

Chapter 5

Collection & Analysis of Rate Data

There are some basic steps in Analysis of Rate Data

1. Postulate a rate law:

a) Power law model for homogeneous rxns:

$$-r_A = k \cdot C_A^\alpha \cdot C_B^\beta$$

b) Langmuir – Hinshelwood for heterogeneous rxns:

$$-r_A' = \frac{k \cdot P_A \cdot P_B}{(1 + K_A \cdot P_A + P_B)^2}$$

2. Select reactor type; i.e.; Batch, CSTR, PFR, PBR.....

3. Process your data in term of measured variables (N_A , C_A or P_A)

4. Do simplifications (assumptions), if $-r_A = k C_A C_B$ and $C_A \gg C_B$
 $\rightarrow -r_A \approx k C_B$

5. For batch reactors, find reaction order

i. Find $(-dC_A / dt)$ from C_A vs t data.

Take \ln .

Find the order of rxn by $\ln (-dC_A / dt) = \ln k + \alpha \ln C_A$

Find the rate constant, k .

ii. Integral Form:

$$-\frac{dC_A}{dt} = k \cdot C_A^\alpha$$

Integrate

$$t = \frac{1}{k} [C_{A0}^{1-\alpha} \dots \dots \dots]$$

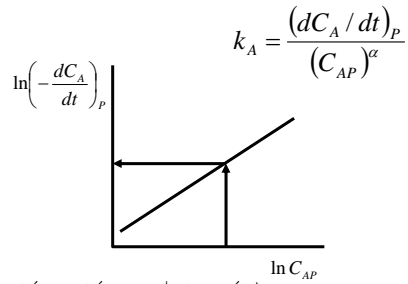
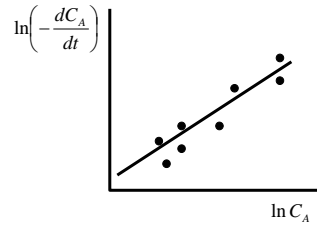
6. For PBR, find $-r_A'$ as a function of C_A or P_A .

SUMMARY

Differential Method:

$$-\frac{dC_A}{dt} = k_A \cdot C_A^\alpha \quad \ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + \alpha \ln C_A$$

slope = α



We should differentiate the concentration-time data either graphically or numerically.

1. Graphical differentiation
2. Numerical differentiation formula
3. Differentiation of a polynomial fit to the data.

1. Graphical

Tabulate (C_{Ai}, t_i) observations and for each interval calculate

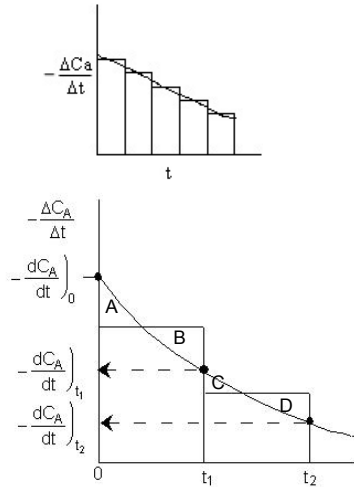
$$\Delta C_n = C_n - C_{n-1} \quad \Delta t_n = t_n - t_{n-1}$$

t_i	C_i	Δt	ΔC_A	$\Delta C_A / \Delta t$	(dC_A / dt)
t_0	C_0	$t_1 - t_0$	$C_1 - C_0$	$(\Delta C_A / \Delta t)_1$	$(dC_A / dt)_1$
t_1	C_1				
t_2	C_2	$t_2 - t_1$	$C_2 - C_1$	$(\Delta C_A / \Delta t)_2$	$(dC_A / dt)_2$
t_3	C_3	$t_3 - t_2$	$C_3 - C_2$	$(\Delta C_A / \Delta t)_3$	

