REACTION KINETICS AND REACTION MECHANISMS

Different levels of dealing with reaction rates:

I. REACTION KINETICS
  macroscopic level – mathematical description

II. REACTION MECHANISMS
  molecular level– interpretation

III. THEORIES OF REACTION RATES
  Arrhenius equation, collision and activated complex theories

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INTRODUCTION

History of reaction kinetics:

- 183X *Berzelius*: catalysis
- 1850 *Wilhelmy*: sugar inversion measurements
- 188X *van't Hoff*: rate equations
- 189X *Arrhenius*: a $k = f(T)$ equation
- 1918 *McLewis*: collision theory
- 193X *Eyring-Polányi*: activated complex theory
- more than ten Nobel prizes awarded for achievements in reaction kinetics

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I. REACTION KINETICS

- Concept of reaction rate
- Experimental method of measuring reaction rates
  - initiation and monitoring
  - sampling and online methods
  - investigation of slow and fast reactions
- Types and condition of investigated systems:
  - based on the number of phases: homogeneous (g, l, s) or heterogeneous (g/l, g/s, l/s, …)
  - closed or open (batch, tank and tube reactors)
  - isothermal and adiabatic conditions (exothermic and endothermic)
  - significance of homogeneity (mixing)

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I. REACTION KINETICS

- Rate equation, rate, order of reaction, rate constant
  - The $v = f(c)$ connection, measured and calculated $c = f(t)$ curves
  - Analytical or numerical integration of the rate equation
  - Concept of half-life ($t_{1/2}$)
  - Single term rate equations and their properties:
    - first, second and third order
  - Multiterm rate equations:
    - reversible, consecutive and parallel reactions
  - The *rapid pre-equilibrium* and *steady state* approximations, rate determining steps

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I. REACTION KINETICS

- **Before kinetic investigations, one should clarify**:
  - the stoichiometric equation,
  - the identity of reactants (A, B, …) and products (P, …),
  - possibility of an intermediate (I) – [*vs.* activated complex].

- **After the investigation of reaction kinetics,** taking the stoichiometry and the rate equation into account, **a mechanism is postulated**.
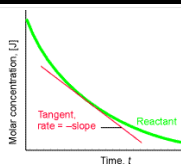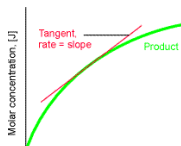
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Concept of reaction rate

- Change in amount of substance/time (open systems)
  - $v_n = dn/dt$ v_n units: mol s^{-1}
- Change in concentration/time (closed system, constant V)
  - $v_c = dc/dt$ v_c units: mol dm^{-3} s^{-1}
  - Generally: $v = \frac{1}{v_J} \cdot \frac{d[J]}{dt}$, where v_J is the stoichiometric coefficient of substance J
  - For reaction A + 2B → P: $v = -\frac{d[A]}{dt} = -\frac{1}{2} \cdot \frac{d[B]}{dt} = \frac{d[P]}{dt}$
  - Simplified formalism: $v = d\xi/dt$, where ξ is the extent of reaction: $0 < \xi < 1$

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Visualizing the reaction rate – graphical representation

- Rate equation:
  $v = \mathrm{d}c/\mathrm{d}t = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}\ldots$
  - reactant: $\mathrm{d}c/\mathrm{d}t$ negative
  - product: $\mathrm{d}c/\mathrm{d}t$ positive
- The rate of reaction at time t (or concentration c) is determined based on the slopes of the experimentally measured $c - t$ (or $c = f(t)$) curves.

