Kinetics: The Big Picture

1. A reaction's rate, R, is expressed in terms of a change in concentration over a change in time, either as an average rate over a discrete increment in time ($R = \frac{\Delta[\,]}{\Delta t}$) or as an instantaneous rate over an infinitesimal increment in time ($R = \frac{d[\,]}{dt}$).

2. A reaction's rate is always positive and is adjusted for the stoichiometry of the species used to report the rate; thus, for the reaction $a\text{A} \longrightarrow b\text{B}$, the instantaneous rates are $R = -\frac{1}{a}\frac{d[\text{A}]}{dt}$ or $R = \frac{1}{b}\frac{d[\text{B}]}{dt}$.

3. A reaction's rate depends on the concentrations of species that are reactants, products, catalysts, or inhibitors as expressed by an experimental rate law where the concentration of each species is raised to a power called its reaction order; thus, $R = k[A]^{\alpha}[B]^{\beta}\ldots[C]^{\gamma}$. Reaction orders are not equivalent to stoichiometric coefficients.

4. To determine the reaction order for a species, we can (i) find a way to linearize a plot of its concentration vs. time, (ii) look for trends in half-lives, or (iii) use the method of initial rates to determine how a change in initial concentration affects the rate. For (i) and (ii), we can study the affect of one species by making its concentration small relative to all other species, a process called a pseudo-order kinetic analysis.

5. A reaction's rate constant is independent of the concentrations of reactants and products, but is affected by temperature, T, by the frequency of effective collisions, A, and by the activation energy, E_a; thus $k = Ae^{-E_a/RT}$.

6. A reaction's experimental rate law reflects its underlying mechanism, which consists of a sequence of steps that involve no more than two reactants (plus solvent, if needed) and that combine to give the reaction's overall stoichiometry. The rate law for any individual step in a mechanism is the product of that step's rate constant and the concentration of each reactant raised to a power equivalent to its stoichiometry in that step.

7. A reaction's experimental rate law depends on the slowest step in the mechanism (the rate-determining step, or RDS) and any steps before the RDS; steps that occur after the RDS have no affect on the rate law. To incorporate earlier steps into the experimental rate law for the RDS, we make the simplifying assumption that they are at equilibrium.