Plot these values as a histogram

Draw a smooth curve

Read estimates of (dC_A/dt) at t_1, t_2, \dots



$$\Delta x = x_n - x_{n-1}$$

$$\Delta y = y_n - y_{n-1}$$

Plot these

$$y_n - y_1 = \sum_{i=2}^n \frac{\Delta y}{\Delta x_i} \cdot \Delta x_i$$

$$y_n - y_1 = \int_{x_1}^{x_n} \frac{dy}{dx} \cdot dx$$

Try to find

$$\text{Area(A)} \approx \text{Area(B)}$$

$$A + C \approx B + D$$

Numerical Methods

If the data points are equally spaced, i.e., $t_1 - t_0 = t_2 - t_1 = \Delta t$

time (min)	t_0	t_1	t_2
Conc'n (mol/dm ³)	C_{A0}	C_{A1}	C_{A2}

$$\text{For initial point } \left(\frac{dC_A}{dt} \right)_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$$

$$\text{interior point } \left(\frac{dC_A}{dt} \right)_{t_i} = \frac{1}{2\Delta t} [C_{A(i+1)} - C_{A(i-1)}]$$

$$\text{End point } \left(\frac{dC_A}{dt} \right)_{t_n} = \frac{1}{2\Delta t} [C_{A(n-2)} - 4C_{A(n-1)} + C_{A(n)}]$$

Polynomial fit:

Fit the conc'n – time data to an n^{th} order polynomial as:

$$C_A = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + \dots + a_n t^n$$

Find best values for $\{a_0, a_1, a_2, \dots, a_n\}$

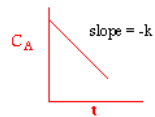
$$\frac{dC_A}{dt} = a_1 + 2a_2 t + 3a_3 t^2 + \dots + n a_n t^{n-1}$$

Integral Method

We first guess the rxn order and integrate the differential equation used to model the batch system. If the order is correct, the plot of conc'n time data should be linear.

This method is used when rxn order is known but E_A and k_A are unknown.

Zero Order, $\alpha = 0$

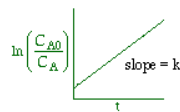


$$\frac{dC_A}{dt} = r_A = -k$$

$$\text{at } t = 0, C_A = C_{A0}$$

$$\Rightarrow C_A = C_{A0} - kt$$

First Order, $\alpha = 1$

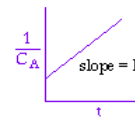


$$\frac{dC_A}{dt} = r_A = -kC_A$$

$$\text{at } t = 0, C_A = C_{A0}$$

$$\Rightarrow \ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

Second Order, $\alpha = 2$



$$\frac{dC_A}{dt} = r_A = -kC_A^2$$

$$\text{at } t = 0, C_A = C_{A0}$$

$$\Rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

Non – Linear Regression

Non – Linear Least-Square Analysis

We want to find the parameter values (alpha, k, E) for which the sum of the squares of the differences, the measured rate (r_m), and the calculated rate (r_c) is a minimum.

$$\sigma^2 = \sum_{i=1}^n \frac{(r_{mi} - r_{ci})^2}{N - K}$$

of parameters to be determined

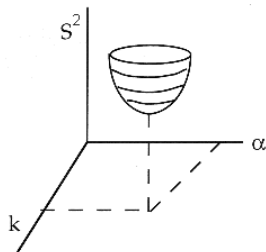
of runs

That is we want σ^2 to be a minimum.

For concentration-time data, we can integrate the mole balance equation for $-r_A = k C_A^{\alpha}$ to obtain

$$S^2 = \sum_{i=1}^N (C_{A_{mi}} - C_{A_{ci}})^2 = \sum_{i=1}^N \left(C_{A_{mi}} - \left[C_{A0}^{1-\alpha} - (1-\alpha)kt_i \right]^{1/1-\alpha} \right)^2$$

We find the values of alpha and k which minimize S^2



$$\frac{dC_A}{dt} = k \cdot C_A^\alpha$$

$$k \cdot dt = dC_A \cdot C_A^{-\alpha}$$

$$k \cdot t = \frac{1}{1-\alpha} C_A^{1-\alpha} + Const$$

$$Const = -\frac{C_{A0}^{1-\alpha}}{1-\alpha}$$

$$C_A = \sqrt[1-\alpha]{C_{A0}^{1-\alpha} - (1-\alpha)k \cdot t}$$

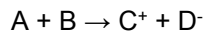
Vary α and k , obtain S^2 (or use a search technique)

$S(\alpha', k')$ is a minimum (optimization methods)

Concentration vs Time Equations for the proposed rate equations can be done by differential or integration method.