Experimental methods

Experimental methods of reaction rate measurements
- two key points: <u>**initiation**</u> and **monitoring**
  - <u>Initiation</u>:
    - manual mixing of solutions (s)
    - automated fast mixing (ms)
    - rapid disturbance of an equilibrium (µs, ns): relaxation,
    - photolysis
    - dynamic NMR (exchange processes)

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Experimental methods

Experimental methods of reaction rate measurements
- two key points: **initiation** and <u>**monitoring**</u>
  - <u>Monitoring</u>: **Sampling (offline) methods**:
    - individual samples and analysis (*e.g.* titration)
    - concentration *versus* time traces
    - high consumption of chemicals (and time)
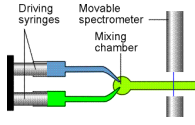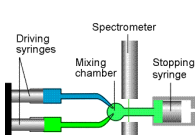
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Experimental methods

- <u>Monitoring</u>: **Continuous (online) detection**:
  - detection of a signal proportional to the concentration
  - the measurement should not interfere with the reaction!
  - types of measured property:
    - net data (non-selective) : p, V, T, pH, ...
    - reactant-selective: A_{λ}, ε_{pot}, optical rotation, NMR, ESR ...
  - concentration *versus* time traces (several different)
  - analogous or digital; computational data processing is common today
  - low consumption of chemicals (and time)
- **Gas and heterogeneous phases**: specific methods

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Experimental methods

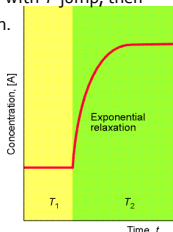**Special methods for fast reactions**:
- <u>continuous flow</u>
  - Principle:
  - Result: concentration *vs.* time trace
  - **Advantage**: ms mixing time,
  - **Drawback**: high consumption of chemicals.
- <u>stopped flow</u> (*stopped flow*)
  - Principle:
  - Result: concentration *vs.* time trace
  - **Advantage**: ms mixing time,
    low consumption of chemicals,
    possibility of multiple measurements.

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Experimental methods

- <u>Relaxation methods</u>: *e.g.* temperature jump (T-jump)
  - rapid perturbation of on equilibrium system with T-jump, then
  - monitoring the approach to new equilibrium.
  - M. Eigen: Nobel prize (1967)
  - Principle of T-jump:
    - initiation: capacitor discharging
    - monitoring: spectrophotometry
  - Result: concentration *vs.* time trace
  - **Advantage**: µs – ns initiation time,
    many repetitions.
  - **Drawback**: only reversible reactions.
- Also: p-jump, E-jump.

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Experimental methods

- <u>flash photolysis</u> (*flash photolysis*)
  - Norrish and Porter (<u>Nobel prize, 1967</u>)
  - fast reactions of photogenerated reactants
  - ns–s time scale
- <u>dynamic NMR methods</u>:
  - fast exchange reactions in equilibrium systems,
  - e.g. proton exchange, ligand exchange, …
- <u>cross beam experiments</u> (gas phase):
  - study of elementary reactions

Even the most rapid chemical reactions can be studied.

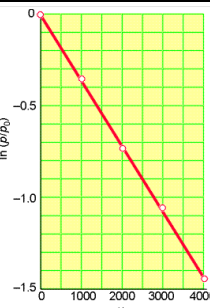**Time scales**: <u>10^{19} year</u> – days – minutes – fs (10^{-15} s)

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Rate equation

- $v = dc/dt = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}...$
  - v: rate of reaction
  - k: rate constant (= rate coefficient)
  - α, β, γ: order of reaction; $\alpha + \beta + \gamma$: net order f reaction
- The rate equation is $v - c$ (i.e. $v = f(c)$) connections, differential equation
- Measurement results: $c - t$ traces
- Integration of the differential equation (analytical or numerical) is needed for comparison
- The reaction orders are decided based on the comparison of integrated forms and then, the k rate constant(s) are calculated
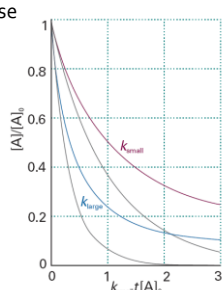
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First order kinetics

- Stoichiometry: $A \to P$ (the reverse reaction is negligible)
- Rate equation: $-\dfrac{d[A]}{dt} = k_1[A]$

  or: $\dfrac{d[P]}{dt} = k_1[A]$
- Integrated form: $[A] = [A]_0 e^{-k_1 t}$; $[P]$

  linearized: $\ln\dfrac{[A]}{[A]_0} = -k_1 t$
- Half-life: $t_{1/2} = \ln 2/k_1$
  - $t_{1/2}$ is independent of the initial concentration in first order reactions.
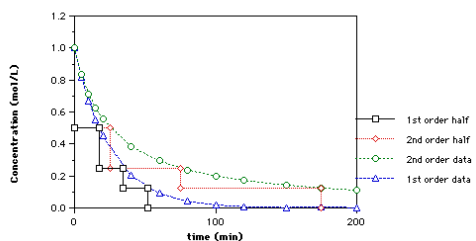

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Second order kinetics I.

