Lecture # 11.1 CHE331A

- Basics of reactions and ideal reactors
- Design/Analysis of CSTRs, PFRs, PBRs, Batch and Semi-batch reactors
- Collection and Analysis of Rate Data
- Non-linear regression and other methods of rate data analysis

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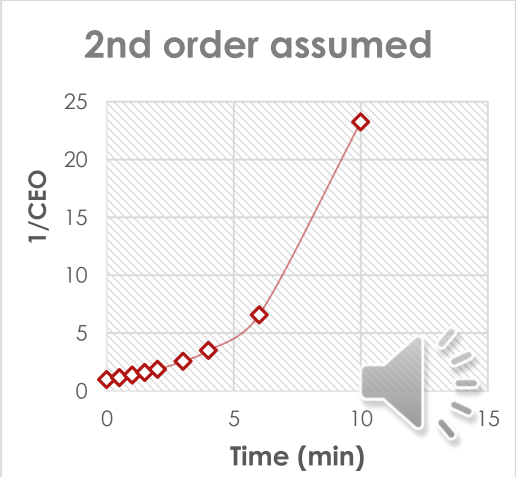
Differential method

Given C_A vs t, methods to determine $\frac{dC_A}{dt}$ are:

- Graphical differentiation
- Numerical differentiation
- Differentiation of a polynomial fit

Integral Method



Nonlinear regression involves search for parameters that minimize “errors”

- Minimize the sum of the square of difference between measured values and estimated values
  - Determines the best parameter values by “searching” different values – this usually required an initial guess obtained by linear regression
  - Also used to discriminate rate law models, → heterogeneous catalysis
- For example, we want to find $k\ and\ \alpha$ from set of rate data
- Minimize the difference between measured reaction rates, r_m, and the reaction rates calculated, r_c, based on “search” values → $(r_m - r_c)^2$
- Based on the initial value the best value $k\ and\ \alpha$ is obtained by following some search technique

The function to be minimized also depends on the number of experiments and parameters

- (Objective) Function to be minimized given by:

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

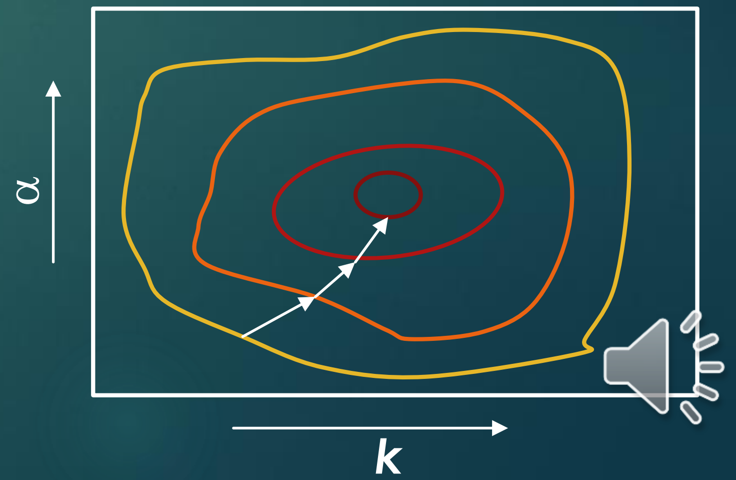
- N = number of runs K = number of parameters to be determined
- r_{im} = measured reaction rate r_{ic} = calculated reaction rate for run *i*
- $EO + H_2O \rightarrow EG$ measured 10 C_{EG} values (N=10) → 10 values of $r_{EG,m}$
- For a specific $k\ and\ \alpha$ (K = 2), we have 10 values of $r_{EG,c} (= k'_{EO} C_{EO}^{\alpha})$

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

Calculations for the objective function

time (min)	Rate, meas.	Rate, calcu (k=0.5, α = 1)	sigma^2	Rate, calcu (k=0.5, α = 2)	sigma^2	Rate, calcu (k=0.31, α = 2)	sigma^2	Rate, calcu (k=0.31, α = 1)	sigma^2
0	**0.31**	0.50000	0.00451	0.50000	0.00451	0.31000	0.00000	0.31000	0.00000
0.5	**0.27**	0.42750	0.00310	0.36551	0.00114	0.22662	0.00024	0.26505	0.00000
1	**0.231**	0.36500	0.00224	0.26645	0.00016	0.16520	0.00054	0.22630	0.00000
1.5	**0.197**	0.31200	0.00165	0.19469	0.00000	0.12071	0.00073	0.19344	0.00000
2	**0.234**	0.26650	0.00013	0.14204	0.00106	0.08807	0.00266	0.16523	0.00059
3	**0.248**	0.19500	0.00035	0.07605	0.00370	0.04715	0.00504	0.12090	0.00202
4	**0.238**	0.14250	0.00114	0.04061	0.00487	0.02518	0.00566	0.08835	0.00280
6	**0.242**	0.07600	0.00344	0.01155	0.00664	0.00716	0.00689	0.04712	0.00475
10	**0.194**	0.02150	0.00372	0.00092	0.00466	0.00057	0.00468	0.01333	0.00408
Date Measured		total =	**0.02030**		**0.02673**		**0.02644**		**0.01424**

- Parameter values are found by minimizing σ^2 using some optimization technique (MatLab/PolyMath/Mathematica)



The objective function can be also in terms of concentration vs. time data

- Combined mol balance-stoichiometry for constant volume Batch Reactor: $\frac{dC_A}{dt} = -k.C_A^{\alpha}$ and for $\alpha \neq 1$ by integrating

$$C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)k.t \quad \rightarrow \quad C_A = [C_{A0}^{1-\alpha} - (1-\alpha)k.t]^{1/_{1-\alpha}}$$

- For 10 runs, where C_A *vs. time* is measured and 2 parameters

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

- Time, instead of conc is used then

$$\sigma^2 = \sum_{i=1}^{10} \frac{(t_{im} - t_{ic})^2}{10-2} \ where\ t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{(1-\alpha)k}$$

Example 5-3 as a reading assignment