

Chemical reaction engineering

Chapter 7: Collection and analysis of rate data

reactors
for rate
data

Common reactors for obtaining rate data

- Batch reactor: transient data
 - ⇒ Conc., temp., volume are measured at different time
 - ⇒ used for homogeneous reactions
- Differential reactor: steady state data
 - ⇒ product conc. is monitored for different feed conditions
 - ⇒ Used for solid-fluid heterogeneous reactions.

methods
of
analysis

Methods of analyzing rate data

- ⇒ Integral method
- ⇒ differential method
- ⇒ nonlinear regression

} Batch reactor data

Solve a minimization problem.

rate law

Rate law: Algebraic equation that relates $-r_A$ to the species concentrations.

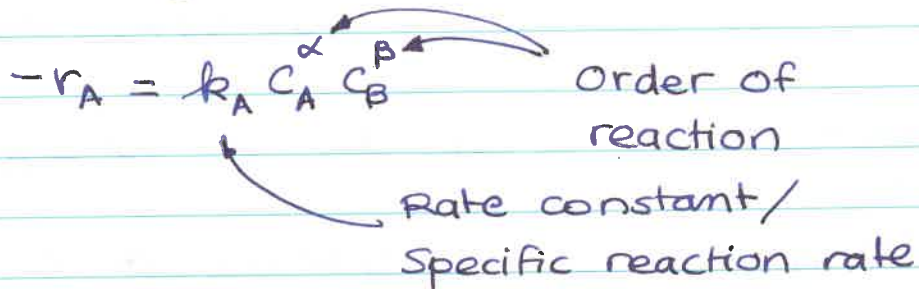
⇒ kinetic expression

$$-r_A = k_A(T) f(C_A, C_B, \dots)$$

⇒ Almost always determined experimentally.

For homogeneous reactions :

