Kinetics

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Chemical Kinetics

Reaction Rates

Reaction rate is the change in the concentration of a reactant or a product with time (*M*/s).

$$A \longrightarrow B$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

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Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$

- A plot of concentration vs. time for this reaction yields a curve like this.

- The slope of a line tangent to the curve at any point is the **instantaneous rate** at that time.

$$\frac{\Delta[A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

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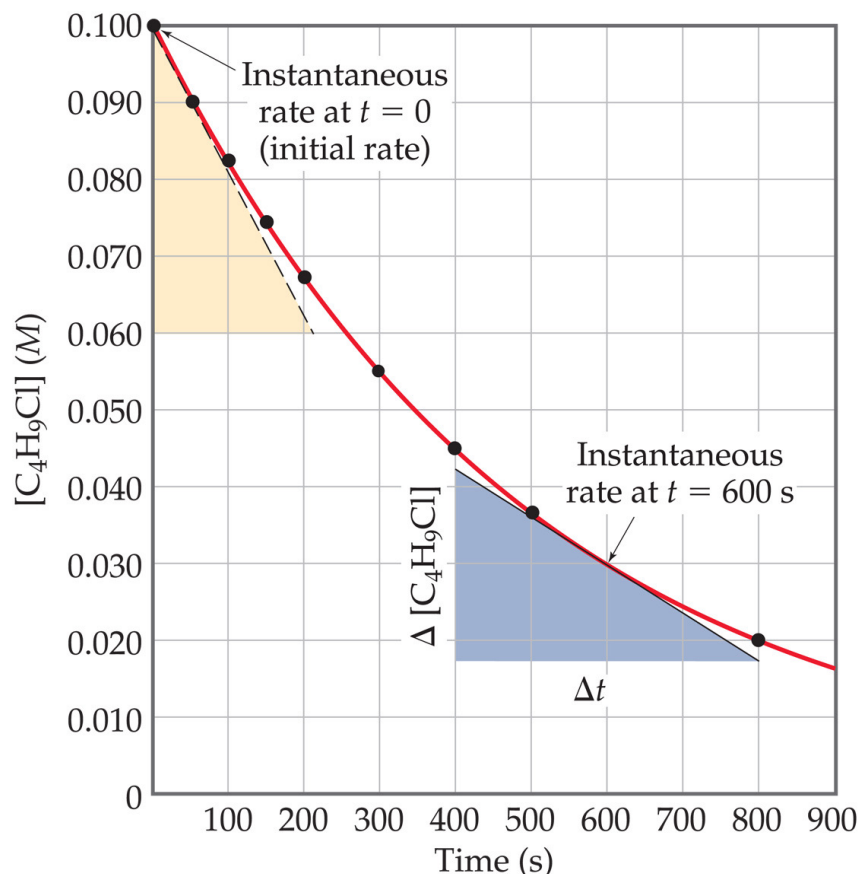
Reaction Rates and Stoichiometry

- To generalize, for the reaction

$$aA + bB \longrightarrow cC + dD$$

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

Reactants (decrease)   Products (increase)

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Rate in Terms of Concentration

Each reaction has its own equation that expresses its **rate as a function of the concentrations** of the involved species (e.g., reactants, products, catalysts).

This is called its **Rate Law**

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Rate Laws

- In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.

- The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.

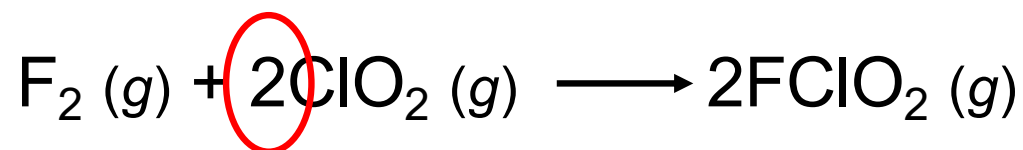- For reactions follow *simple rate laws*:

$$v = k\,[A]^m\,[B]^n\ldots$$

- [A], [B]: reactant concentrations

- The exponents m and n: **reaction order** (w.r.t. specific reactant)

- The constant k: **rate constant**

- The **overall reaction order** is the sum of the reaction orders:
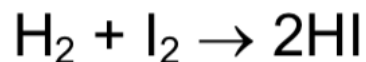
$$m + n$$

Determination of Rate Laws

- Rate laws, rate constants, and orders are **determined** *experimentally*.

