First Order Reactions

- **Rate Law:** Concentration with exponent of one

$$\frac{d[A]}{dt} = k[A]$$

- **Basic Reaction:** R → P
  - Rate doesn't depend on the product; spontaneous

- **Example:** Radioactive decay

First Order Reactions

- **Example:**

$$A \xrightarrow{k} B$$

- Rate Law for A and B:
  - *"The rate of decay of A is proportional to the amount of A."*

$$\frac{d[A]}{dt} = -k[A] \text{ and } \frac{d[B]}{dt} = k[A]$$

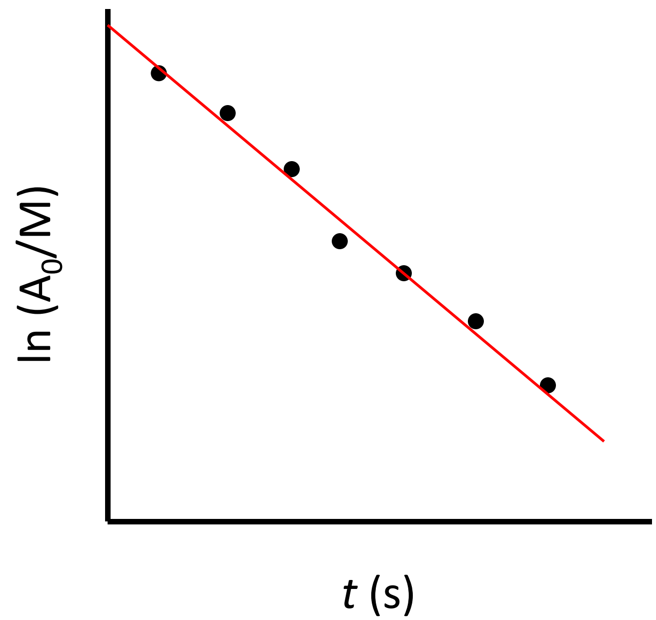
- Starting conditions (at t = 0):

$$[A] = A_0 \text{ and } [B] = B_0$$

Plotting First Order Reactions

- Plotting $\ln A$ vs. t:
  $\ln A = \ln A_0 - kt$

- **Fit Parameters:**
  - Intercept: $\ln A_0$
  - Slope: $-k$



Second Order Reactions (Class I)

- **Rate Law:** Concentration with exponent of two

$$\frac{d[A]}{dt} = k[A]^2$$

- **Basic Reaction:** R+R → P
  - Rate doesn't depend on the product; spontaneous
  - Two reactant molecules collide and form product

- **Example:** 2(Cysteine) → Cystine

Second Order Reactions (Class I)

- **Example:**

$$2A \xrightarrow{k} B$$

- Rate Law for A and B:
  - *"The rate of decay of A is proportional to amount of A^2."*

$$\frac{d[A]}{dt} = -k[A]^2 \text{ and } \frac{d[B]}{dt} = k[A]^2$$

- Starting conditions (at t = 0):