Ex.: Liquid phase rxn btw trimethylamine(A) and n-propyl bromide (B) was studied by Winkler & Hinshelwood. The results at 139.4°C are shown below. Initial sol'ns of A & B in benzene, 0.2 molal, were mixed and placed in constant temperature bath. After certain times, they were cooled to stop the rxn. Determine the first order and second order specificrates, k_1 and k_2 , assuming the rxn is irreversible. Use integration & differential methods.

Run	t, min	x (%)
1	13	11.2
2	34	25.7
3	59	36.7
4	120	55.2

Sol'n:

Volume is constant

$$1^{\text{st}} \text{ order} \quad -r_A = \frac{dC_A}{dt} = k_1 \cdot C_A$$

$$2^{\text{nd}} \text{ order} \quad -r_A = \frac{dC_A}{dt} = k_2 \cdot C_A \cdot C_B$$

Integration Method

1st order

$$-\ln \frac{C_A}{C_{A0}} = k_1 \cdot t \quad [1]$$

2nd order

Stoichiometric coefficients are equal and $C_{A0} = C_{B0} = 0.1$ molal

$$-\frac{dC_A}{dt} = k_2 \cdot C_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = k_2 \cdot t \quad [2]$$

$$x = \frac{C_{A0} - C_A}{C_{A0}} \quad C_A = C_{A0}(1 - x)$$

For the first run $C_A = 0.1 \cdot 0.888$

Substitute in [1]

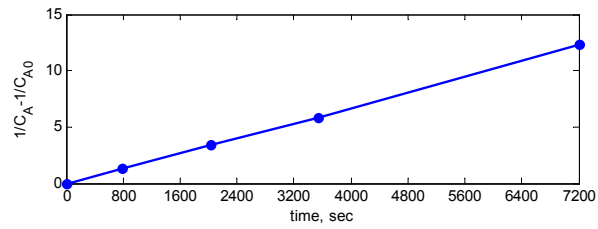
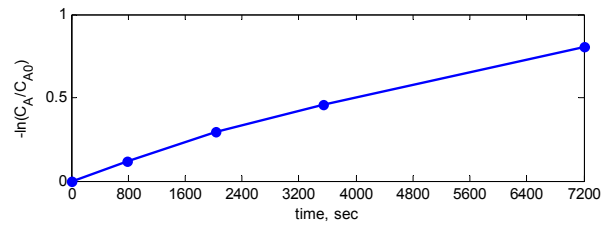
$$k_1 = \frac{1}{t} \cdot \ln \frac{C_{A0}}{C_A} = \frac{1}{13 \cdot 60} \ln \frac{0.1}{0.0888} = 1.54 \times 10^{-4} \text{ s}^{-1}$$

Substitute in [2]

$$k_2 = \frac{1}{t \cdot C_{A0}} \left(\frac{1}{1-x} - 1 \right) = \frac{0.112}{(13 \cdot 60) \cdot 0.1 \cdot (1 - 0.112)} = 1.63 \times 10^{-3} \frac{L}{\text{mol} \cdot \text{s}}$$

If you repeat for four of the runs:

Run	t, sec	$k_1 \times 10^{-4} (\text{s}^{-1})$	$k_2 \times 10^{-3} (\text{L/mol s})$	C_D
1	780	1.54	1.63	0.0112
2	2040	1.46	1.70	0.0257
3	3540	1.30	1.64	0.0367
4	7200	1.12	1.71	0.0552

