Chemical Kinetics

All rates written as $\frac{\Delta \text{conc}}{\Delta \text{time}}$ or $\frac{\Delta[A]}{\Delta t}$. Instantaneous rate is the slope of a concentration vs time plot and is shown by the differential equation: $\frac{d[A]}{dt}$. Overall rates for forward reactions are shown as POSITIVE rates, therefore, all reactants (which have negative rate of change) must have their rates negated $\frac{-d[A]}{dt}$.

In general for the overall reaction:

$$aA + bB \rightarrow cC + dD$$
 overall rxn rate $= \frac{-\Delta[A]}{a\Delta t} = \frac{-\Delta[B]}{b\Delta t} = \frac{-\Delta[C]}{c\Delta t} = \frac{-\Delta[D]}{d\Delta t}$

Note that each individual rate is divided by it's coefficient in the balanced chemical equation.

Half-life $(t_{1/2})$: The time it takes for the concentration to drop to one half its current value during the course of the reaction. Note that the "current value" is typically the initial starting value - but not always.

Equation	Zero Order	First Order	Second Order
rate law	rate $= k$	rate = $k[A]$	rate = $k[A]^2$
integrated rate law	$[\mathbf{A}]_0 - [\mathbf{A}] = kt$	$\ln[A]_0 - \ln[A] = kt$ $\ln\left(\frac{[A]_0}{[A]}\right) = kt$	$\frac{1}{[\mathbf{A}]} - \frac{1}{[\mathbf{A}]_0} = kt$
straight line plot	$[\mathbf{A}] = -kt + [\mathbf{A}]_0$	$\ln[\mathbf{A}] = -kt + \ln[\mathbf{A}]_0$	$\frac{1}{[\mathbf{A}]} = kt + \frac{1}{[\mathbf{A}]_0}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Rate Laws for: $A \longrightarrow$ products

Temperature dependence of rate:

$$k = A e^{-(E_a/RT)}$$

This is the Arrhenius Equation. This equation can be converted into the straight line plot version by taking natural log of each side and then rearranging:

$$\ln k = -\frac{E_{\rm a}}{R} \left(\frac{1}{T}\right) + \ln A$$

When finding the new k value at a new T...

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note this is another form of the Arrhenius Equation where you have 2 specific rate constants at 2 specific temperatures. Remember they come in pairs. Also note how the Arrhenius factor *A*, has factored OUT of the equation.

$$\ln\left(\frac{t_1}{t_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This is still the Arrhenius Equation, EXCEPT we now show TIME in place of rate constant. Time is inversely proportional to rate so the positions are switched. Any common timed event will work – half-life is the most common.