Elementary Reactions

- When reactant molecules collide with the right orientation and energy level to form new bonds.
- Many “observable” reactions are really just combinations of elementary reactions.

Starting out with some A and B, we observe that E and F are the end products:

\[ A + B \rightarrow C + D \quad \text{slow} \]
\[ 2C \rightarrow E \quad \text{fast} \]
\[ A + D \rightarrow C + F \quad \text{fast} \]

\[ 2A + B \rightarrow E + F \]
Cont.

- Elementary reactions
  - A single step in a reaction sequence
  - Involves 1 or 2 reactants and 1 or 2 products
  - Can be described by classical chemical kinetics

Kinetics

- Examples
  - Fe^{+2} oxidation by O_2
    - almost instantaneous at high pH
    - quite slow at low pH
    - high D.O. may help
  - Oxidation of organic material
  - Formation of solid phases
    - Aluminum hydroxide
    - Quartz sand
Kinetics

- Base Hydrolysis of dichloromethane (DCM)
  - Forms chloromethanol (CM) and chloride

\[
\begin{align*}
\text{H}_2\text{Cl}_2 + \text{OH}^- & \rightarrow \text{H}_2\text{Cl} + \text{Cl}^- \\
\end{align*}
\]

- Classic second order reaction (molecularity of 2)

\[\text{Rate} = k[D\text{CM}][OH^-] = \frac{-d[DCM]}{dt} = \frac{-d[OH^-]}{dt} = \frac{d[CM]}{dt} = \frac{d[Cl^-]}{dt}\]

- First order in each reactant, second order overall

Reaction Kinetics

- Irreversible reaction
  - is one in which the reactant(s) proceed to product(s), but there is no significant backward reaction,
  - In generalized form, irreversible reactions can be represented as:
    - \(aA + bB \rightarrow \text{Products}\)

i.e., the products do not recombine or change to form reactants in any appreciable amount. An example of an irreversible reaction is hydrogen and oxygen combining to form water in a combustion reaction. We do not observe water spontaneously separating into hydrogen and oxygen.
Reaction Kinetics: Reversibility

- A reversible reaction
  - is one in which the reactant(s) proceed to product(s), but the product(s) react at an appreciable rate to reform reactant(s).
  - \[ aA + bB \leftrightarrow pP + qQ \]
  - Most reactions must be considered reversible

An example of a reversible biological reaction is the formation of adenosine triphosphate (ATP) and adenosine diphosphate (ADP). All living organisms use ATP (or a similar compound) to store energy. As the ATP is used it is converted to ADP, the organism then uses food to reconvert the ADP to ATP.

Kinetic principles

- Law of Mass Action
  - For elementary reactions

\[ aA + bB \xrightarrow{k} \text{products} \]

where,

- \( C_A \) = concentration of reactant species A, [moles/liter]
- \( C_B \) = concentration of reactant species B, [moles/liter]
- \( a \) = stoichiometric coefficient of species A
- \( b \) = stoichiometric coefficient of species B
- \( k \) = rate constant, [units are dependent on \( a \) and \( b \)]
Reaction Kinetics (cont.)

- Reactions of order “n” in reactant “c”
  \[
  \frac{dc}{dt} = -kc^n
  \]

- When n=0, we have a simple zero-order reaction
  \[
  \frac{dc}{dt} = -k
  \]
  \[c = c_o - kt\]

- When n=1, we have a simple first-order reaction
  \[
  \frac{dc}{dt} = -kc^1
  \]
  \[c = c_o e^{-kt}\]
  \[k = 0.032 \text{ min}^{-1}\]
Reaction Kinetics (cont.)

- This equation can be linearized
- good for assessment of “k” from data

\[
\frac{dc}{dt} = -kc^1
\]

\[
\ln c = \ln c_o - kt
\]

Slope

\[k = 0.032 \text{ min}^{-1}\]

---

Reaction Kinetics (cont.)

- When n=2, we have a simple second-order reaction
- This results in an especially wide range in rates
- More typical to have 2nd order in each of two different reactants

\[
\frac{dc}{dt} = -kc^2
\]

\[
c = c_o \frac{1}{1 + kc_o t}
\]

\[k = 0.0015 L/\text{mg/min}\]
Reaction Kinetics (cont.)

- Again, the equation can be linearized to estimate “k” from data

\[ \frac{dc}{dt} = -kc^2 \]

\[ \frac{1}{c} = \frac{1}{c_o} + kt \]

\[ k = 0.0015 \text{L/mg/min} \]

Comparison of Reaction Orders

- Curvature as order changes: 2\text{nd}>1\text{st}>zero
Reaction Kinetics (cont.)

- For most reactions, $n=1$ for each of two different reactants, thus a second-order overall reaction.

\[ \frac{dc}{dt} = -kc_1c_2 \]

- Many of these will have one reactant in great excess.
- These become "pseudo-1st order in the limiting reactant, as the reactant in excess really doesn’t change in concentration.