- Stoichiometry: $2A \to P$ (the reverse reaction is negligible)
- Rate equation: $-\dfrac{d[A]}{⟨2⟩dt} = k_2[A]^2$

  or: $\dfrac{d[P]}{dt} = k_2[A]^2$
- Integrated form: $[A] = \dfrac{[A]_0}{1 + ⟨2⟩k_2 t[A]_0}$

  linearized: $\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = ⟨2⟩k_2 t$
- Half-life: $t_{1/2} = 1/(⟨2⟩k_2[A]_0)$
  - $t_{1/2}$ is dependent on the initial concentration in second order reactions.

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Second order kinetics I.

Concentration vs time data for first and second order reactions

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Second order kinetics II.

- Stoichiometry: $A + B \to P$ (the reverse reaction is negligible)
- Rate equation: $-\dfrac{d[A]}{dt} = k_2[A][B]$

  or: $\dfrac{d[P]}{dt} = k_2[A][B]$
- Integrated form: $\dfrac{1}{[B]_0 - [A]_0} \ln\left(\dfrac{[B]/[B]_0}{[A]/[A]_0}\right) = k_2 t$

  the conversion x is often useful:

  $x = [A]_0 - [A] = [B]_0 - [B] \to \dfrac{1}{[B]_0 - [A]_0} \ln\left(\dfrac{([B]_0 - x)/[B]_0}{([A]_0 - x)/[A]_0}\right) = k_2 t$

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Other simple kinetics

Zeroth order kinetics
- Stoichiometry: $A \rightarrow P$ (the reverse reaction is negligible)
- Rate equation: $-d[A]/dt = k_0$ or $d[P]/dt = k_0$
- Integrated from: $[A] = [A]_0 - k_0 t$
  - the rate is independent of the reactant concentration (e.g. surface reactions)

Third order kinetics
- Stoichiometry: $3A \rightarrow P$ or $A + 2B \rightarrow P$ or $A + B + C \rightarrow P$
- Rate equation: as indicated by the stoichiometry
- Integrated form: by solving the differential equation (not as simple as first order kinetics). Calculating the conversion x is useful.

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Multiterm rate equations: <u>consecutive</u> reactions

- Stoichiometry: $A \xrightarrow{k_a} B \xrightarrow{k_b} P$
- Classical examples: radioactive decay series
$$^{239}U \xrightarrow{23,5\,\text{minutes}} {}^{239}Np \xrightarrow{2,35\,\text{days}} {}^{239}Pu$$
- The rate equation can be stated for each component: $-\dfrac{d[A]}{dt} = k_a[A]$
$$\dfrac{d[B]}{dt} = k_a[A] - k_b[B]$$
$$\dfrac{d[P]}{dt} = k_b[B]$$

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Multiterm rate equations: <u>consecutive</u> reactions

- Integrated form:
  - **reactant**: exponential decay,
    $$[A] = [A]_0 e^{-k_a t}$$
  - **intermediate**: maximum,
    $$[B] = \dfrac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)[A]_0$$
  - **product**: S-shaped curve (*alias* induction period),
    $$[P] = \left\{1 + \dfrac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a}\right\}[A]_0$$

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Multiterm rate equations: <u>parallel</u> reactions

- Relatively simple (close to obvious)
- Stoichiometry:
$$A \xrightarrow{k_1} P_1 \quad d[P_1]/dt = k_1[A] \quad [P_1] = \tfrac{k_1}{k_1 + k_2 + ... + k_i}[A]_0\left(1 - e^{-(k_1 + k_2 + ... + k_i)t}\right)$$
$$A \xrightarrow{k_2} P_2 \quad d[P_2]/dt = k_2[A] \quad [P_2] = \tfrac{k_2}{k_1 + k_2 + ... + k_i}[A]_0\left(1 - e^{-(k_1 + k_2 + ... + k_i)t}\right)$$
$$A \xrightarrow{k_i} P_i \quad d[P_i]/dt = k_i[A]$$
$$-d[A]/dt = (k_1 + k_2 + ... + k_i)[A] \qquad [A] = [A]_0 e^{-(k_1 + k_2 + ... + k_i)t}$$
- Integration gives exponential (first order) formulas.