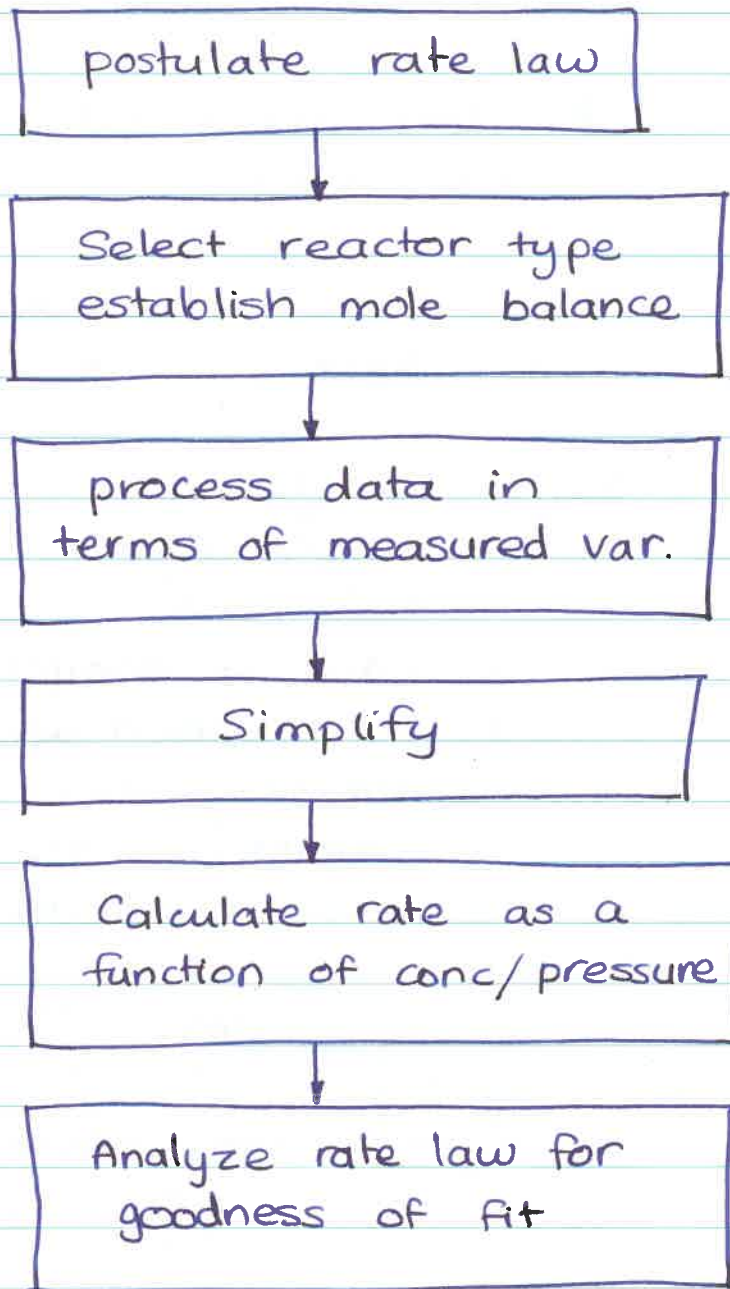
power law model



⇒ Need to determine k_A, α, β

algorithm
for
rate
analysis

Algorithm for data analysis



Rate law
for homogeneous
reactions

Determination of rate law for
homogeneous reactions

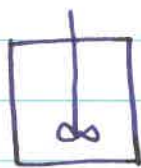
⇒ Most often batch reactors
are used.

Type of reactor chosen will
not affect rate of reaction.

Batch reactor

Why batch
reactor?

- Simple operation
- low cost
- ease of sampling
- easy clean up
- uniform conc. can be
obtained in the reactor
- limited waste.



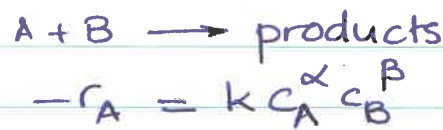
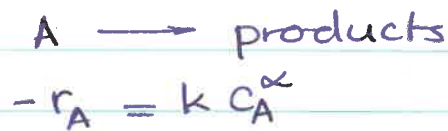
$$\frac{dN_i}{dt} = \int^V r_i dV$$

For constant volume

$$-\frac{dC_A}{dt} = -r_A \quad (\text{in terms of reactant A})$$

model for
homogeneous
reaction

Power law models :



measurements

Typical measurements

- concentration
- pressure
- temperature

- developed heat
during reaction

For simplicity many
times batch reactions
are carried out
isothermally.

Reaction
calorimetry.

Mole balance

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

} isothermal
constant volume
batch reactor

obtaining
rate law

Common Simplification:

One of the reactants is in excess.



excess \Rightarrow Concentration is assumed to be constant.

Calculating $-r_A$ as a function of C_A :

- differential analysis
- integral analysis
- nonlinear regression.

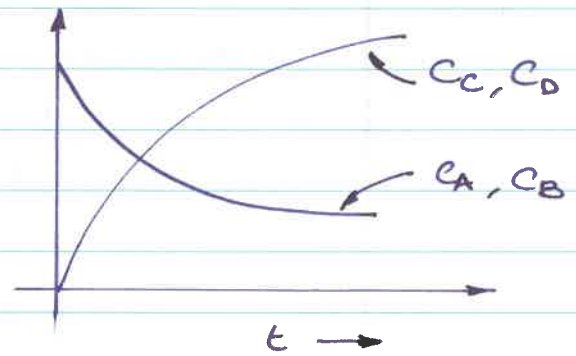
Goodness of fit

- linear correlation coefficient (r^2)
- r^2 should be as close to 1 as possible.

obtaining
reaction
order

Determining reaction order using method of excess

- Given:
- Conc. v time
profile in a
batch experiment,
determine the
order and rate
constant.



rate law: $-r_A = k C_A^\alpha C_B^\beta$

Need to determine: k, α, β .

Determining reaction orders: α, β

- Two separate experiments

① Excess B $\Rightarrow c_B \rightarrow$ constant $c_B \gg c_A$
↳ determine α

② Excess A $\Rightarrow c_A \gg c_B \rightarrow c_A$ constant
↳ Find out β .



$$\text{rate law: } -r_A = k C_A^\alpha C_B^\beta$$

→ if $C_B \gg C_A$ then C_B can be assumed to be constant $C_B \approx C_{B0}$

$$\therefore -r_A = k' C_A^\alpha ; k' \approx k C_{B0}^\beta$$

→ α can be determined by integral / differential method.