- $k = 3.9 \times 10^{-5} \text{ Lmg}^{-1} \text{ min}^{-1}$

\[ c_2 \]

\[ c_1 \]

- Since $c_2$ changes little from its initial 820 mg/L, it is more interesting to focus on $c_1$.
- $C_1$ exhibits simple 1st order decay, called pseudo-1st order.
- The pseudo-1st order rate constant is just the “observed rate” or $k_{obs}$.

\[ c_1 = c_{10}e^{-k_{obs}t} \]
Variable Kinetic Order

- Any reaction order, except $n=1$

$$\frac{dc}{dt} = -kc^n$$

$$\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)kt$$

$$c = c_o \frac{1}{\left[1 + (n-1)kc_o^{n-1}t\right]^{\frac{1}{n-1}}}$$

Half-lives

- Time required for initial concentration to drop to half, i.e., $c=0.5c_o$
  - For a zero order reaction:

$$c = c_o - kt$$

$$0.5c_o = c_o - k\frac{t}{2}$$

- For a first order reaction:

$$c = c_o e^{-kt}$$

$$0.5c_o = c_o e^{-k\frac{t}{2}}$$

$$t^{\frac{1}{2}} = \frac{0.5c_o}{k}$$

$$t^{\frac{1}{2}} = \frac{\ln(2)}{k} = 0.693$$
Reactions in Series

\[ A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C \overset{k_3}{\rightarrow} D \]

\[ k_1 = k_2 = k_3 = 0.1 \text{ day}^{-1} \]

Fig. 2.9
Pg. 68

Reversible reaction kinetics

For a general reversible reaction:

\[ aA + bB \leftrightarrow pP + qQ \]

And the rate law must consider both forward and reverse reactions:

\[ r_A = k_f C_A^a C_B^b - k_b C_P^p C_Q^q \]

where,
- \( k_f \) = forward rate constant, [units depend on a and b]
- \( k_b \) = backward rate constant, [units depend on a and b]
- \( C_P \) = concentration of product species P, [moles/liter]
- \( C_Q \) = concentration of product species Q, [moles/liter]
- \( p \) = stoichiometric coefficient of species P
- \( q \) = stoichiometric coefficient of species Q
Reversible 1st order reactions

- Kinetic law
  \[
  \frac{dB}{dt} = k_1[A] - k_2[B]
  \]
- Eventually the reaction slows and,
  - Reactant concentrations approach the equilibrium values
  \[
  \frac{dB}{dt} = 0 = k_1[A] - k_2[B]
  \]
  \[
  [B] = \frac{k_1}{k_2} \equiv K_{eq}
  \]

Temperature Effects

Temperature Dependence

- Chemist's Approach: Arrhenius Equation
  \[
  \frac{d(\ln k)}{dT_a} = \frac{E_a}{RT_a^2}
  \]
  \[
  k_{T_a} = k_{293^oK} e^{E_a(T_a-293)/RT_a 293}
  \]
- Engineer's Approach:
  \[
  k_T = k_{20^oC} \Theta^{T-20^oC}
  \]
  Or more generally where
  \[
  T_a = \text{any "baseline" temperature}
  \]
  \[
  k_T = k_{T_o} \Theta^{T-T_o}
  \]
  Typical values:
  \[
  0=1.02 \text{ to } 1.15
  \]
Determination of $E_a$ and $A$

- Use Arrhenius equation
  - Take natural log of both sides
  - Evaluate slope and intercept

\[
\ln k_{T_a} = \ln A - \left( \frac{E_a}{R} \right) \left( \frac{1}{T_a} \right)
\]

Catalysis

- A Catalyst enhances rates by providing alternative pathways with lower activation energies
  - It is not “consumed” in the reaction
- Homogeneous
  - Acid/base catalysis
  - Trace metal catalysis
- Heterogeneous
  - Reactions on particle surfaces
  - Reactions mediated by microorganisms (enzymes)
  - Engineered surface catalysis
  - Catalytic converters, activated carbon
Analysis of Rate Data

- Integral Method
  - Least squares regression of linearized form
- Differential Method
  - estimate instantaneous rate at known time and reactant concentration
- Initial rate Method
  - more rigorous, but slow
- Method of Excess
  - only when 2 or more reactants are involved

Kinetic model for equilibrium

- Consider a reaction as follows:
  \[ A + B = C + D \]
  
- Since all reactions are reversible, we have two possibilities
  \[ A + B \xrightarrow{k_f} C + D \]
  \[ A + B \xleftarrow{k_b} C + D \]

- The rates are:
  \[ r_f = k_f \{A\} \{B\} \quad r_b = k_b \{C\} \{D\} \]

- And at equilibrium the two are equal, \( r_f = r_b \)
  \[ k_f \{A\} \{B\} = k_b \{C\} \{D\} \]

- We then define an equilibrium constant \( K_{eq} \)
  \[ K_{eq} \equiv \frac{k_f}{k_b} = \frac{\{C\} \{D\}}{\{A\} \{B\}} \]
Kinetic model with moles

- In terms of molar concentrations, the rates are:
  \[ r_f = k_f [A]^{\gamma_A} [B]^{\gamma_B} \quad r_b = k_b [C]^{\gamma_C} [D]^{\gamma_D} \]

- And at equilibrium the two are equal, \( r_f = r_b \)
  \[ k_f [A]^{\gamma_A} [B]^{\gamma_B} = k_b [C]^{\gamma_C} [D]^{\gamma_D} \]

- And solving for the equilibrium constant \( (K_{eq}) \)
  \[ K_{eq} = \frac{k_f}{k_b} = \frac{[C]^{\gamma_C} [D]^{\gamma_D}}{[A]^{\gamma_A} [B]^{\gamma_B}} = \frac{[C]^{\gamma_C} [D]^{\gamma_D}}{[A]^{\gamma_A} [B]^{\gamma_B}} \]

To next lecture