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Multiterm rate equations: <u>reversible</u> reactions

Reversible first order reaction:
- Stoichiometry: $A \rightleftharpoons B$
- Rate equation:
$$d[A]/dt = -k_1[A] + k_{-1}[B]$$
- Integration: $[A] = \dfrac{k_{-1} + k_1 e^{-(k_1 + k_{-1})t}}{k_1 + k_{-1}}[A]_0$
- These concentration – time traces are exponential.

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Multiterm rate equations: <u>reversible</u> reactions

Reversible second order reaction:
- Stoichiometry: $A + B \rightleftharpoons C + D$
- Rate equation:
$$d[A]/dt = -k_2[A][B] + k_{-2}[C][D]$$
- Integration: …
- Message: **in equilibrium** $d[A]/dt = 0$, so the $\rightleftharpoons$ rates are identical: $k_2[A][B] = k_{-2}[C][D]$.
  Therefore: $\dfrac{k_2}{k_{-2}} = \dfrac{[C][D]}{[A][B]} = K_2$

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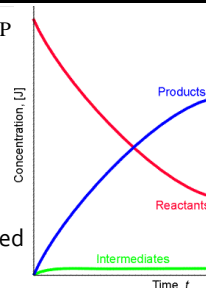## Multiterm rate equations: complex reaction networks

- can be seldom integrated analytically,
- numerical methods are used.

Two useful **approximation methods**:
- *steady state* approximation,
- *rapid pre-equilibrium* approximation.
- Both make it possible to solve complicated kinetics differential equations.
- They are not exact, but practically „perfect" approximations, also contributing to the chemical understanding of systems.
- The usefulness of the two approximations can be assessed by comparing calculated and measured kinetic traces. 25

Steady state approximation (Bodenstein principle):

- Stoichiometry: $A \xrightarrow{k_a} B \xrightarrow{k_b} P$
- If B is very reactive, it is consumed rapidly, so [B] is always very low, which means $d[B]/dt \sim 0$.
- The rate determining step: $A \rightarrow B$
- Differential equations are turned into algebraic equations!
- *Examples: reaction mechanisms (later)*

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Rapid pre-equilibrium approximation:

- Stoichiometry: A + B → P, but intermediate I forms,
- so the scheme A + B ⇌ I → P can be written if the first equilibrium is reached faster than I → P
- Rate determining step: I → P
- [I] can be given from the „pre-equilibrium":
$$K_1 = \frac{k_1}{k_{-1}} = \frac{[I]}{[A][B]} \text{ so } [I] = K_1[A][B]$$
- as d[P]/dt = k_2[I], substituting [I] gives:
$$\frac{d[P]}{dt} = k_{exp}[A][B], \text{ where } k_{exp} = k_2 K_1 = \frac{k_1 k_2}{k_{-1}}$$
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Determining the rate equation:

Rate equation: $v = dc/dt = k[A]^\alpha[B]^\beta[C]^\gamma$
1. Determination of all orders of reaction ($\alpha, \beta, \gamma, ...$) Summing the individual orders gives the **net order of reaction**.
2. Calculation of rate constant k

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Determining the rate equation:

Rate equation: $v = dc/dt = k[A]^\alpha[B]^\beta[C]^\gamma$
1. **Determination of all orders of reaction ($\alpha, \beta, \gamma, ...$)**

A. „**trial-and-error**" based on individual $c – t$ kinetic traces. Plot the $c – t$ pairs of points:
- if first order: $\ln c – t$ (semilogarithmic formula),
- if second order: $1/c – t$ (reciprocal formula) gives a straight line.
- Simple first and second order are common cases, but by no means exclusive, a „more certain" method is needed.
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Determining the rate equation:

