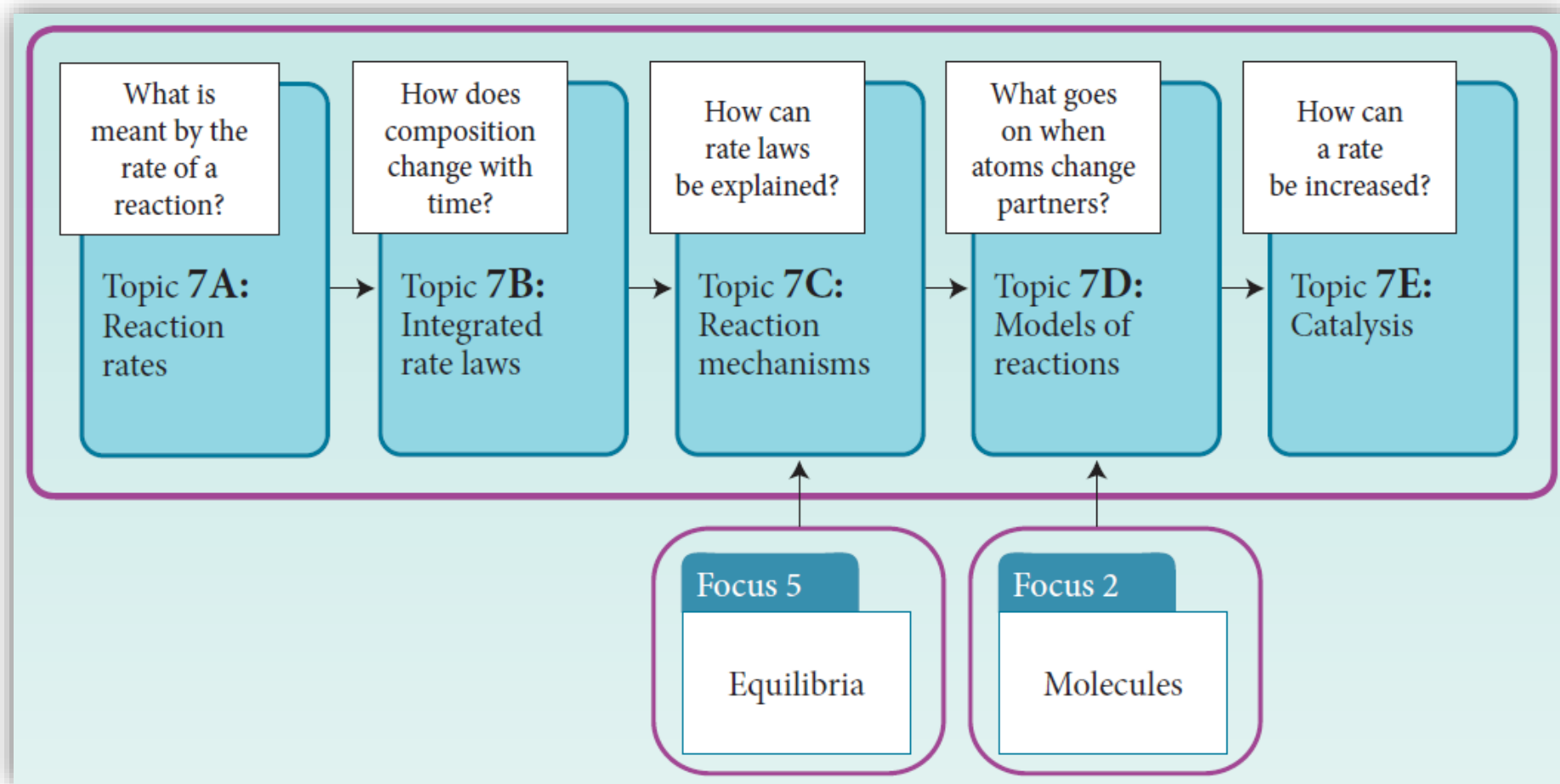


Focus 7. Kinetics Overview



Topic 7A. Reaction Rates

- 7A.1 Concentration and Reaction Rate
- 7A.2 The Instantaneous Rate of Reaction
- 7A.3 Rate Laws and Reaction Order

Concentration and Reaction Rate



Concentration and Reaction Rate

- **Reaction rate:** the 'speed' of a chemical reaction
As the change in concentration of one of the reactants or products at a selected stage of the reaction divided by the time interval over which the change takes place.