- The order of a reactant is **NOT** generally related to its stoichiometric coefficient in a balanced chemical equation.

$$F_2 \ (g) + 2ClO_2 \ (g) \longrightarrow 2FClO_2 \ (g)$$

$$v = k \ [F_2][ClO_2]^1$$

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Expression of Rate Laws

Reactions with **simple rate laws**:

$$H_2 + I_2 \rightarrow 2HI \qquad\qquad v = k\,[H_2][I_2].$$

$$3ClO^- \rightarrow ClO_3^- + 2Cl^- \qquad\qquad v = k\,[ClO^-]^2$$

Reactions with **complex rate laws***:
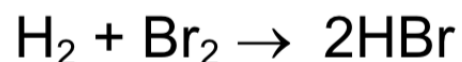
$$H_2 + Br_2 \rightarrow 2HBr \qquad\qquad v = \frac{[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$

* imply multi-step reactions (sequence of elementary steps)

$$Br_2 \rightarrow Br + Br$$
$$Br + H_2 \rightarrow H + HBr$$
$$H + Br_2 \rightarrow Br + HBr$$
$$Br + Br \rightarrow Br_2$$
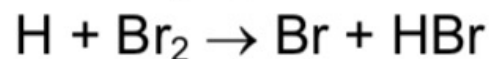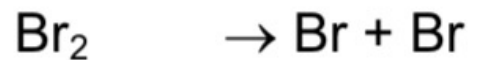
however, the overall rate cannot involve intermediate species

Reaction Kinetics (Vallance)

Elementary Reactions

Always follow simple rate laws

Unimolecular decomposition	$A \rightarrow B$	$v = k\,[A]$
Bimolecular reaction	$A + B \rightarrow P$	$v = k\,[A][B]$
	$A + A \rightarrow P$	$v = k\,[A][A] = k\,[A]^2$
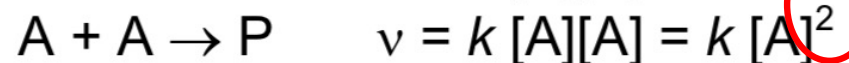
Reactant **order** reflects **molecularity** (# of molecules involved in reaction)

Elementary Reactions

• The **reaction mechanism** gives the path of the reaction.

• The stoichiometry **can** be used to determine the rate law!

• The **molecularity** of a process tells how many molecules are involved in the process.

• **Law of Mass Action**: The rate of a **simple (one step) reaction** is directly proportional to the concentration of the reacting substances.

TABLE 14.3	Elementary Steps and Their Rate Laws	
Molecularity	**Elementary Step**	**Rate Law**
*Uni*molecular	A $\longrightarrow$ products	Rate = $k[A]$
*Bi*molecular	A + A $\longrightarrow$ products	Rate = $k[A]^2$
*Bi*molecular	A + B $\longrightarrow$ products	Rate = $k[A][B]$
*Ter*molecular	A + A + A $\longrightarrow$ products	Rate = $k[A]^3$
*Ter*molecular	A + A + B $\longrightarrow$ products	Rate = $k[A]^2[B]$
*Ter*molecular	A + B + C $\longrightarrow$ products	Rate = $k[A][B][C]$

Integrated Rate Laws

Goal: express concentration as a function of time
Why: fit to the form of typical experimental data
How: integrate the expression of rate law

Reaction	Order	Differential form	Integrated form
$A \xrightarrow{k} P$	zeroth	$\dfrac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \xrightarrow{k} P$	first	$\dfrac{d[A]}{dt} = -k\,[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \xrightarrow{k} P$	second	$\dfrac{1\,d[A]}{2\,dt} = -k\,[A]^2$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + 2kt$
$A + B \xrightarrow{k} P$	second	$\dfrac{d[A]}{dt} = -k\,[A][B]$	$kt = \dfrac{1}{[B]_0 - [A]_0} \ln \dfrac{[B]_0[A]}{[A]_0[B]}$

differential rate
expression

integrated rate
expression

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Order of Reaction

- A reaction is 0th order in a reactant if the change in concentration of that reactant produces <u>no effect</u>.

- A reaction is 1st order if <u>doubling</u> the concentration causes the rate to <u>double.</u>

- A reaction is 2nd order if <u>doubling</u> the concentration causes a <u>quadruple</u> increase in rate.