→ Repeat the experiments with excess A to determine β

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

differential
method

Differential method

- Irreversible reaction
- The rate is essentially a function of the concentration of only one reactant

e.g. $A \rightarrow \text{products}$

$$-r_A = k C_A^\alpha$$

Consider :

- Isothermal, constant volume batch reactor

• mole balance

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

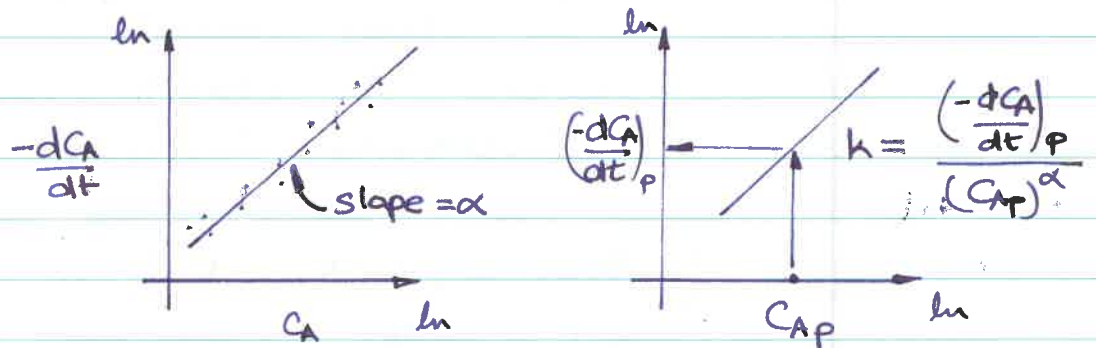
• rate law

$$-r_A = k C_A^\alpha$$

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

Taking natural logarithm

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$



\Rightarrow slope of plot of $\ln\left[-\frac{dC_A}{dt}\right]$ vs $\ln(C_A)$ is the reaction order

\Rightarrow Specific reaction rate can be determined using a specified point P $k = \frac{\left(-\frac{dC_A}{dt}\right)_P}{(C_{AP})^\alpha}$

⇒ Need to evaluate $-\frac{dC_A}{dt}$

- Graphical differentiation
- Numerical differentiation
- differentiation of a polynomial fit to the data.

graphical
method

Graphical method

- very old method
- disparities in the data are easily seen.
 - ↳ can clearly indicate bad data
- useful to visualize data before performing additional experiments.

⇒ Plot $(-\Delta C_A / \Delta t)$ as a function of time.

⇒ use equal area differentiation to obtain $(-dC_A/dt)$

graphical
differentiation

Equal area graphical differentiation

Objective: find derivative of y
with respect to x

steps:

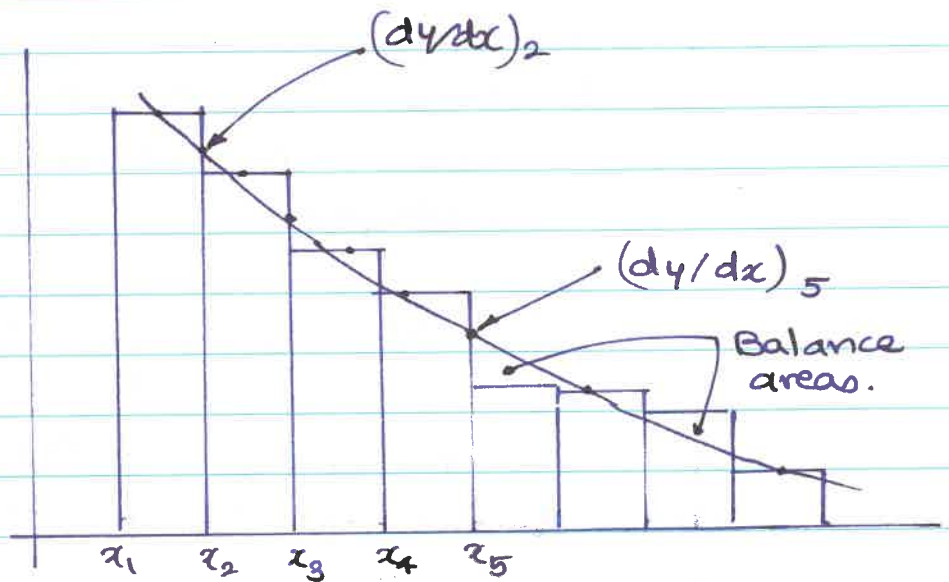
1. Tabulate (y_i, x_i)
2. Calculate $\Delta x_n = x_n - x_{n-1}$ and
 $\Delta y_n = y_n - y_{n-1}$
3. Calculate $\Delta y_n / \Delta x_n \in R$
↳ Estimate of the average
slope in interval $x_{n-1} - x_n$
4. Plot values as a histogram vs x_i
5. Draw a smooth curve that
best approximates the area under
histogram