- Average reaction rate for a reaction $R \rightarrow P$

$$\Delta[R] = [R]_{t_2} - [R]_{t_1}, \Delta t = t_2 - t_1$$

$$\text{Average rate of consumption of R} = -\frac{\Delta[R]}{\Delta t}$$

$$\text{Average rate of formation of P} = \frac{\Delta[P]}{\Delta t}$$

Concentration and Reaction Rate

- For a reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

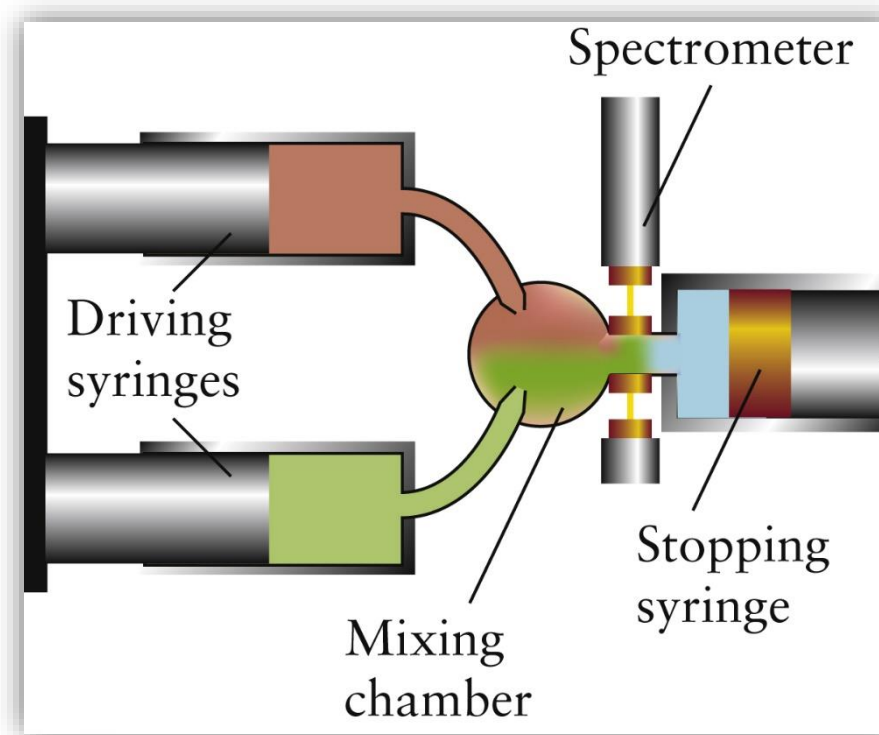
$$\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

- Unique average rate for $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\text{Unique average reaction rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

Concentration and Reaction Rate

- How can we measure reaction rates?
- Stopped-flow method
- Spectrometry



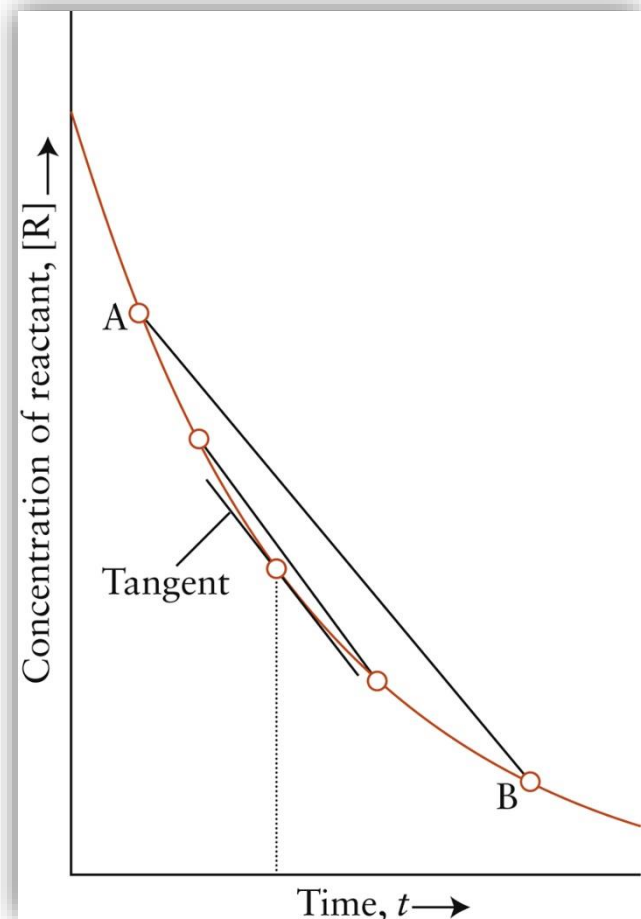
The Instantaneous Rate of Reaction

- Instantaneous rate of reaction
the slope of a tangent drawn to the graph of
concentration as a function of time

