Physical Chemistry

Lecture 6

Reaction mechanisms and reaction-velocity predictions

Elementary reactions

- Reactions of interest are often complex
- Some reactions do occur in a single step -- elementary reactions
  - Generally involve simple mono- or bimolecular interactions
  - "Order" (correctly, molecularity) in elementary reactions is always the stoichiometry number of the reactant
  - Examples: $H_2 + O \rightarrow H_2O$
    $H + Br \rightarrow HBr$

"Simple" reaction sequences

- Reversible two-step reaction

$$A \xrightarrow{k_f} B$$
$$B \xrightarrow{k_r} A$$

- Irreversible sequential two-step reaction

$$A \xrightarrow{k_1} B$$
$$B \xrightarrow{k_2} C \ (a\ product)$$

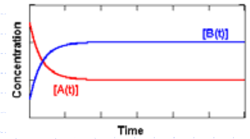
- Irreversible parallel two-step reaction

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

Mathematics of simple reaction sequences

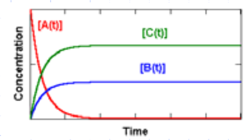
- Reversible two-step
- Both first order

$$v = k_f[A] - k_r[B]$$



- Irreversible parallel
- Both first order

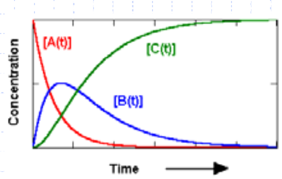
$$v = k_1[A] + k_2[A]$$



Two-step irreversible process

$$A \xrightarrow{k_1} B$$
$$B \xrightarrow{k_2} C \ (a\ product)$$

- Both steps first order
- Exactly soluble
- Gives complex result
- Can be understood qualitatively, as well as quantitatively



Reaction mechanism

- A description of the course of a reaction that gives a set of elementary reactions
- Example from Bodenstein's work:

$$H_2\,(g) + Br_2\,(g) \rightarrow 2\,HBr\,(g)$$

$$\begin{array}{lll} Br_2 & \xrightarrow{k_1} 2\,Br & v_1 \\ Br + H_2 & \xrightarrow{k_2} HBr + H & v_2 \\ H + Br_2 & \xrightarrow{k_3} HBr + Br & v_3 \\ H + HBr & \xrightarrow{k_4} H_2 + Br & v_4 \\ Br + Br & \xrightarrow{k_5} Br_2 & v_5 \end{array}$$

- Reaction mechanisms are not necessarily unique

Finding reaction velocity

- Assuming that every step is elementary allows one to know its rate equation
- Find expressions for disappearance of reactant or appearance of product
- Include terms for every step that affects reactants (or products), with stoichiometry
- Example from Bodenstein's work:

$$-\frac{d[H_2]}{dt} = v_2 - v_4 \qquad \frac{d[HBr]}{dt} = v_2 + v_3 - v_4$$

$$-\frac{d[Br_2]}{dt} = v_1 + v_3 - v_5$$

Reducing rate equations

- Eliminate dependence on reactive species (reactive intermediates such as radicals)
- Use approximations
  - Steady state for reactive species
  - Fast-equilibrium approximation when two fast steps precede a slow one

Steady-state approximation

- Reactive species have very low concentrations
- After initiation, this concentration is presumed to be independent of time

$$\frac{d[reactive\ species]}{dt} = 0$$

- Gives relation between velocities
- Example from Bodenstein's work:

$$\frac{d[Br]}{dt} = 2v_1 - v_2 + v_3 + v_4 - 2v_5 = 0$$

Fast-equilibrium approximation

- One step containing an intermediate is rate-limiting
- Prior step is reversible

$$\begin{array}{llll} (1) & A + B \rightarrow C & & fast \\ (2) & C \rightarrow A + B & & fast \\ (3) & C \rightarrow Product & & slow \end{array}$$

- One presumes a quasi-equilibrium in the first two steps to relate the concentrations

$$K_{eq} = \frac{k_1}{k_2} \approx \frac{[C]}{[A][B]} \Rightarrow \frac{d[Product]}{dt} = k_3[C] = k_3 K_{eq}[A][B]$$

Steady-state rate of formation of HBr

- From the reaction mechanism, identify time changes of reactive species and use the steady-state approximation

$$\left.\frac{d[Br]}{dt}\right|_{ss} = 2v_1 - v_2 + v_3 + v_4 - 2v_5 = 0$$

$$\left.\frac{d[H]}{dt}\right|_{ss} = v_2 - v_3 - v_4 = 0$$

- These two equations give relations

$$v_1 = v_5 \Rightarrow [Br]_{ss} = \left(\frac{k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}$$

$$\Rightarrow [H]_{ss} = \left(\frac{k_1 k_2^2}{k_5}\right)^{1/2} \frac{[H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]}$$

Example: H_2 + Br_2 continued

- Identify the reaction velocity in terms of change of a reactant or product

$$v = -\frac{d[Br_2]}{dt} = v_1 + v_3 - v_5$$
$$= v_3$$

- Substitution gives the final prediction of the steady-state reaction rate by this mechanism

$$v_{ss} = \left(\frac{k_1 k_2^2 k_3^2}{k_5}\right)^{1/2} \frac{[H_2][Br_2]^{3/2}}{k_3[Br_2] + k_4[HBr]}$$

Summary

- Every reaction is described by an equation

$$H_2\,(gas) \;+\; Br_2\,(gas) \;\rightarrow\; 2\,HBr\,(gas)$$

- "Simple" reaction sequences solved exactly
- Generally, equation like above does NOT describe reaction course
- Often cannot get exact time dependence of concentrations for reactions
  - Use a mechanism
    - Overall reaction expressed in terms of elementary steps
    - Not unique
  - "Solve" mechanism, using approximations if necessary
    - Rate-limiting steps
    - Steady-state approximation
    - Fast-equilibrium approximation