$$y_n - y_1 = \sum_{i=2}^n \frac{\Delta y}{\Delta x_i} \Delta x_i$$
$$\Rightarrow y_n - y_1 = \int_{x_1}^{x_n} \frac{dy}{dx} dx$$

} Area under $\Delta y / \Delta x$ is
same as
that under
 dy/dx every-
where.

6. Read dy/dx from the smooth
curve.

x_i	y_i	Δx	Δy	$\frac{\Delta y}{\Delta x}$	$\frac{dy}{dx}$
x_1	y_1				$(dy/dx)_1$
		$x_2 - x_1$	$y_2 - y_1$	$(\frac{\Delta y}{\Delta x})_2$	
x_2	y_2				$(dy/dx)_2$
		$x_3 - x_2$	$y_3 - y_2$	$(\frac{\Delta y}{\Delta x})_3$	
x_3	y_3				$(dy/dx)_3$
		$x_4 - x_3$	$y_4 - y_3$	$(\frac{\Delta y}{\Delta x})_4$	
x_4	y_4				\vdots



Differentiation is less accurate than integration.

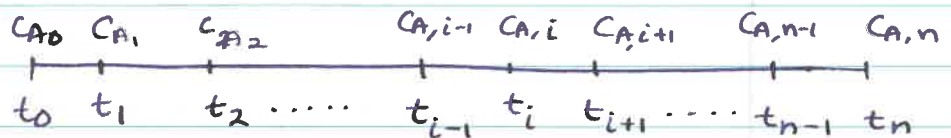
⇒ Only valid when data can be differentiated smoothly.

numerical
differentiation

Numerical method

- Finite difference
- Independent variable are equally spaced

$$t_1 - t_0 = t_2 - t_1 \Rightarrow \Delta t$$



Initial point

$$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A,0} + 4C_{A,1} - C_{A,2}}{2\Delta t}$$

Interior points

$$\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t} (C_{A,i+1} - C_{A,i-1})$$

$$\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{1}{2\Delta t} (C_{A,i+1} - C_{A,i-1})$$

Last point

$$\left(\frac{dC_A}{dt}\right)_n = \frac{1}{2\Delta t} [C_{A,n-2} - 4C_{A,n-1} + 3C_{A,n}]$$

polynomial
derivative

Polynomial derivative :

- Fit a polynomial to C_A vs t data.

e.g. $C_A = f(t)$

$$C_A = a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$$

↓
4th order polynomial.

↳ analytical derivative

$$\frac{dC_A}{dt} = a_1 + 2a_2 t + 3a_3 t^2 + 4a_4 t^3$$

- create table

time	conc	derivative
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- determine reaction order and specific rate from plot of $\ln(-dC_A/dt)$ vs $\ln C(A)$

Integral
method

Integral method

- Quickest method to use to determine the rate law if the order is 0, 1, or 2.
- ⇒ Guess reaction order
- ⇒ Integrate the differential equation to obtain conc. as a function of time.
- ⇒ If guessed order is correct appropriate plot (determined from integration) should be linear
- ⇒ Used when reaction order is known.
- ⇒ Determine specific reaction rate constant at different temperatures to determine activation energy.

Need to know appropriate function of conc. corresponding to a rate law that is linear with time

Reaction : $A \rightarrow \text{products}$.

