rate = \frac{dA}{dt} = -kA \quad \text{(rate of change in A is proportional to A)} \quad \text{(A is ANYTHING)}

rate = \frac{dA}{A} = -kdt \quad \text{(fractional change is directly proportional to time)}

How much do we have after time passes?
What is the SUM of FRACTIONAL changes???

\int \frac{dN}{N} = \pm k \int dt

\ln \left( \frac{N_2}{N_1} \right) = \pm k(t_2 - t_1)

or, what is the same thing:

\frac{N(t_2)}{N(t_1)} = f = e^{\pm k(t_2 - t_1)}

The first order mantra:

\frac{N(t_2)}{N(t_1)} = f = e^{\pm k(t_2 - t_1)}

Given any 2 of k, t, or f, find the 3rd
\( t_f = \frac{-\ln(f)}{k} = \text{time for } A_{t_2}/A_{t_1} \text{ to } = f \)

**half life:** \( f = 0.5 = \exp(-kt_{1/2}) \)

\[ \ln(0.5) = -kt_{1/2} \]

\[-\ln(0.5)/k = t_{1/2} \]

**exponential increase instead of decrease**

\[ \frac{dA}{dt} = +kA \text{ gives } \frac{A(t_2)}{A(t_1)} = f = e^{k(t_2 - t_1)} \]

**Doubling time**

\( f = 2 \)

\[ t_{\text{double}} = \ln(2)/k = -\ln0.5/k = t_{1/2} \text{ (same number)} \]
f can be anything e.g., 0.123456 but even more popular than ½ is

\( f = \frac{1}{e} \)

\( \tau = -\ln(\frac{1}{e})/k = \ln(e)/k = 1/k \)

Called “lifetime”, “time constant” ...

\[
\frac{dN}{dt} = -kN \quad \text{gives} \quad \frac{N(t_2)}{N(t_1)} = f = e^{-k(t_2 - t_1)} = e^{-\frac{(t_2-t_1)}{\tau}}
\]
The exact same math is used to calculate growth of living objects, e.g., humans, decline of populations, growth and decay of bank accounts and investments, etc.

And: the meaning of sedimentation coefficient

\[ \text{mass} \times \text{acceleration} = \text{Force} = \text{speed} \times \text{frictional coef.} \]
\[ \text{mass} \times \frac{du}{dt} = -uf \]
\[ \frac{du}{dt} = -(\text{frictional coef/mass})u = -\frac{u}{s} \]

\[ u = u_0 e^{-t/s} \]
\[ A + B \rightarrow C \]

If first order: \[ \ln[A](t) = -kt + \ln[A]_0 \]

\[ \text{Slope} = -k \ (s^{-1}) \]

If second order & rate = \[ k[A]^2 \]

\[ \ln[A] \]

\[ \text{Not straight line.} \]

Units of \( k \) = \?

\[ \frac{1}{6} \text{ rate } = k[A][B] \] and \[ [B] \gg [A] \] then what will not \( \text{ln}[A] \) vs \( t \) look like? (pseudo first order)
A rate law **CANNOT** be deduced from a STOICHIOMETRIC Equation. This is *abundantly* clear from the table below.

### TABLE 9.1 Rate Laws and Kinetic Order for Some Reactions

<table>
<thead>
<tr>
<th>Stoichiometric reaction</th>
<th>Rate law</th>
<th>Kinetic order</th>
</tr>
</thead>
<tbody>
<tr>
<td>sucrose + H₂O $\rightarrow$ fructose + glucose</td>
<td>$v = k[\text{sucrose}]$</td>
<td>1</td>
</tr>
<tr>
<td>L-isoleucine $\rightarrow$ D-isoleucine</td>
<td>$v = k[\text{L-isoleucine}]$</td>
<td>1</td>
</tr>
<tr>
<td>$^{14}\text{C} \rightarrow 14\text{N} + \beta^-$</td>
<td>$v = k[^{14}\text{C}]$</td>
<td>1</td>
</tr>
<tr>
<td>2 proflavin $\rightarrow$ proflavin dimer</td>
<td>$v = k[\text{proflavin}]^2$</td>
<td>2</td>
</tr>
<tr>
<td>$p$-nitrophenylacetate + 2 OH$^- \rightarrow$</td>
<td>$v = k[\text{p-nitrophenylacetate}][\text{OH}^-]$</td>
<td>2 (overall)</td>
</tr>
<tr>
<td>$p$-nitrophenolate + acetate + H₂O (pH 9)</td>
<td>$v = k[\text{Hb}\cdot 3\text{O}_2][\text{O}_2]$</td>
<td>2 (overall)</td>
</tr>
<tr>
<td>hemoglobin·3O₂ + O₂ $\rightarrow$ hemoglobin·4O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ + I₂ $\rightarrow$ 2 HI</td>
<td>$v = k[H_2][I_2]$</td>
<td>2 (overall)</td>
</tr>
<tr>
<td>H₂ + Br₂ $\rightarrow$ 2 HBr</td>
<td>$v = k[H_2][Br_2]^{1/2}$</td>
<td>Complex</td>
</tr>
<tr>
<td>$v = \frac{k[H_2][Br_2]^{1/2}}{k' + [HBr]/[Br_2]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CHO $\rightarrow$ CH₄ + CO</td>
<td>$v \approx [\text{CH}_3\text{CHO}]^{3/2}$</td>
<td>3/2 (approx.)</td>
</tr>
<tr>
<td>C₂H₅OH $\rightarrow$ CH₃CHO (liver enzymes)</td>
<td>$v$ constant</td>
<td>0</td>
</tr>
</tbody>
</table>
**Mechanism:** a set of hypothetical elementary reactions that are microscopic descriptions of supposed events. *(might)* Mechanism may be correct if it predicts the observed rate law (or might be wrong.)