$$\text{Rate of consumption of R} = -\frac{d[R]}{dt}$$

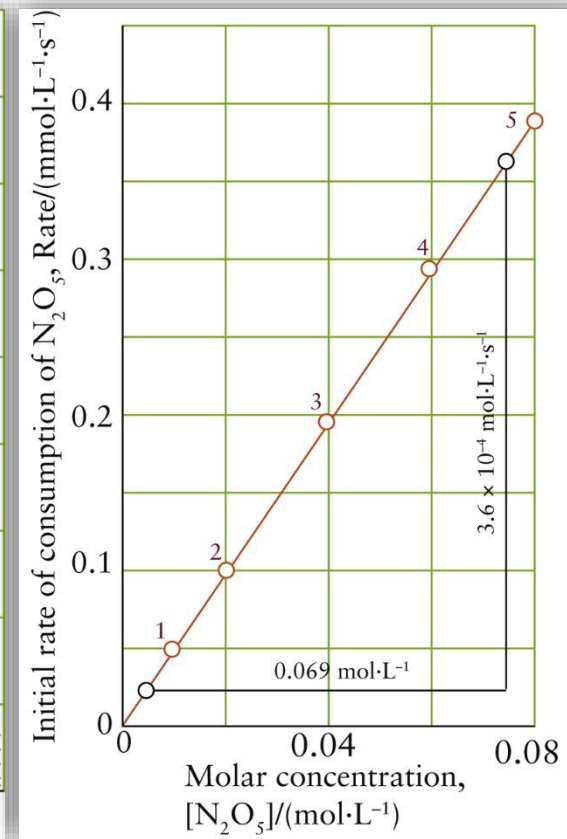
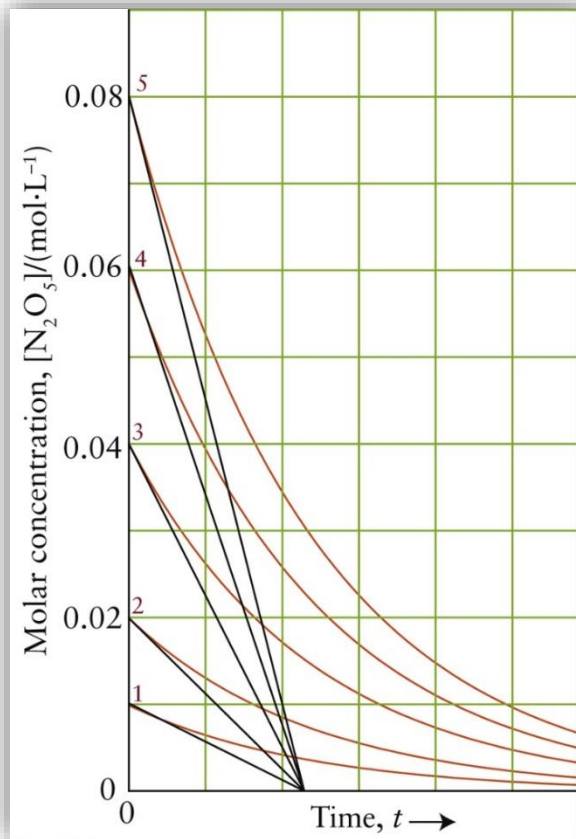
$$\text{Rate of formation of P} = \frac{d[P]}{dt}$$

$$\text{Reaction rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$



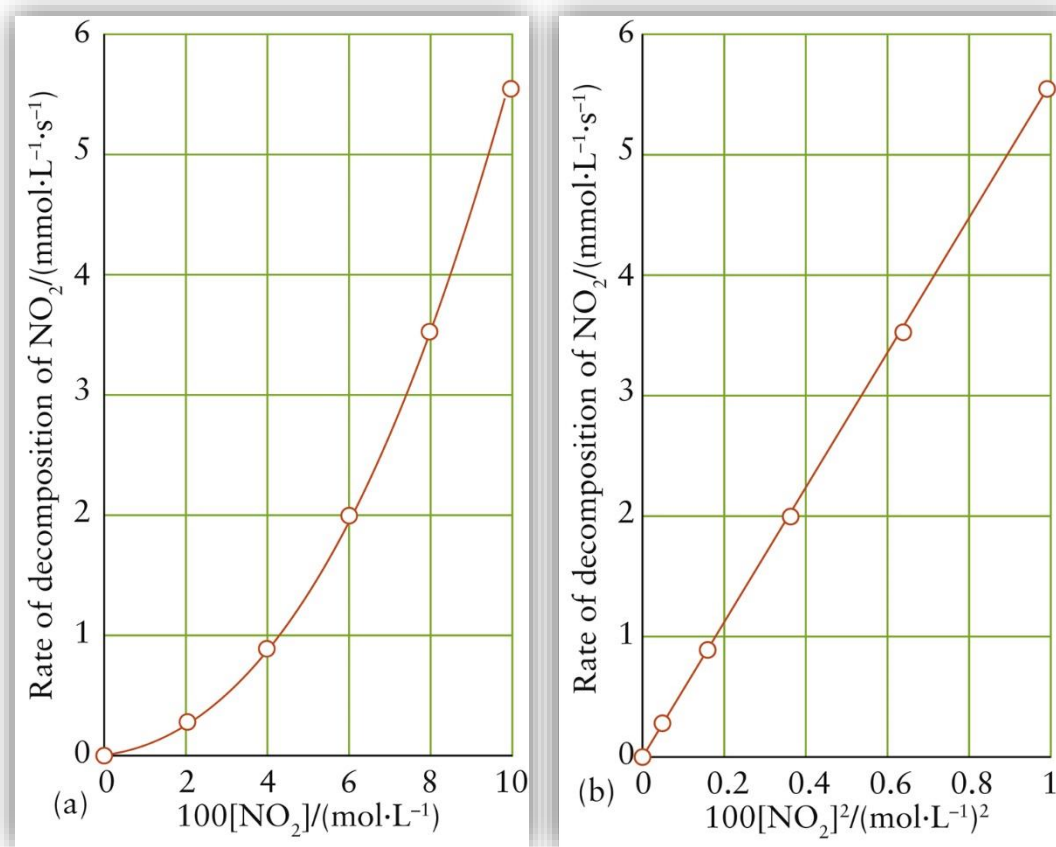
Rate Laws and Reaction Order

- Initial rate
The rate can be calculated without intervention of products.
- $2 \text{N}_2\text{O}_5 (\text{g}) \rightarrow 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$
Initial rate of consumption of N_2O_5
 $\propto [\text{N}_2\text{O}_5]_{\text{initial}} = k_r \times [\text{N}_2\text{O}_5]_{\text{initial}}$
- k_r : Rate constant



