I. Experimental Kinetic Data:
- concentration vs. time – c(t)
- concentration vs. rate – ∆[A]/∆t (rate laws)
- rate vs. time – initial, intermediate, final (equilibrium)

II. Rate law for \( a \, A + b \, B \rightarrow c \, C + d \, D \)
- in general
  - forward rate = \( k_f [A]^i [B]^j [\text{cat.}]^k \)
  - backward rate = \( k_b [C]^n [D]^m [\text{cat.}]^p \)
  - reaction rate = forward rate – backward rate
  - initial rate = \( k_f [A]^i [B]^j [\text{cat.}]^k \) (since [cat.] = constant for a good catalyst)

III. Determination of Rate Laws using either c(t), rate(t), or rate(c):
\[2 \, \text{ICl}_2(g) + \text{H}_2(g) \rightarrow I_2(g) + 2 \, \text{HCl}(g)\]

<table>
<thead>
<tr>
<th>Time, s</th>
<th>[H(_2)], M</th>
<th>Rate = (\Delta[H_2]/\Delta t), M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000</td>
<td>0.326</td>
</tr>
<tr>
<td>1</td>
<td>0.674</td>
<td>0.148</td>
</tr>
<tr>
<td>2</td>
<td>0.526</td>
<td>0.090</td>
</tr>
<tr>
<td>3</td>
<td>0.436</td>
<td>0.062</td>
</tr>
<tr>
<td>4</td>
<td>0.374</td>
<td>0.046</td>
</tr>
<tr>
<td>5</td>
<td>0.328</td>
<td></td>
</tr>
</tbody>
</table>

1. determining the order of the kinetics:
\[
\text{rate at } t=1 \text{ s} = \frac{k \cdot ([H_2]_0)^n}{[H_2]_0} = 0.326 \quad \text{rate at } t=5 \text{ s} = \frac{k \cdot ([H_2]_0)^n}{[H_2]_0} = 0.374 \quad \Rightarrow n = 1.984
\]
(simple logic: consider rate(c) function, half the concentration = half the rate \(\Rightarrow 1^{\text{st}}\) order kinetics)

2. determining the rate constant (k): use any of the measured points and substitute [H\(_2\)] and rate \(\Rightarrow 0.326 \text{ M/s}\)

3. The above procedure in general using the methods of initial rates
  - consider: \( a \, A + b \, B \rightarrow .... \)
  - focus only on the initial rates (maximal rates):
    \[\ln \left( \frac{\text{rate } x}{\text{rate } y} \right) = i \cdot \ln \left( \frac{[A(x)]_0}{[A(y)]_0} \right) + j \cdot \ln \left( \frac{[B(x)]_0}{[B(y)]_0} \right)\]
  - need at least three experiments:
    1. arbitrary A(x), B(x) \(\rightarrow\) define initial rate x (reference)
    2. A(x) = A(y) \(\rightarrow\) obtain j from initial rate y
    3. B(x) = B(y') \(\rightarrow\) obtain i from initial rate y'
(please take the time and resolve the worked out exercises in the book \textit{without using the book!})
IV. Integrated rate law:

We would like to know the actual concentration at any given time (recall plots from last lecture).

- **1st order dissociation of a** $A \rightarrow ...$

  \[
  \frac{\Delta [A]}{\Delta t} = k \cdot [A] \\
  \text{consider very small } \Delta t\text{-s} \Rightarrow \quad \frac{d[A]}{dt} = k \cdot [A] \quad \rightarrow [A](t) = \text{constant } e^t
  \]

  
  \[ [A] = [A]_0 \cdot e^{kt} \text{ with the boundary condition of } t=0 \; [A] = [A]_0 \Rightarrow \ln [A] = -kt + \ln [A]_0 \]

  - experimental plots of $\ln [A]$ vs. time: slope = $-k$; intercept = $\ln [A]_0$ (nice quick test)
  - how much has already reacted? $\Rightarrow \quad \ln \frac{[A]_0}{[A]} = k \cdot t \; \text{half-life } t_{1/2} = \ln 2 / k$ (not depend on $[A]_0$)

- **2nd order reaction of a single reactant (NO disproportionation):**

  \[
  \frac{\Delta [A]}{\Delta t} = k \cdot [A]^2 \Rightarrow \ldots \quad \frac{1}{[A]} = kt + \frac{1}{[A]_0}
  \]

  - experimental plots of $\frac{1}{[A]}$ vs. time: slope = $k$; intercept = $\frac{1}{[A]_0}$
  - how much has already reacted? $\Rightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = k \cdot t \; \text{half-life } t_{1/2} = \frac{1}{k \cdot [A]_0}$ (depends on $[A]_0$)

- **0th order reaction of a single reactant (enzyme, heterogeneous catalysis – reaction is limited by diffusion):**

  \[
  \frac{\Delta [A]}{\Delta t} = k \Rightarrow \ldots \quad [A] = -kt + [A]_0
  \]

  - experimental plots of $[A]$ vs. time: slope = $-k$; intercept = $[A]_0$
  - how much has already reacted? $\Rightarrow \quad [A] - [A]_0 = k \cdot t \; \text{half-life } t_{1/2} = [A]_0 / 2k$ (depends on $[A]_0$)