  − 3rd order…doubling concentration leads to 2^3 (or 8 times) the rate.
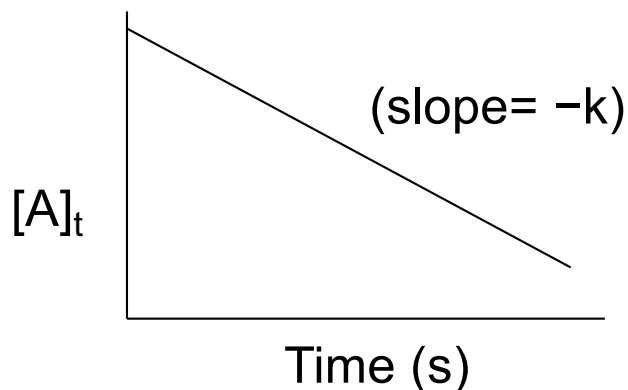
  - extremely rare.

Zero-Order Reaction

$$A \rightarrow P \qquad \text{zeroth} \qquad \frac{d[A]}{dt} = -k$$

$$\text{reaction rate} = -\frac{\Delta[A]_t}{\Delta t} = k \textbf{ (constant)}$$

Integrated rate law: $[A]_t = -kt + [A]_0$

• This equation has the general form for a straight line, y=mx+b, so a plot of **$[A]_t$** vs. t is a straight line with slope (-k) and intercept $[A]_0$.

(slope= −k)

$[A]_t$

Time (s)

First-Order Reaction

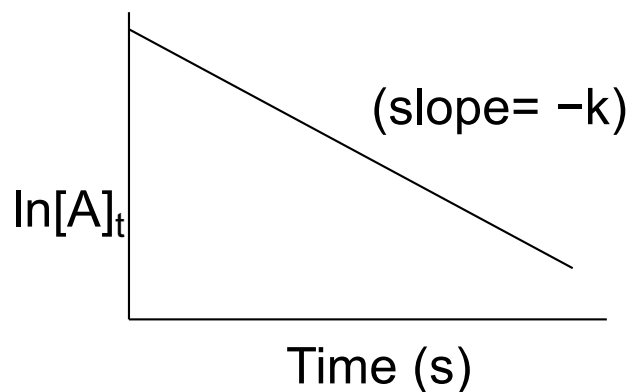Integrated rate law: $\ln[A]_t = -kt + \ln[A]_0$

where $[A]_t$ = concentration of [A] after some time, t

k = reaction rate constant in units of s^{-1}

t = time in seconds

$[A]_o$ = initial concentration of A

- This equation has the general form for a straight line, y=mx+b, so a plot of **ln[A]$_t$** vs. t is a straight line with slope (-k) and intercept $\ln[A]_0$.

$\ln[A]_t$ (slope= −k)

Time (s)

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Second-Order Reaction
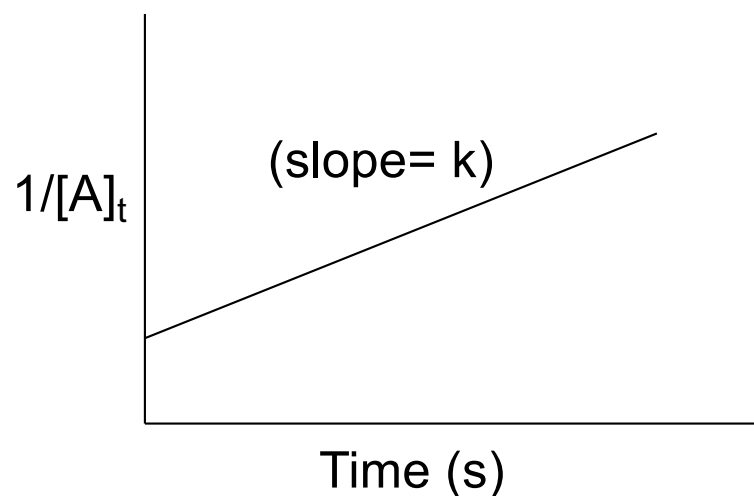
Integrated rate law: $1/[A]_t = kt + 1/[A]_0$

where $[A]_t$ = concentration of [A] after some time, t
k = reaction rate constant in units of $M^{-1}s^{-1}$
t = time in seconds
$[A]_o$ = initial concentration of A

- This equation has the general form for a straight line, y=mx+b, so a plot of **1/[A]$_t$** vs. t is a straight line with slope (k) and intercept of $1/[A]_0$.