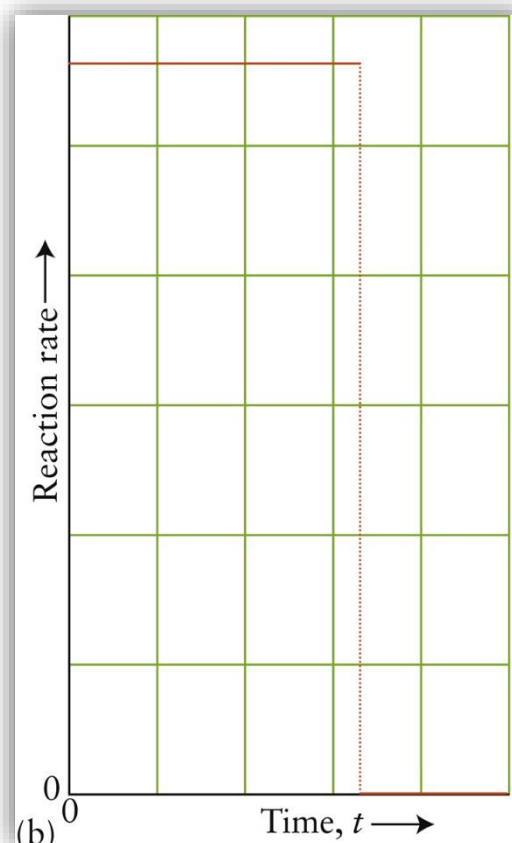
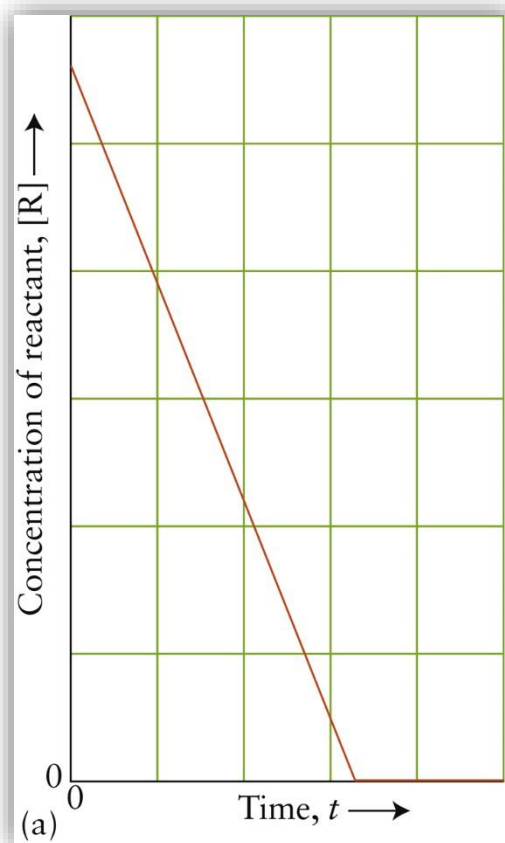
Rate Laws and Reaction Order

- Second order: $2 \text{NO}_2 (\text{g}) \rightarrow 2 \text{NO} (\text{g}) + \text{O}_2 (\text{g})$
Rate of consumption of $\text{NO}_2 = k_r \times [\text{NO}_2]^2$



Rate Laws and Reaction Order

- Zeroth order: $2 \text{NH}_3 (\text{g}) \rightarrow \text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g})$
Rate of consumption of $\text{NH}_3 = k_r$