mole balance : const. vol. batch reactor

$$-\frac{dC_A}{dt} = -r_A \quad \text{--- (1)}$$

① For zero order reaction

$$-r_A = k$$

Integrating eq. ① with $C_A = C_{A0}$ @ $t = 0$

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

② First order reaction

$$-r_A = kC_A$$

Integration with $C_A = C_{A0}$ @ $t = 0$ of ①

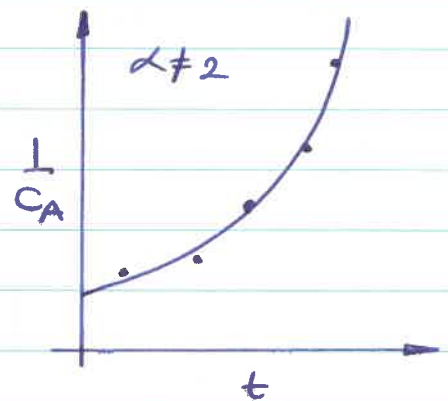
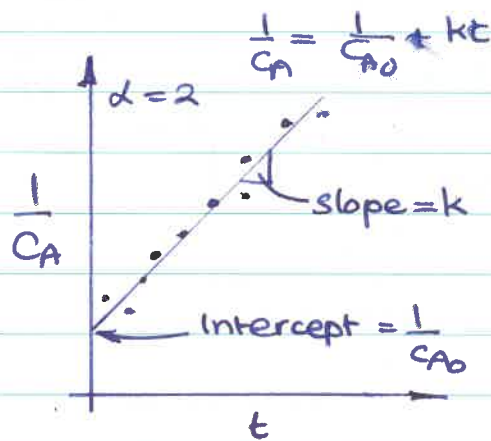
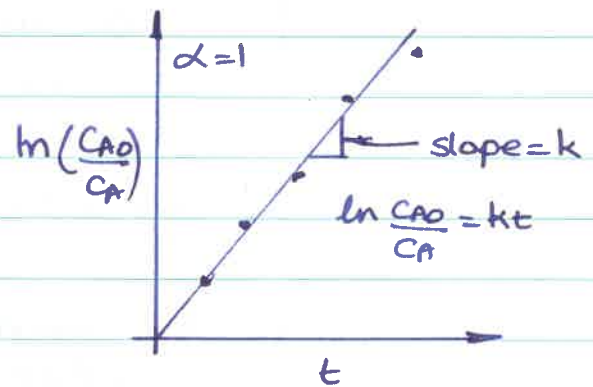
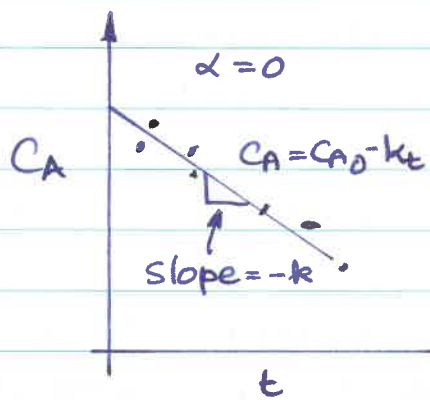
$$\ln \frac{C_{A0}}{C_A} = kt$$