Rate equation: $v = dc/dt = k[A]^\alpha[B]^\beta[C]^\gamma$
1. **Determination of all orders of reaction ($\alpha, \beta, \gamma, ...$)**

B. **van't Hoff method (initial rate method)**:
- Logarithm of the rate equation with initial values: $\lg v_0 = \lg k + \alpha \lg[A]_0 + \beta \lg[B]_0 + \gamma \lg[C]_0$
- Set $[B]_0$ and $[C]_0$ so that [B] = constant and [C] = constant (pseudo-zeroth order).
- Rate v_0 is measured at different $[A]_0$, then the data pairs $\lg v_0 – \lg[A]_0$ are plotted.
- The slope of the straight line is the α order of reaction with respect to reactant A. 30

Determining the rate equation:

Rate equation: $v = \mathrm{d}c/\mathrm{d}t = k[A]^\alpha[B]^\beta[C]^\gamma$

1. **Determination of all orders of reaction (α, β, γ, …)**

- B. **van't Hoff method (initial rate method):**
  - Then change $[B]_0$ and keep [A] and [C] constant, so <u>order β with respect to B</u> is obtained.
  - …..
  - **Initial values** may be used, but rates at any other time may be useful for evaluation.

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Determining the rate equation:

Rate equation: $v = \mathrm{d}c/\mathrm{d}t = k[A]^\alpha[B]^\beta[C]^\gamma$

1. **Determination of all orders of reaction (α, β, γ, …)**
   The individual orders of reactions may be:
   - small positive integers (1, 2, 3)
     - no explanation needed, a natural case
   - small negative integers (-1, -2, -3)
     - *e.g.* interpretation by rapid pre-equilibrium
   - small positive/negative fractional numbers (1/2, 3/2)
     - (*e.g.* parallel paths with different orders of reaction)
     - *e.g.* dimer dissociation as a pre-equilibrium
     - *e.g.* chain reactions
   - 0 (this can be directly seen from the data, no plot needed)
     - *e.g.* pre-equilibrium (iodination of acetone)
     - *e.g.* certain surface reactions, drug intake processes

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Determining the rate equation:

Rate equation: $v = \mathrm{d}c/\mathrm{d}t = k[A]^\alpha[B]^\beta[C]^\gamma$

1. **Determination of all orders of reaction (α, β, γ, …)**
   The individual orders of reactions may be:
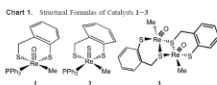
Inorganic Chemistry
: Communication

A Non-Radical Chain Mechanism for Oxygen Atom Transfer with a Thiorhenium(V) Catalyst

Katalin Ösz† and James H. Espenson*

Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

The compound MeRe(S)(mtp)(PPh₃), **2**, where mtpH₂ is 2-(mercaptomethyl)thiophenol, was used to catalyze the reaction between pyridine *N*-oxides, PyO, and triphenylphosphine. The rate law is −d[PyO]/dt = k₁′[2]·[PyO]¹ᐟ², with k₁′ at 25.0 °C in benzene == 0.68 (4-picoline *N*-oxide) and 3.5 × 10⁻³ dm³·² mol⁻¹ᐟ² s⁻¹ (4-NO₂-pyridine *N*-oxide). A chain mechanism with three steady-state thiorhenium species as chain carriers is implicated.

Chart 1. Structural Formulas of Catalysts **1–3**

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Determining the rate equation:

Rate equation: $v = \mathrm{d}c/\mathrm{d}t = k[A]^\alpha[B]^\beta[C]^\gamma$

1. Determination of all orders of reaction (α, β, γ, …)
2. **Calculation of the rate constant k**

- Numerical calculations from measured v rates (mol dm⁻³ s⁻¹) and the known form of the rate equation.
- dimension of k: $[k_1] = $ s⁻¹, $[k_2] = $ mol⁻¹ dm³ s⁻¹ etc.
- Equilibrium constant K is the ratio of the rate constants k_+ and k_- – both numerically and dimensionally:

$$K = k_+/k_-$$

- It is useful to compare these to other values of K obtained from independent measurements.

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