Rate Laws and Reaction Order

TABLE 7A.1 Rate Laws and Rate Constants

Reaction	Rate law*	Temperature, T/K†	Rate constant
Gas phase			
$\text{H}_2 + \text{I}_2 \longrightarrow 2 \text{HI}$	$k_r[\text{H}_2][\text{I}_2]$	500	$4.3 \times 10^{-7} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
		600	4.4×10^{-4}
		700	6.3×10^{-2}
		800	2.6
$2 \text{HI} \longrightarrow \text{H}_2 + \text{I}_2$	$k_r[\text{HI}]^2$	500	$6.4 \times 10^{-9} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
		600	9.7×10^{-6}
		700	1.8×10^{-3}
		800	9.7×10^{-2}
$2 \text{N}_2\text{O}_5 \longrightarrow 4 \text{NO}_2 + \text{O}_2$	$k_r[\text{N}_2\text{O}_5]$	298	$3.7 \times 10^{-5} \text{ s}^{-1}$
		318	5.1×10^{-4}
		328	1.7×10^{-3}
		338	5.2×10^{-3}
		1000	0.76 s^{-1}
$2 \text{N}_2\text{O} \longrightarrow 2 \text{N}_2 + \text{O}_2$	$k_r[\text{N}_2\text{O}]$	1050	3.4
$2 \text{NO}_2 \longrightarrow 2 \text{NO} + \text{O}_2$	$k_r[\text{NO}_2]^2$	573	$0.54 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
$\text{C}_2\text{H}_6 \longrightarrow 2 \text{CH}_3$	$k_r[\text{C}_2\text{H}_6]$	973	$5.5 \times 10^{-4} \text{ s}^{-1}$
cyclopropane \longrightarrow propene	$k_r[\text{cyclopropane}]$	773	$6.7 \times 10^{-4} \text{ s}^{-1}$
Aqueous solution			
$\text{H}_3\text{O}^+ + \text{OH}^- \longrightarrow 2 \text{H}_2\text{O}$	$k_r[\text{H}_3\text{O}^+][\text{OH}^-]$	298	$1.5 \times 10^{11} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
$\text{CH}_3\text{Br} + \text{OH}^- \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$	$k_r[\text{CH}_3\text{Br}][\text{OH}^-]$	298	$2.8 \times 10^{-4} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \longrightarrow 2 \text{C}_6\text{H}_{12}\text{O}_6$	$k_r[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}^+]$	298	$1.8 \times 10^{-4} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$

*For the unique instantaneous rate.

†Three significant figures.

Rate Laws and Reaction Order

- Rate = constant \times [concentration]^{*a*}
*n*th reaction order according to *a*

Order in A	Rate law
0	Rate = k_r
1	Rate = $k_r[A]$
2	Rate = $k_r[A]^2$

The rate law for a reaction is determined experimentally and cannot in general be inferred from the chemical equation for the reaction.

Rate Laws and Reaction Order

- For general case, $\text{Rate} = k_r \times [\text{A}]^a [\text{B}]^b$

- Overall order = $a + b$

- Units of k_r

Overall order:	1	2	3
Units of k_r :	s^{-1}	$\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$\text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$
Overall order:	1	2	3
Units of k_r :	s^{-1}	$\text{kPa}^{-1} \cdot \text{s}^{-1}$	$\text{kPa}^{-2} \cdot \text{s}^{-1}$

Rate Laws and Reaction Order

- $2 \text{O}_3 (\text{g}) \rightarrow 3 \text{O}_2 (\text{g})$ with a negative reaction order

$$\text{Rate} = k_r \frac{[\text{O}_3]^2}{[\text{O}_2]} = k_r [\text{O}_3]^2 [\text{O}_2]^{-1}$$

- $2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{SO}_3 (\text{g})$ with a fractional reaction order

$$\text{Rate} = k_r \frac{[\text{SO}_2]}{[\text{SO}_3]^{1/2}} = k_r [\text{SO}_2] [\text{SO}_3]^{-1/2}$$

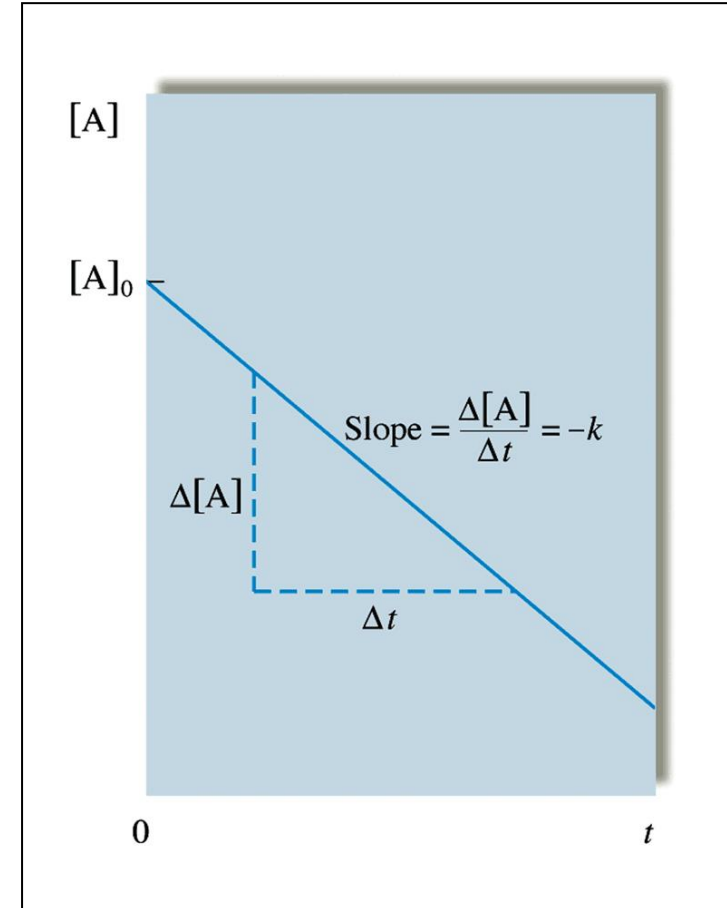
Topic 7B. Integrated Rate Laws

- 7B.1 First-Order Integrated Rate Laws
- 7B.2 Half-Lives for First-Order Reactions
- 7B.3 Second-Order Integrated Rate Laws