③ Second order reaction

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

Integrating (1) $C_A = C_{A0}$ @ $t=0$

$$\boxed{\frac{1}{C_A} = \frac{1}{C_{A0}} + kt}$$

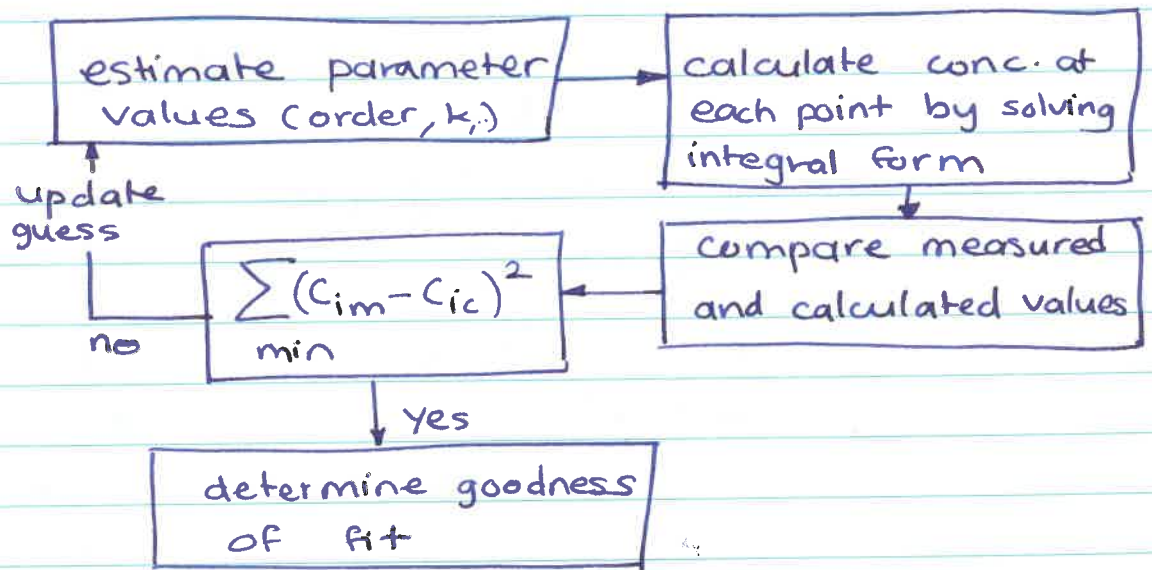


Non linear regression

- Search for parameter values that minimize the sum of squares of the difference between the measured values and calculated values for all data points.

- ⇒ Best estimate of parameter values
- ⇒ discriminate between different rate law models. ⇒ ~~minimum~~
 - Smallest s^2
 - F-Test
 - residual plots

Procedure





mole balance

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

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^\alpha} = \int_0^t k dt$$

For $\alpha \neq 1$

$$C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt$$

$$\therefore C_A = \left[C_{A0}^{(1-\alpha)} - (1-\alpha)kt \right]^{1/(1-\alpha)}$$

$$\text{minimize : } S^2 = \sum_{i=1}^N (C_{Aim} - C_{Aic})^2$$

can also use time

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

$$\text{minimize : } S^2 = \sum_{i=1}^N (t_{im} - t_{ic})^2$$

Other numerical methods

- ODE regression : combine regression program with ODE solver
- least square / weighted least square.

Other methods to determine kinetics

- Method of half life
- method of initial rates

Method of half life

- $t_{1/2}$ \rightarrow time taken for the conc. of reactant to fall to half of its initial value
- determine half life as a function of initial conc.
- requires several experiments.

Reaction: $A \rightarrow \text{products}$.

rate law: $-r_A = kC_A^\alpha$

mole. balance: $-\frac{dC_A}{dt} = kC_A^\alpha$

integration $C_A = C_{A0}$ @ $t = 0$

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

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

$$t = t_{1/2} \quad \text{when} \quad C_A = \frac{1}{2} C_{A0}$$

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

in general:

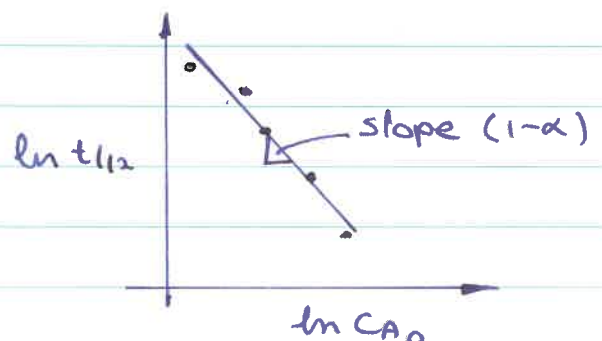
$$t_{1/n} = \frac{n^{\alpha-1} - 1}{k(\alpha-1)} \left[\frac{1}{C_{A0}^{\alpha-1}} \right]$$

taking log of ①

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

intercept slope

\Rightarrow plot $\ln t_{1/2}$ vs $\ln C_{A0}$



method of initial rates

— Differential analysis method is not effective for reversible reactions.

→ method of initial rates

- perform series of experiments at different initial concentrations C_{A0}
- determine initial rate of reaction $-r_{A0}$
- determine rate law parameters by relating $-r_{A0}$ to C_{A0} .

Reaction: $A \rightarrow \text{products}$

rate law: $-r_A = kC_A^\alpha$

mole balance: $dC_A/dt = kC_A^\alpha$

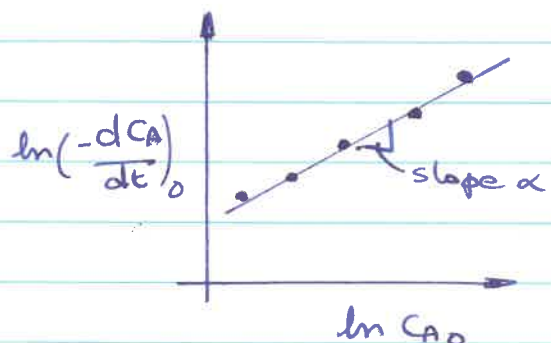
Initial rate:

$$-r_{A0} = \left(-\frac{dC_A}{dt}\right)_0 = kC_{A0}^\alpha$$

taking log:

$$\ln\left(-\frac{dC_A}{dt}\right)_0 = \ln k + \alpha \ln C_{A0}$$

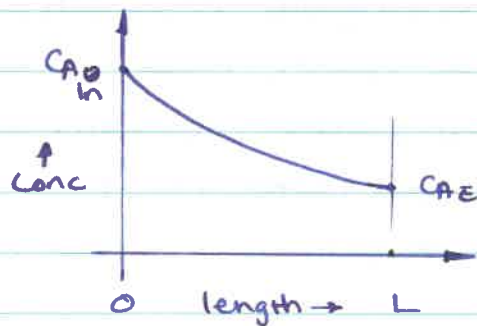
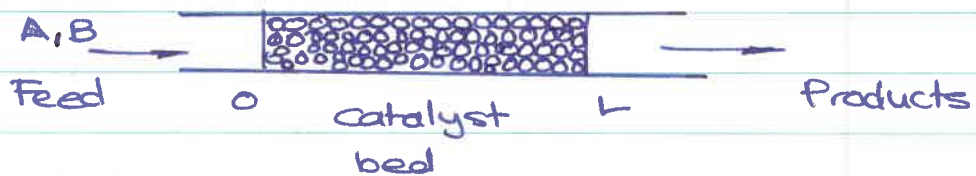
plot ~~r_{A0}~~ $\ln\left(-\frac{dC_A}{dt}\right)_0$ vs $\ln C_{A0}$



Reaction rate data from differential reactors

- Heterogeneous reactions
- rate is determined by carrying out number of experiments with varying inlet concentrations.
- Packed bed reactor (PBR) is commonly used \Rightarrow differential reactor

PBR :



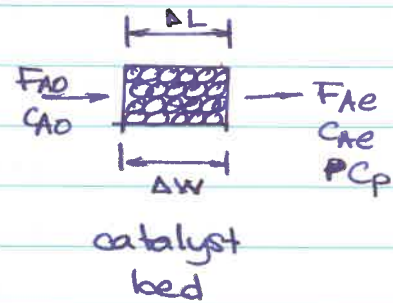
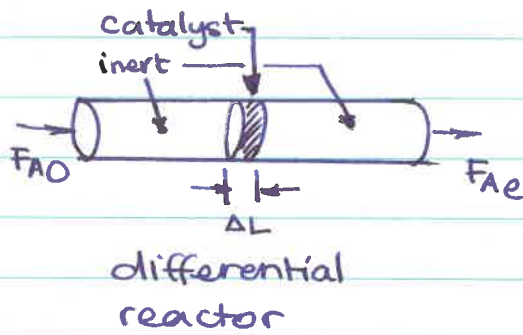
\Rightarrow Drawbacks

- conc. gradients
- axial and radial temp. gradients

\rightarrow steady state operations

\Downarrow Differential reactor

- very small amount of catalyst (thin wafer / disk)
- very small c & T gradient
- extremely low conversion, ΔH_R



Assumptions:

- No C & T gradients
 \Rightarrow gradientless
- high volumetric flow rate
- small catalyst particles
 \hookrightarrow no mass transfer limitations
- very low conversion
- low/negligible heat release
 \hookrightarrow isothermal
- no bypassing / channeling
 \hookrightarrow uniform flow across catalyst layer

Disadvantages / limitations

- ~~not~~ cannot be used with rapidly decaying catalyst
- difficulties in analysis \rightarrow multicomponent mixtures with low conc.