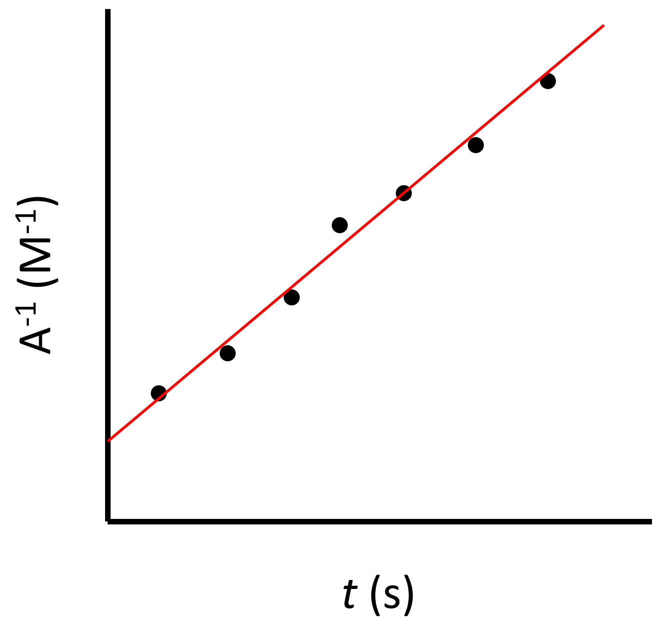
$$[A] = A_0 \text{ and } [B] = B_0$$

Plotting Second Order Reactions

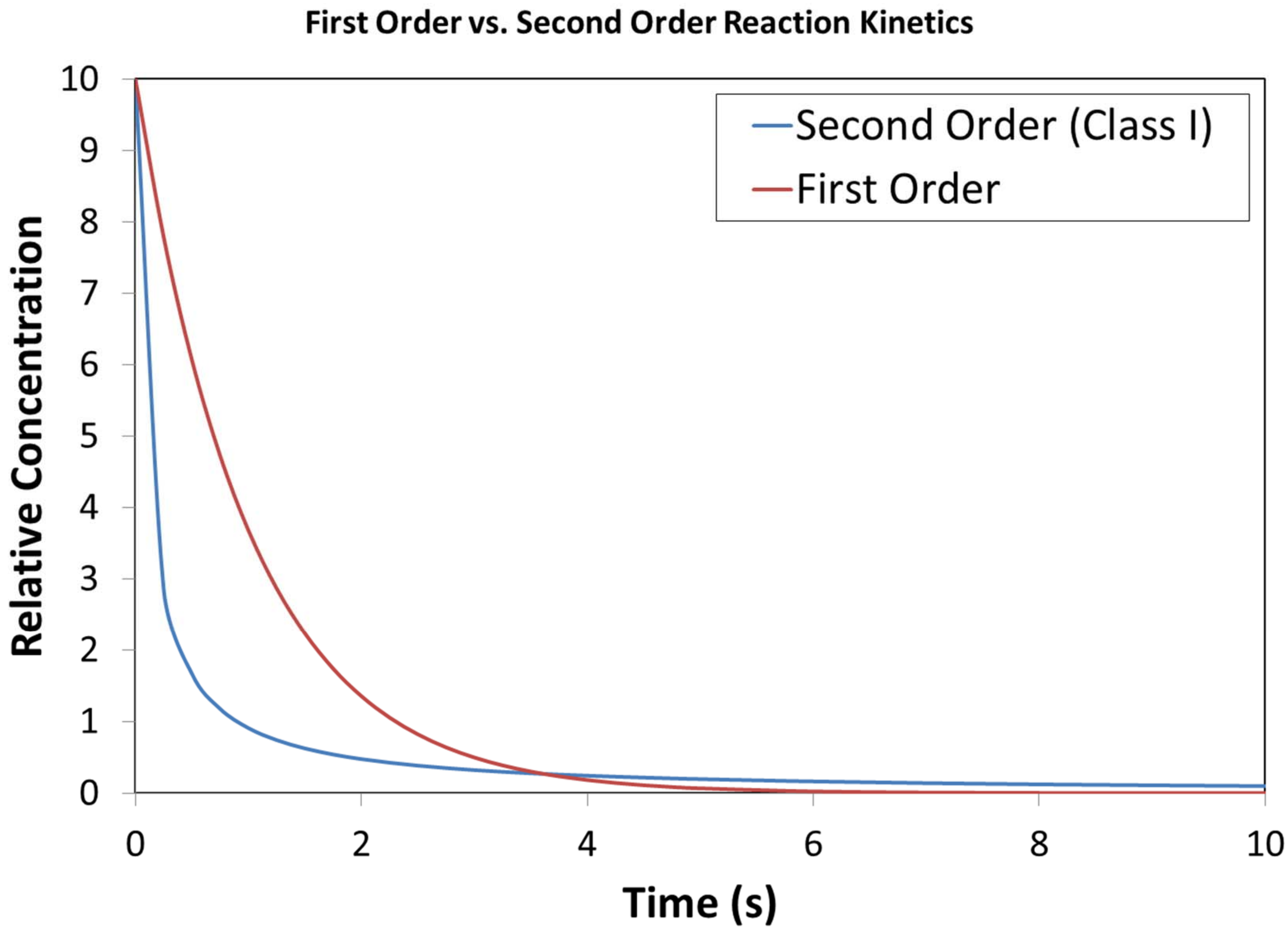
- Plotting A^{-1} vs. t:

  $A^{-1} = A_0^{-1} + kt$

- **Fit Parameters:**
  - Intercept: A_0^{-1}
  - Slope: k



First vs. Second Order: Single Species



Second Order Reactions (Class II)

- **Rate Law:** Concentration with overall order of two

$$\frac{d[A]}{dt} = k[A][B]$$

- **Basic Reaction:** $R_1 + R_2 \rightarrow P$
  - Rate doesn't depend on the product; spontaneous
  - Two *different* reactant molecules collide and form product

- **Example:** DNA_1 + DNA_2 → Duplex DNA

Second Order Reactions (Class II)

- **Example:**

$$A + B \xrightarrow{k} C$$

- Rate Law for A and B:
  - *The rate laws for A and B are the same (Why?)*
  - *A and B must collide in order to react*