First-Order Integrated Rate Laws

- For zeroth order reaction

$$[A]_0 - [A] = k_r t \quad \text{or} \quad [A] = [A]_0 - k_r t$$



First-Order Integrated Rate Laws

- For first order reaction

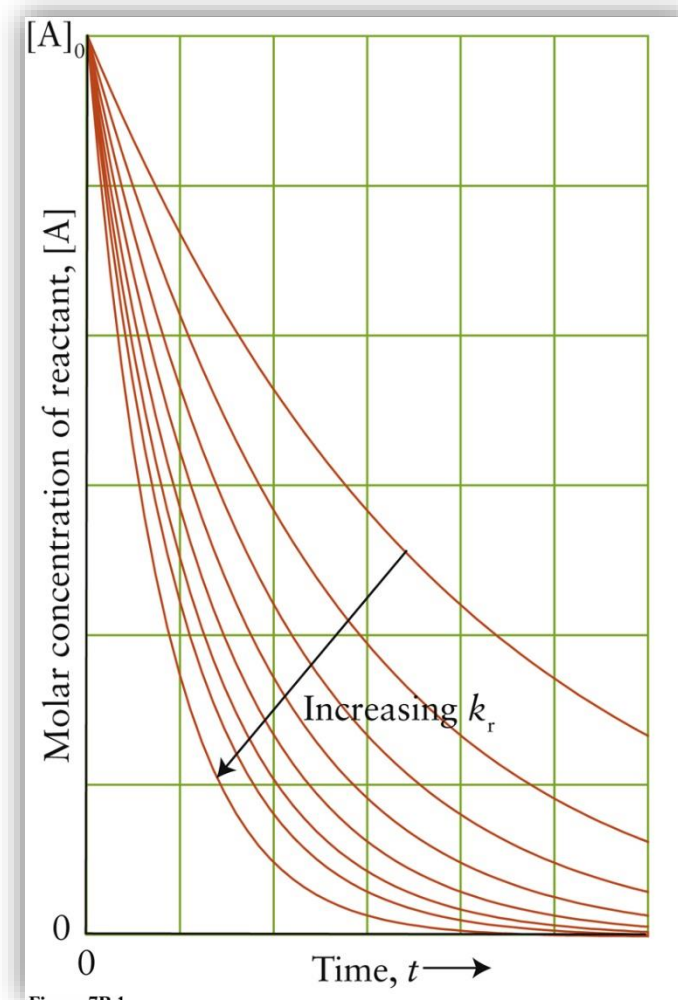
$$\text{Rate of consumption of A} = -\frac{d[A]}{dt} = k_r[A]$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k_r \int_0^t dt = -k_r t$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = (\ln [A]_t + \text{constant}) - (\ln [A]_0 + \text{constant})$$

$$\ln \frac{[A]_t}{[A]_0} = -k_r t$$

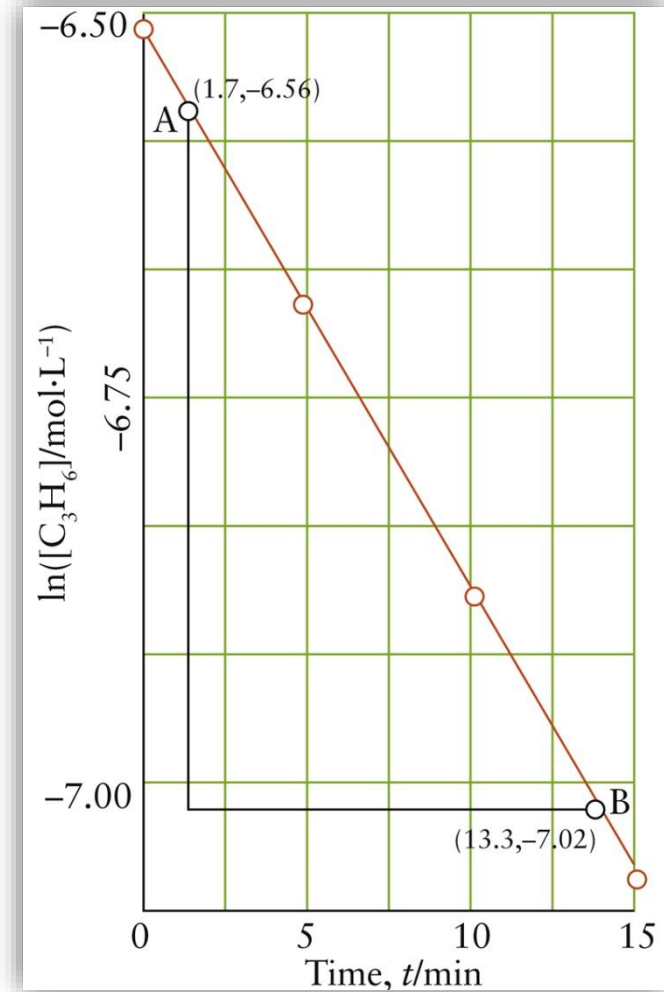
$$[A]_t = [A]_0 e^{-k_r t}$$



First-Order Integrated Rate Laws

- For first order reaction

$$\overbrace{\ln [A]_t}^y = \overbrace{\ln [A]_0}^{\text{intercept}} \overbrace{-k_r t}^{\text{slope } x}$$