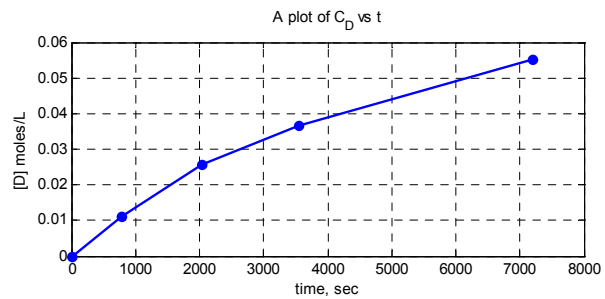


So, it is SECOND ORDER

Differential Method

$$C_D = C_{A0} - C_A \quad (\text{moles of D produced} = \text{moles of A reacted})$$

$$C_D = x C_{A0}$$



$$r = -\frac{dC_A}{dt} = \frac{dC_D}{dt} \quad (\text{the slope of the curve})$$

Slopes determined from the curve are given as follows

C_D	C_A	$r = dC_D/dt$ (10^5 gmol/L)
0.0	0.10	1.58
0.01	0.09	1.38
0.02	0.08	1.14
0.03	0.07	0.79
0.04	0.06	0.64
0.05	0.05	0.45

$$\log r_A = \log k_1 + \log C_A \quad (\text{from } -r_A = k_1 C_A)$$

$$\log r_A = \log k_2 + \log C_A^2 = \log k_2 + 2 \log C_A \quad (\text{from } -r_A = k_2 C_A^2)$$

1st: $\log r$ vs $\log C_A$ should yield a straight line with a slope of 1.0.

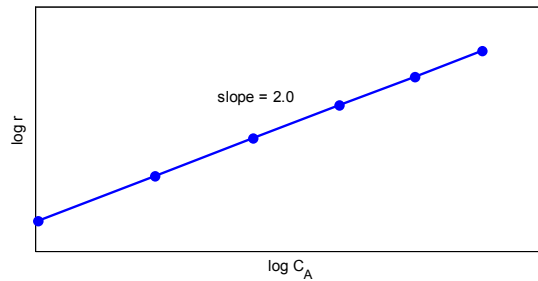
2nd: $\log r$ vs $\log C_A$ should yield a straight line with a slope of 2.0.

$$\log r = -2.76 + 2.0 \log C_A$$

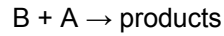
The data suggest a slope of 2!

$$\log k_2 = -2.76$$

$$k_2 = 1.73 \times 10^{-3} \text{ L / mol s}$$



Another Way (Batch Reactor Data)



$-r_A = k_A C_A^\alpha C_B^\beta$ if α and β are both unknown, the rxn could be run in an excess of B so that C_B remains essentially unchanged

$-r_A = k' C_A^\alpha$ where $k' = k_A C_B^\beta \approx k_A C_{B0}^\beta$

In determining α , the rxn is carried (excess of A)

$-r_A = k'' C_B^\beta$ where $k'' = k_A C_A^\alpha \approx k_A C_{A0}^\alpha$

Solving with search

$$S^2 = \sum_{i=1}^4 \left(C_{Am,i} - \left[C_{A0}^{1-\alpha} - (1-\alpha)k \cdot t_i \right]^{1/(1-\alpha)} \right)^2$$

t	C _D	C _A
780	0.0112	0.0888
2040	0.0257	0.0743
3540	0.0367	0.0633
7200	0.0552	0.0448

$$S^2 = \sum_{i=1}^n \left(C_{Am,i} - \text{abs} \left[C_{A0}^{1-\alpha} - (1-\alpha)k \cdot t_i \right]^{1/(1-\alpha)} \right)^2 \quad \text{fminsearch}$$

Method of Initial Rates

If there is a reverse rxn, it could render the differential method ineffective. In these cases, initial rates could be used for k & α .

Carry out a series of experiments with different C_{A0} .

Determine $-r_{A0}$ for each run.

$$-r_{A0} = k C_{A0}^\alpha \rightarrow \ln(-r_{A0}) \text{ vs } \ln(C_{A0})$$

Instead of doing at different time steps, repeat the rxn.