→ 3 Types only:

1. **Unimolecular**
   \[ \text{O}_2 + \text{N}_2 \rightarrow \text{O}_2 \cdot \text{N}_2 \cdot \text{C} \]

2. **Bimolecular**
   \[ \text{H}_2 + \text{I}_2 \rightarrow \text{ZHI} \]

3. **Ter molecular**
   \[ 2\text{I} + \text{H}_2 \rightarrow \text{ZHI} \]

**Molecularity does imply order**

**Unimolecular step** is **1st order** \[ K[\text{O}_2 \cdot \text{N}_2 \cdot \text{C}] \]

**Bimolecular**

" " **2nd**

\[ K[\text{H}_2][\text{I}_2] \]

**Ter molecular**

" " **3rd**

\[ K[\text{I}]^2[\text{H}_2] \]

**Sum of steps must = stoichiometric eq.**

Steps → predicted rate law

**Stoichiometric chemical eq. says nothing about the rate law**

But, experimentally, observed order does not imply molecularity

At high temperature, experiments show I atoms exist and rate given by this
Find Rate Law (overall) from Mechanism:

- The Rate Determining Step (RDS)

Slowest Step & the Bottleneck

Be able to "find" rate law given a two-step mechanism & which step is RDS.

Guiding Principle: Rate Law = That from RDS

* But must not contain any hypothetical transient species
EXAMPLE: STOICHI.: \[ A + 2B \rightarrow C \] overall balanced reaction

MECH: 1) \[ A + B \xrightarrow{K_1} D \xleftarrow{K_{-1}} \] proposed reactive intermediate

2) \[ D + B \xrightarrow{K_2} C \]

Sum \[ D + A + 2B \rightarrow C + D \]

- IF 1st step is RDS, RATE = \( K_1[A][B] \)
- IF 2nd step is RDS, RATE = \( K_2[B][D] \)

must reexpress \([D]\) by saying Step (1) reaches EQUILIBRIUM

BACK RATE = FORWARD RATE \( K_{-1[D]} = K_1[A][B] \)

\([D] = \frac{K_1[A][B]}{K_{-1}}\)

\( \text{RATE} = \frac{K_2[B]}{K_{-1}} \frac{K_1[A][B]}{K_{-1}} = \frac{K_2K_1[A][B]^2}{K_{-1}} \)
Microscopic Reversibility

MUST ACCOUNT FOR REVERSE OF ALL PROPOSED PROCESSES

At equilibrium: Forward rate = Backward rate
For any pair

NEVER
A \rightarrow B
C \rightarrow D

implies that\ G_A > G_B > G_C > G_A

But \Delta G = 0 for cyclic process.

Consider: C \xrightarrow{K} A

IF BOTH ARE 1st order:
Forward rate = K[C]
Back rate = K'[A]

AT EQUIL: K[C] = K'[A]
K_{eq} = \left(\frac{K[C]}{[A]}\right)_{eq} = \frac{K}{K'}

Perpetual Motion!
What about really fast, violent reactions, i.e., **EXPLOSIONS**?

Chain reaction mechanism (typical of explosions):
Arrhenius: Explanation of why most reactions have rate increase as temp. increases.

Example: $\text{O-C-N} \rightarrow \text{O-N-C}$

[Diagram showing the reaction coordinate, activation energy, and activated complex with labels: $E_a$, $\Delta H_{\text{reaction}}$, OCN (reactant), and ONC (product).]
Arrhenius was a student of Boltzmann

Arrhenius: rate constant $K = A \exp \left( \frac{-E_a}{RT} \right)$

$\ln \frac{K_2}{K_1} = -\frac{E_a}{RT} \left( \frac{T_2}{T_1} \right)$

Exactly the form as Van’t Hoff when applied to equilibrium constants!

RULE OF THUMB: $10^\circ C$ doubles rate

What is $E_a$?

$\ln 2 = -\frac{E_a}{R} \left( \frac{1}{310} - \frac{1}{300} \right)$

$E_a = \frac{-R \ln 2}{310^{-1} - 300^{-1}} = \frac{8.3145 \times 0.693}{-1.075 \times 10^{-4}} \approx 52,500 \frac{J}{mol}$