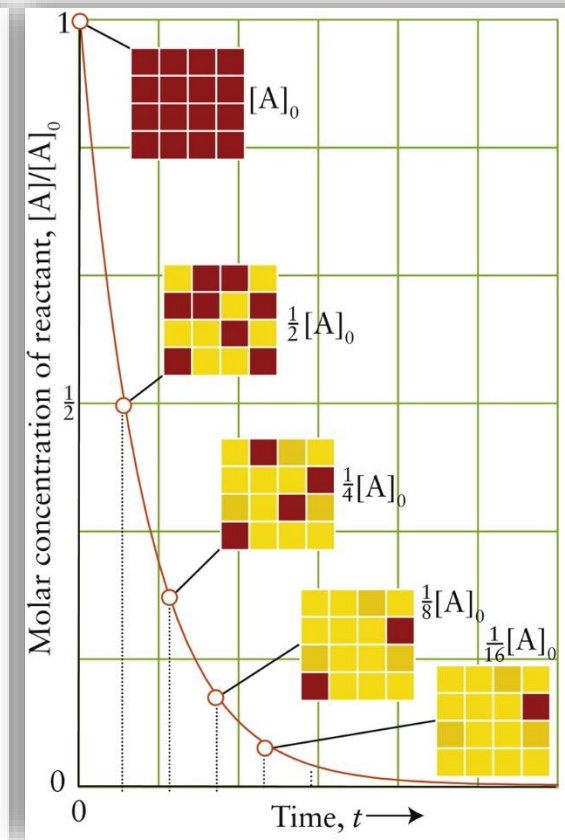
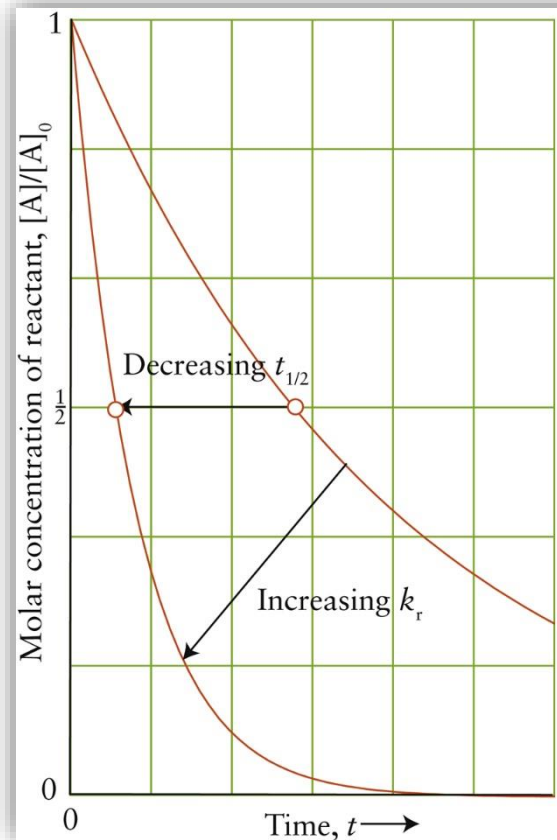
Half-Lives for First-Order Reactions

From $\ln([A]_t/[A]_0) = -k_r t$ and $\ln(1/x) = -\ln x$

$$t = \frac{1}{k_r} \ln \frac{[A]_0}{[A]_t}$$

Now set $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$

$$t_{1/2} = \frac{1}{k_r} \ln \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{1}{k_r} \ln 2$$



Second-Order Integrated Rate Laws

- For second order reaction

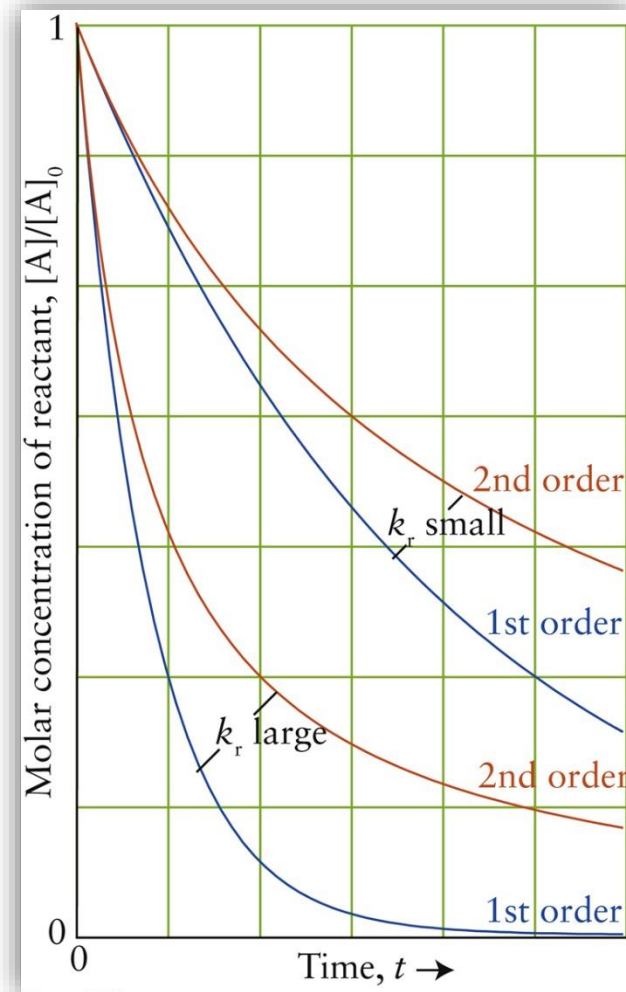
$$-\frac{d[A]}{dt} = k_r[A]^2$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k_r \int_0^t dt = -kt$$

