: \( k = Ae^{-\frac{E_a}{RT}} \) (A is the frequency factor for the number of collisions with the proper orientation)

Do the natural log to both sides to get \( \ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A \)

This will make \(-\left(\frac{E_a}{R}\right)\) the slope of a \( k \) vs. \( \frac{1}{T} \) graph (linear)

Arrhenius Equation for two temperatures: \( \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \)

USE OTHER R CONSTANT (8.3145)

Rate is also, therefore, dependent on the activation energy

A lower activation energy means a faster reaction

In order to compare two temperatures to compare rates, you must have an assumption that initial concentrations are equal

14.6 – Reaction Mechanisms

If the rate equation has an intermediate in it with a fast reversible initial step it needs to be substituted:

\[ A + B \leftrightarrow C \] (fast)

\[ B + C \rightarrow D \] (slow)

Therefore, the rate equation is not \( k[B][C] \). It is \( k[A][B]^2 \)

The molecularity of an elementary reaction tells how many molecules are involved (based on stoichiometry)

How many relative minima are on a potential energy diagram are how many intermediates

How many relative maxima there are on the potential energy diagram are how many transitional states there are

If there is a two step reaction with a very fast irreversible initial step, the two steps can be broken up because the first product will accumulate

Pre-Equilibrium is a fast equilibrium that precedes the rate determining step in a multi step system
Inhibitors are found with a negative exponent in a rate law.

Catalysts work by adsorbing the reactants (bringing them to the surface and close to one another) to help bonds break.

Catalase catalyzes decomposition of hydrogen peroxide (has four Fe$^{3+}$ ions as active centers that amino acids hold and create a special environment around).