1/[A]$_t$ (slope= k)

Time (s)
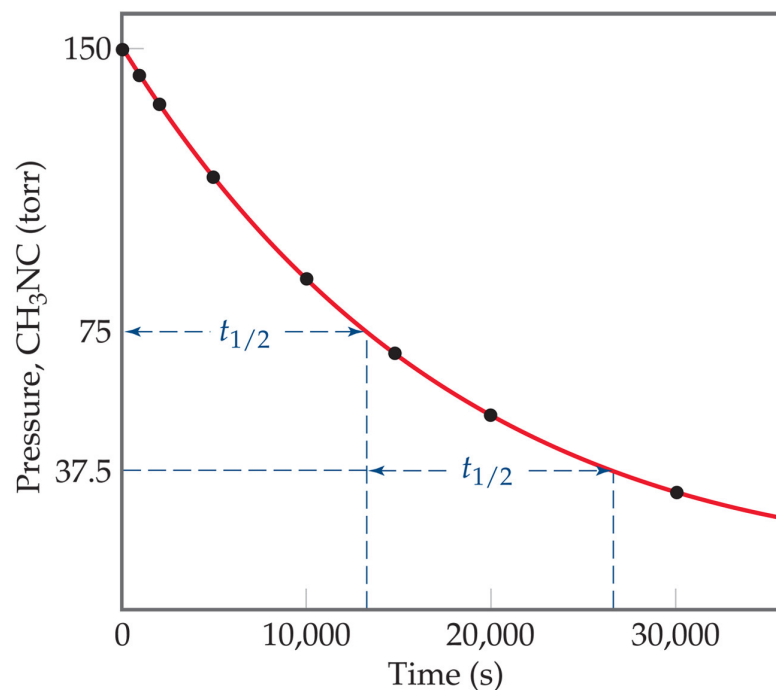
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Reaction Half-Life

- **Half-life** is the time taken for the concentration of a reactant to drop to half its original value.
- Substitute into integrated rate laws: $t_{1/2}$ is the time taken for [A] to reach $\frac{1}{2}[A]_0$

Zeroth order reaction $\quad t_{1/2} = \dfrac{[A]_0}{2k}$
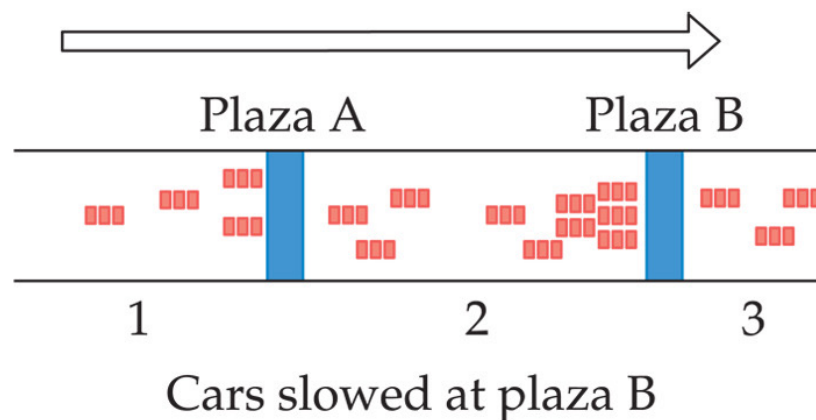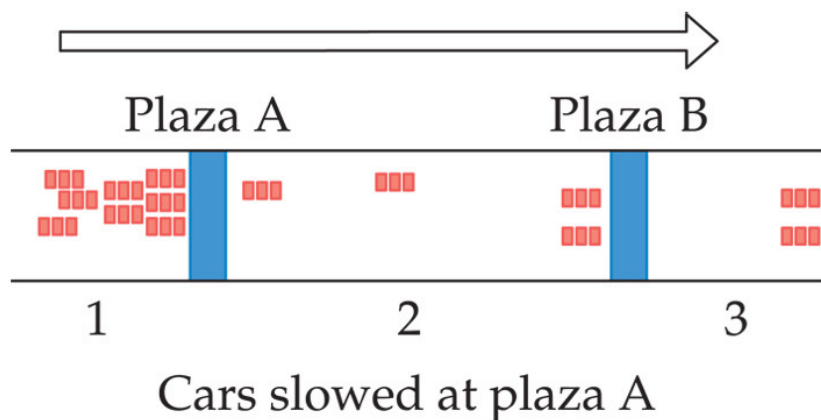
First order reaction $\quad t_{1/2} = \dfrac{\ln 2}{k}$

Second order reaction $\quad t_{1/2} = \dfrac{1}{k[A]_0}$

NOTE: For a first-order process, the half-life does not depend on $[A]_0$.

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Multi-Step Process

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.

Cars slowed at plaza A

Cars slowed at plaza B

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Activation Energy

The minimum amount of energy required to initiate a reaction:

Activation energy (*E_a*)

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