$$\begin{aligned} \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} &= \left(-\frac{1}{[A]_t} + \text{constant} \right) - \left(-\frac{1}{[A]_0} + \text{constant} \right) \\ &= \frac{1}{[A]_0} - \frac{1}{[A]_t} \end{aligned}$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_r t$$

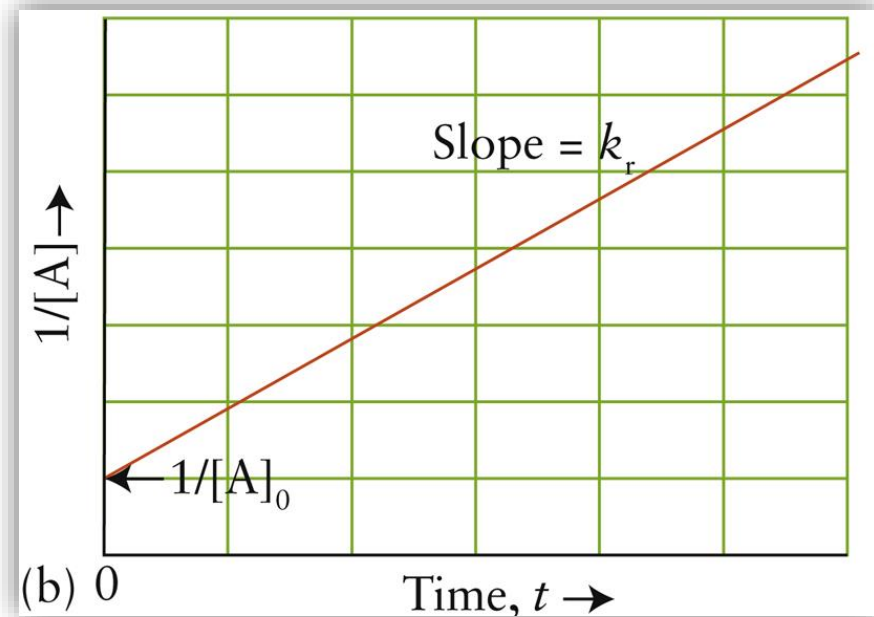
$$[A]_t = \frac{[A]_0}{1 + k_r t [A]_0}$$



Second-Order Integrated Rate Laws

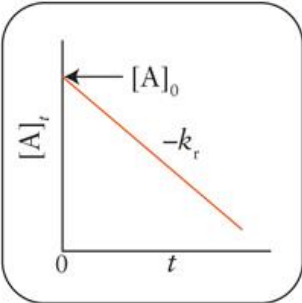
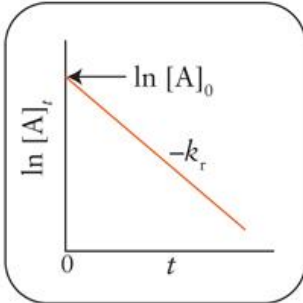
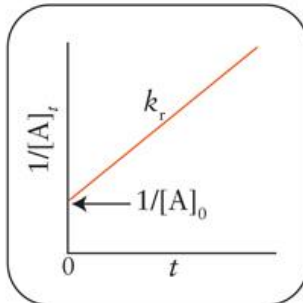
- For second order reaction

$$\frac{\overbrace{1}^y}{[A]_t} = \frac{\overbrace{1}^{\text{intercept}}}{[A]_0} + \overbrace{k_r}^{\text{slope}} \overbrace{t}^x$$



Second-Order Integrated Rate Laws

TABLE 7B.1 Integrated Rate Laws, Rate Law Plots, and Half-Lives

	Order of reaction		
	0	1	2
Rate law	Rate = k_r	Rate = $k_r[A]$	Rate = $k_r[A]^2$
Integrated rate law	$[A]_t = -k_r t + [A]_0$	$[A]_t = [A]_0 e^{-k_r t}$	$[A]_t = \frac{[A]_0}{1 + k_r t [A]_0}$ $\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_r t$
Plot to determine order			
Slope of the line plotted	$-k_r$	$-k_r$	k_r
Half-life	$t_{1/2} = \frac{[A]_0}{2k_r}$ <p>(not used)</p>	$t_{1/2} = \frac{\ln 2}{k_r} \approx \frac{0.693}{k_r}$	$t_{1/2} = \frac{1}{k_r [A]_0}$ <p>(not used)</p>