Lecture # 11.2 CHE331A

- Basics of reactions and ideal reactors
- Design/Analysis of CSTRs, PFRs, PBRs, Batch and Semi-batch in terms of conversions and molar flow rates or concentrations
- Collection and Analysis of Rate Data – Other methods and differential reactors

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Non-linear Regression

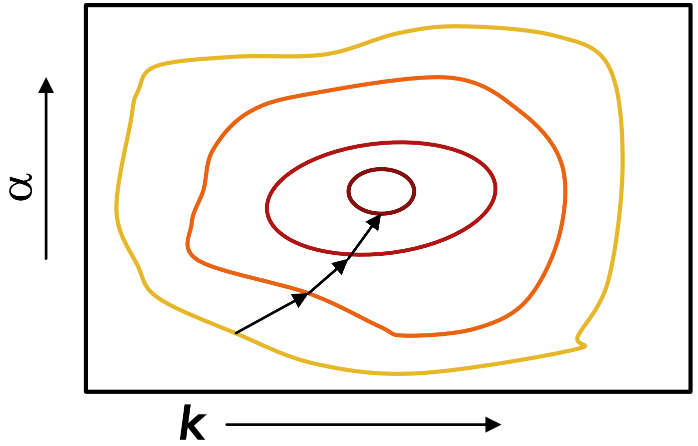
$$-r_A = k.C_A^{\alpha}$$

$$\boldsymbol{\sigma^2 = \frac{s^2}{N-K} = \sum_{i=1}^{N} \frac{(y_{im} - y_{ic})^2}{N-K}}$$

$$\sigma^2 = \sum_{i=1}^{10} \frac{(C_{A,im} - C_{A,ic})^2}{10-2}$$

$$\sigma^2 = \sum_{i=1}^{10} \frac{(t_{im} - t_{ic})^2}{10-2}$$

Finding the best value of α and *k*



Other methods to determine rate law parameters: Method of Initial Rates

- **Method of Initial Rates**: rates are determined by using initial conc
  - Useful for reversible reactions $A \leftrightharpoons B$ $\qquad -r_A = k_A C_A^{\alpha} - k_B C_B^{\beta}$
- Several reactions are carried out with different C_{A0} and with $C_{B0} = 0$, $-r_{A0}$ is determined, e.g., by numerical differentiation
  - Use plot of $ln(-r_{A0})\ vs\ \ ln(C_{A0})$ to determine order with respect to A
- Similarly, reactions are carried out with different C_{B0} and with $C_{A0} = 0$, $-r_{B0}$ is determined , e.g., by numerical differentiation
  - Use plot of $ln(-r_{B0})\ vs\ \ ln(C_{B0})$ to determine order with respect to B

Other methods to determine rate law parameters: Methods of Half-Lives

- **Method of Half-Lives**: Half-life of a reaction is defined as the time taken to reduce the conc of the reactant to half of its initial value
  - Used for irreversible reactions $A \rightarrow Products$ $-r_A = k_A C_A^{\alpha}$
- Combining the mole balance with stoichiometry $\frac{dC_A}{dt} = r_A = -k.C_A^{\alpha}$
- Integrating with known initial conditions: $t = \frac{1}{k(\alpha-1)}\left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}}\right)$
- $t = \frac{1}{k(\alpha-1)C_{A0}^{\alpha-1}}\left[\left(\frac{C_{A0}}{C_A}\right)^{\alpha-1} - 1\right]$ and with $C_A = 0.5C_{A0}$ $at\ t = t_{1/2}$

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(\alpha-1)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right)$$

Methods of Half-Lives continued

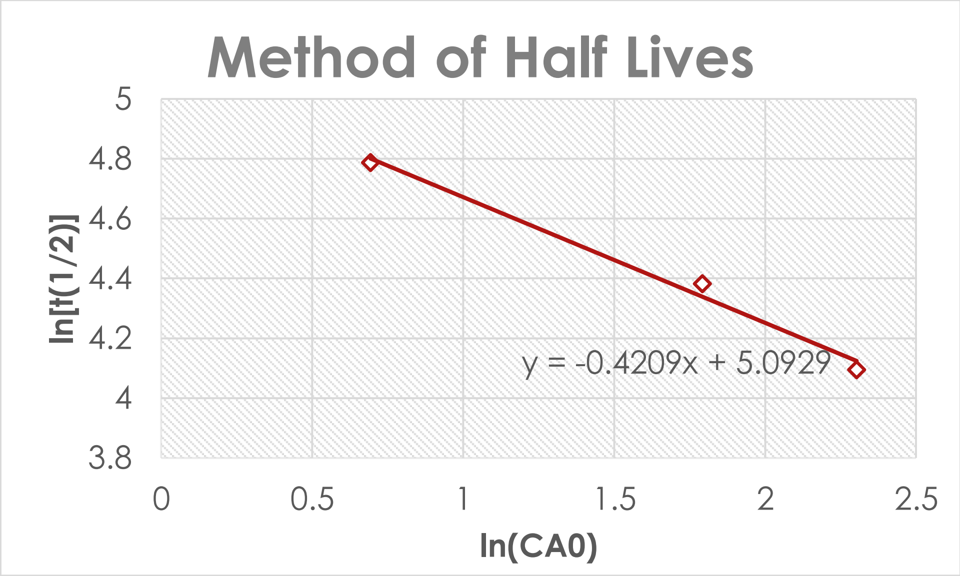
- $t_{1/2} = \frac{2^{\alpha-1}-1}{k(\alpha-1)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right)$ using several C_{A0} $then$ $t_{1/2}$ can be measured
- Plot $ln\left(t_{1/2}\right)$ vs $ln(C_{A0})$ and $slope = 1 - \alpha$

  Slope = -0.42, $\alpha = 1.42$

  Choosing C_{A0} at $t_{1/2}$

  $$k = \frac{2^{1.42-1}-1}{t_{1/2}(1.12-1)}\left(\frac{1}{C_{A0}^{1.42-1}}\right)$$

CA0	t(1/2), s
10	60
6	80
2	120



- In general, the time required for the concentration to drop to 1/n of the initial value, i.e., $C_A = \frac{1}{n}C_{A0}$ at $t = t_{1/n}$

$$t_{1/n} = \frac{n^{\alpha-1}-1}{k(\alpha-1)}\left(\frac{1}{C_{A0}^{\alpha-1}}\right)$$