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

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**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
  \[ \text{HClO}_2 + \text{OH}^- \rightarrow \text{HClO} + \text{Cl}^- + \text{H}_2\text{O} \]
  - Classic second order reaction (molecularity of 2)

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

- 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 for, 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).
  
  \[ aA + bB \rightleftharpoons pP + qQ \]

- 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”
  \[ \frac{dc}{dt} = -k c^n \]

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

- When n=1, we have a simple first-order reaction
  \[ \frac{dc}{dt} = -k c^1 \]
  \[ c = c_o e^{-kt} \]

- This results in an “exponential decay”
  \[ k = 0.032 \text{ min}^{-1} \]
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

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

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

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

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

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

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

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

\[
\frac{1}{c} = \frac{1}{c_0} + kt
\]

\[
k = 0.0015 L/mg/min
\]

Comparison of Reaction Orders

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

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

\[
\frac{dc}{dt} = -kc_1^1c_2^1
\]

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

\[k = 3.9 \times 10^{-5} \text{ L mg}^{-1} \text{ min}^{-1}\]

\[c_1 = c_{1o} e^{-k_{obs} t}\]

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

\[k_{obs} \approx kc_2 = 3.9 \times 10^{-5} \times 820 \approx 0.032 \text{ min}^{-1}\]

The pseudo-1st order rate constant is just the "observed rate" or $k_{obs}$
Variable Kinetic Order

• Any reaction order, except n=1

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

\[ \frac{1}{c^{n-1}} = \frac{1}{c_0^{n-1}} + (n-1)kt \]

\[ c = c_0 \frac{1}{\left[ 1 + (n-1)kc_0^{n-1}t \right]^{\frac{1}{n-1}}} \]

Half-lives

• Time required for initial concentration to drop to half, i.e., c=0.5c_o

• For a zero order reaction:

\[ c = c_o - kt \]

\[ 0.5c_o = c_o - kt_{1/2} \]

• For a first order reaction:

\[ c = c_o e^{-kt} \]

\[ 0.5c_o = c_o e^{-kt_{1/2}} \]

\[ t_{1/2} = \frac{0.5c_o}{k} \]

\[ t_{1/2} = \frac{\ln(2)}{k} \]

\[ = \frac{0.693}{k} \]
Reactions in Series

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

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

Fig. 2.9  
Pg. 68

Reversible reaction kinetics

For a general reversible reaction:

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

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
  \[
  \frac{d(B)}{dt} = 0 = k_1[A] - k_2[B]
  \]
  \[
  [B] = \frac{k_1}{k_2} \equiv K_{eq}
  \]

Temperature Effects

Temperature Dependence

- Chemist's Approach: Arrhenius Equation
  \[
  \frac{d(\ln k)}{dT_a} = \frac{E_a}{RT_a^2}
  \]
  \[
  k_{T_a} = k_{293^o} \times e^{E_a(T_a-293)/RT_a}
  \]

- Engineer's Approach:
  \[
  k_T = k_{20^o} \times \theta^{T-20^o}
  \]
  Or more generally where
  \[
  k_T = k_{T_o} \theta^{T-T_o}
  \]
  Typical values:
  \[
  \theta = 1.02 \text{ to } 1.15
  \]
Determination of $E_a$ and $A$

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

\[ k_{T_a} = A e^{-E_a/RT_a} \]

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

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

\[ \Delta G \]

Reaction coordinate

\[ G^0 \]

reactants

products
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
  \[ A + B \rightleftharpoons \]

\[ \begin{align*}
  r_f &= k_f \{A\} \{B\} \\
  r_b &= k_b \{C\} \{D\}
\end{align*} \]

- The rates are:
  \[ r_f = r_b \]

- 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:
  \[ r_f = k_f [A]^{\gamma_A} [B]^{\gamma_B} \quad \text{and} \quad r_b = k_b [C]^{\gamma_C} [D]^{\gamma_D} \]

- 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 (\( K_{\text{eq}} \))

\[
K_{\text{eq}} = \frac{k_f}{k_b} = \frac{[C]^{\gamma_C} [D]^{\gamma_D}}{[A]^{\gamma_A} [B]^{\gamma_B}} = \frac{[C]^{\gamma_C} [D]^{\gamma_D}}{[A]^{\gamma_A} [B]^{\gamma_B}}
\]

To next lecture