Method of Half Lives:

The half life of a rxn, $t_{1/2}$, is defined as the time it takes for the concentration of the reactant to fall to half of its initial value.

If you know $t_{1/2}$, find k & α .

If there are more than 1 reactant, use method of excess.

$$-r_A = k \cdot C_A^\alpha \quad (A \rightarrow \text{products})$$

$$-\frac{dC_A}{dt} = -r_A = k \cdot C_A^\alpha$$

$$@ t = 0 \quad C_A = C_{A0} \quad @ t = t_{1/2} \quad C_A = \frac{1}{2} C_{A0}$$

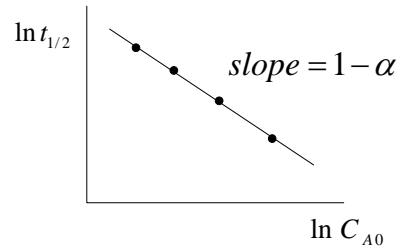
$$t = \frac{1}{k(\alpha-1)} \left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}} \right)$$

$$t = \frac{1}{k(\alpha-1)} \left(\left(\frac{C_{A0}}{C_A} \right)^{\alpha-1} - 1 \right)$$

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

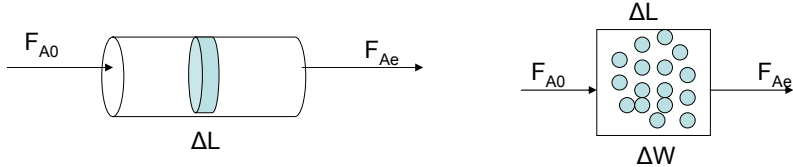
$$\text{Similarly} \quad t_{1/n} = \frac{n^{\alpha-1} - 1}{k(\alpha-1)} \left(\frac{1}{C_{A0}} \right)^{\alpha-1}$$

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



Differential Reactors

A differential reactor is used to determine the rate of a rxn as a function of either concentration or partial pressure



Conversion is very small in bed
 C_A is constant $\approx C_{A0}$ (gradientless)
 Rxn rate is uniform
 (almost isothermal)

Design Equation is similar to a CSTR:

$$F_{A0} - F_{Ae} + \frac{\text{Rate of rxn}}{\text{mass of cat}} (\text{mass of cat}) = 0$$

$$F_{A0} - F_{Ae} + r_A' \cdot \Delta w = 0$$

$$r_A' = \frac{F_{A0} - F_{Ae}}{\Delta w}$$

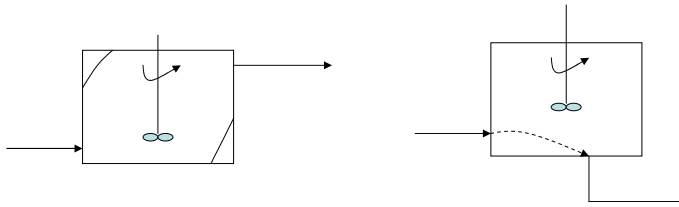
$$r_A' = \frac{v_0 C_{A0} - v \cdot C_{Ae}}{\Delta w} \quad (\text{in terms of conc'n})$$

$$r_A' = \frac{F_{A0} \cdot x}{\Delta w} = \frac{F_P}{\Delta w} \quad (\text{in terms of flow rate})$$

$$r_A' = \frac{v_0 (C_{A0} - C_{Ae})}{\Delta w} = \frac{v_0 (C_P)}{\Delta w}$$

Deviations from Ideal Reactors

When the mixing criteria of ideal reactors are not satisfied, mathematical expressions for the conservation equations become more difficult.



Deviations from ideal stirred – tank reactors

- a) Stagnant regions
- b) by – passing

Deviations from tubular-flow

- a) Longitudinal mixing due to vortices and turbulence
- b) Laminar flow (poor radial mixing)
- c) By-passing in fixed-bed catalytic reactor.