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B] \text{ and } \frac{d[C]}{dt} = k[A][B]$$

- Starting conditions (at t = 0):

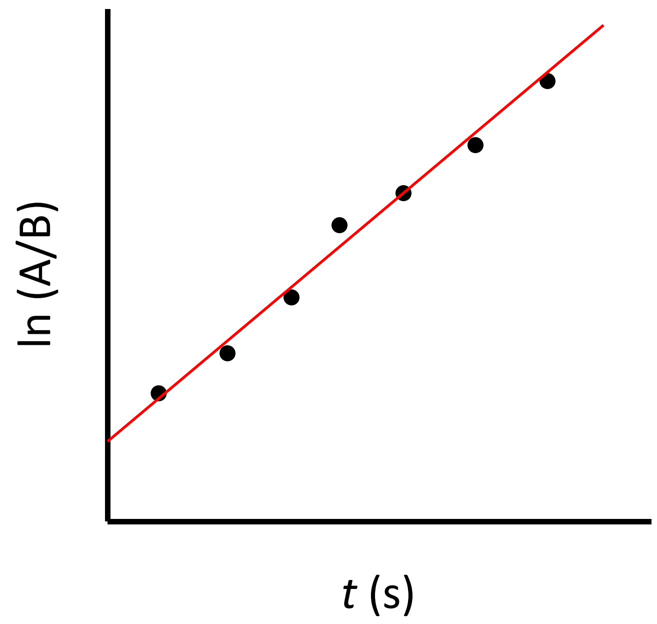
$$[A] = A_0 \text{ and } [B] = B_0 \text{ and } [C] = C_0$$

Plotting Second Order Reactions

- Plotting A^{-1} vs. t:

$$\ln\frac{A}{B} = \ln\frac{A_0}{B_0} + (A_0 - B_0)kt$$

- **Fit Parameters:**
  - Intercept: $\ln\frac{A_0}{B_0}$
  - Slope: $(A_0 - B_0)k$



Class I vs. Class II: A Special Case

- **Example:**

$$A + B \xrightarrow{k} C$$

- What if $A_0 = B_0$?

$$\ln\frac{A}{B} = \ln\frac{A_0}{B_0} + (A_0 - B_0)kt$$

  – This won't work! $(A_0 - B_0 = 0)$

- If initial concentrations are the same, Class II → Class I, **even though actual species are different!**
  – A and B are used up identically and [A] is not distinguishable from [B]

General Case

- **Rate Law:** Concentration with exponent of two

$$\frac{d[A]}{dt} = k[A]^n$$

- **Solution:** (Integration after separation of variables)
  - Same species, or $A_0=B_0=C_0=\ldots$

$$\frac{1}{n-1}\left[\frac{1}{A^{n-1}} - \frac{1}{A_0^{n-1}}\right] = kt$$

- **Half Life:**

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)kA_0^{n-1}}$$

Summary of Rate Laws

TABLE 7.3 The Characteristics of Simple-order Reactions

Reaction order	Linear plot	Rate proportional to	Units of k
Zero-order	c vs. t	$dc/dt = k$	M time^{-1}
First-order	$\ln c$ vs. t	$dc/dt = kc$	time^{-1}
Second-order (I)	$1/c$ vs. t	$dc/dt = kc^2$	M^{-1} time^{-1}
Second-order (II)	$\ln (c_A/c_B)$ vs. t	$dc_A/dt = kc_Ac_B$	M^{-1} time^{-1}
nth-order ($n \neq 1$)	$1/c^{n-1}$ vs. t	$dc/dt = kc^n$	$M^{-(n-1)}$ time^{-1}

Tinoco, p. 339.

Determining Orders and Rate Constants

- **Critical:** Make sure you know the stoichiometry!

- **Method 1:** Plot concentration vs. time
  - Linear indicates zero-order
  - Can use non-linear fitting techniques

- **Method 2:** Plot $\frac{d[A]}{dt}$ vs. time
  - Does it look linear, parabolic, etc.?
  - Drawback: many points are needed to get slope

Determining Orders and Rate Constants

- **Method 3:** Initial velocities
  - Initial velocity should reflect initial concentrations
  - *Assumption:* concentrations don't change much
  - *Example*: If $v = k[A][B]^2$, doubling $[B_0]$ should quadruple initial rate
  - If $[A_0]$, $[B_0]$, v, and orders are known, solve for k algebraically

Determining Orders and Rate Constants

- **Method 4:** Elimination by excess
  - Add B in large molar excess compared to A
  - [B] won't change much, so

$$v = k[A]^a[B]^b \rightarrow v = k'[A]^a$$

  - B will "drop out" of the rate law, measure [A] vs. t.