Reaction $A \rightarrow \text{products}$

- volumetric flow rate through the bed is monitored.

design equation:

gradientless reactor \rightarrow CSTR design equations

at steady state

$$\left[\begin{array}{c} \text{flow} \\ \text{rate} \\ \text{in} \end{array} \right] - \left[\begin{array}{c} \text{flow} \\ \text{rate} \\ \text{out} \end{array} \right] + \left[\begin{array}{c} \text{rate of} \\ \text{generation} \end{array} \right] = \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \end{array} \right]$$

$$F_{A0} - F_{Ae} + r'_A \Delta W = 0$$

r'_A : $\frac{\text{rate of reaction}}{\text{mass of catalyst}}$; ΔW , mass of catalyst.

other commonly used reaction $\frac{\text{rate}}{\text{units}}$

r'_A : rate of rxn / surface of catalyst

r'_A : rate of rxn / volume of catalyst

$$-r'_A = \frac{F_{A0} - F_{Ae}}{\Delta W}$$

$$\therefore -r'_A = \frac{v_0 C_{A0} - v C_{Ae}}{\Delta W} \quad \text{— in terms of conc.}$$

$$-r'_A = \frac{F_{A0} X}{\Delta W} = \frac{F_P}{\Delta W} \quad \text{— in terms of product flow rate.}$$

↑
stoichiometric coeff
of A and P are
identical.

For constant volumetric flow

$$-r'_A = \frac{v_0 (C_{A0} - C_{Ae})}{\Delta W} = \frac{v_0 C_P}{\Delta W}$$

→ for small conversion

(little catalyst, large flowrate)

$$C_{A0} \approx C_{Ae} \quad (C_{A0} - C_{Ae}) \rightarrow \text{very small}$$

→ $-r'_A$ can be expressed as a function of the reactant conc. in catalyst bed

$$-r'_A = -r'_A(C_{Ab}) \quad C_{Ab} = \frac{C_{A0} + C_{Ae}}{2} \approx C_{A0}$$

$$-r_A' = -r_A'(C_{A0})$$

Langmuir - Hinshelwood model for heterogeneous reaction:

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

Evaluation of laboratory reactors

- Need reliable kinetic data for successful scale up ⇒ Important to design equipment and experiments properly.
- Several lab reactor types exist

Criteria to evaluate lab reactors

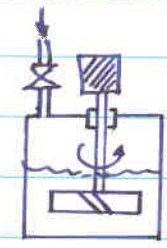
- Ease of sampling and product analysis
- degree of isothermality
- effectiveness of contact between catalyst and reactant
- handling of catalyst decay
- reactor cost and ease of construction

Types of lab reactors

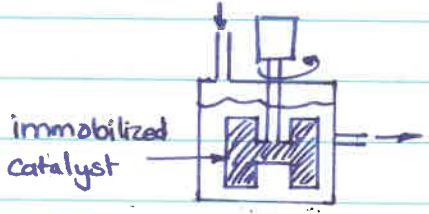
Integral reactor



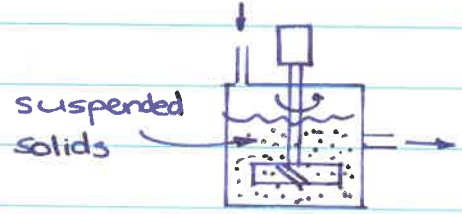
stirred batch reactor



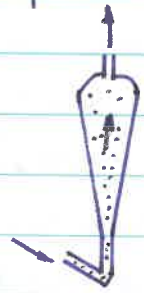
Stirred contained solids reactor



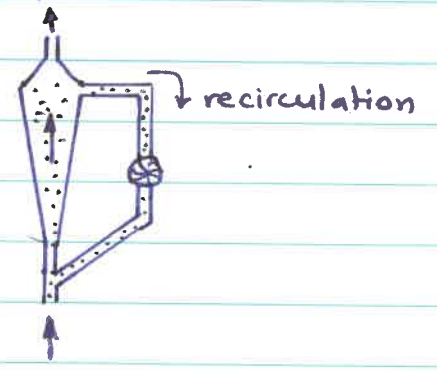
solids in CSTR



straight through transport reactor



recirculating transport reactor



Reactor comparison

Reactor type	Sampling and analysis	isothermality	F-S Contact	Cat. decay	ease of const.
Differential	P-F	F-G	F	P	G
Fixed batch	G	P-F	F	P	G
Stirred batch	F	G	G	P	G
Stirred-contained solids	G	G	F-G	P	F-G
continuous stirred tank	F	G	F-G	F-G	P-F
straight through transport	F-G	P-F	F-G	G	F-G
recirculating transport	F-G	G	G	F-G	P-F
Pulse	G	F-G	P	F-G	G

G : good

F : fair

P : poor