Lecture 4

Mole balance: calculation of membrane reactors and unsteady state in tank reactors.

Analysis of rate data

Mole Balance in terms of Concentration and Molar Flow Rates

- Working in terms of **number of moles** (N_A, N_B,..) or **molar flow rates** (F_A, F_B etc) rather than conversion could be more convenient at some instances
- The difference in calculation: we will write mole balance for **each and every species** in the reactor

Isothermal reaction design algorithm

$$A + 2B \rightleftarrows C$$

Mole Balance

① Write mole balance on each species[7]

e.g., $\frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B, \quad \frac{dF_C}{dV} = r_C$

↓

Rate Law

② Write rate law in terms of concentration

e.g., $-r_A = k_A\left(C_A C_B^2 - \frac{C_C}{K_C}\right)$

↓

Stoichiometry

③ Relate the rates of reaction of each species to one another

e.g., $r_B = 2r_A, \quad r_C = -r_A$

↓

Stoichiometry

④ **(a)** Write the concentrations in terms of molar flow rates for isothermal *gas-phase* reactions

e.g., $C_A = C_{T0}\frac{F_A}{F_T}\frac{P}{P_0}, \quad C_B = C_{T0}\frac{F_B}{F_T}\frac{P}{P_0}$

with $F_T = F_A + F_B + F_C$

(b) For *liquid-phase* reactions use concentration, e.g., $C_A, \ C_B$

↓

Pressure Drop

⑤ Write the *gas-phase* pressure drop term in terms of molar flow rates

$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{F_T}{F_{T_0}}, \quad$ with $\quad y = \frac{P}{P_0}$

↓

Combine

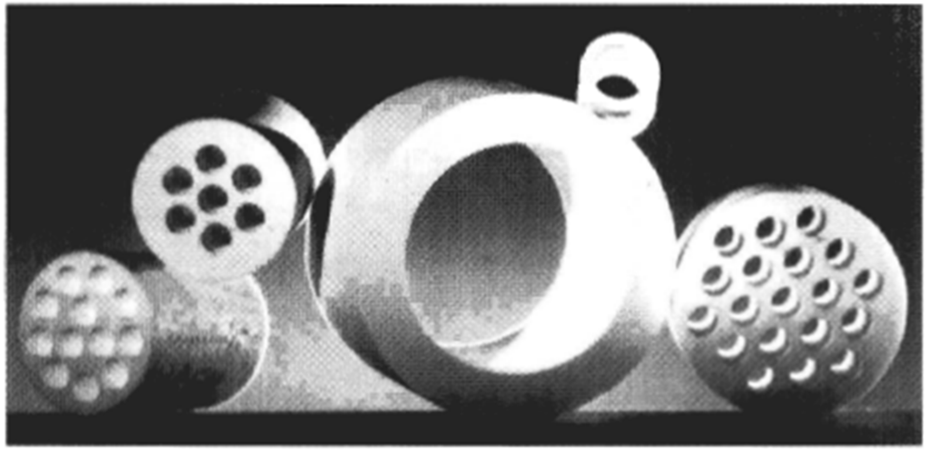
⑥ Use an ODE solver or a nonlinear equation solver (e.g., Polymath) to combine Steps ① through ⑤ to solve for, for example, the profiles of molar flow rates, concentration and pressure.

Membrane reactors

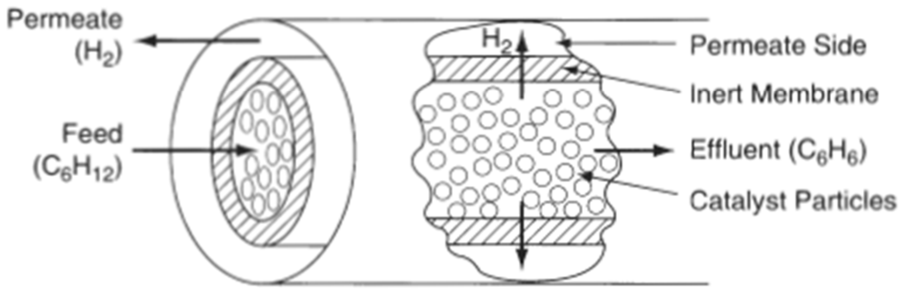
- used to **increase conversion** when the reaction is thermodynamically limited (e.g. with small K)
- or to **increase selectivity** in when multiple reactions are occurring

$$C_6H_{12} \rightleftarrows 3H_2 + C_6H_6$$

(a)

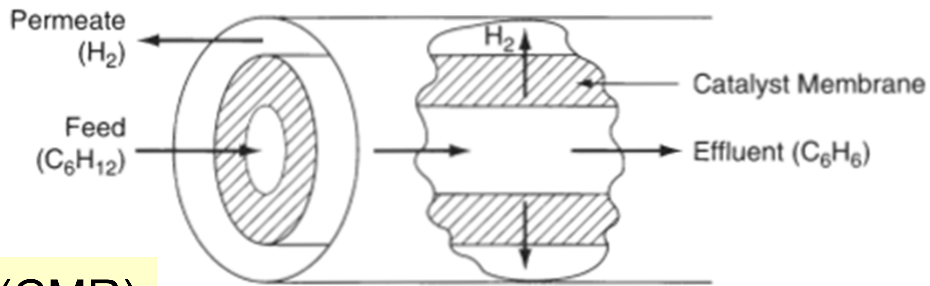


(b)



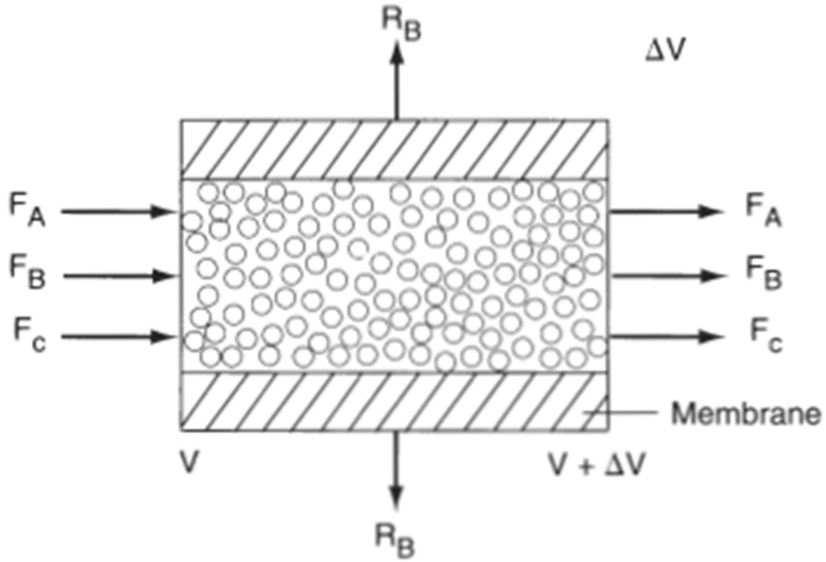
inert membrane reactor with catalyst pellet on the feed side (IMRCF)

(c)



catalyst membrane reactor (CMR)

Membrane reactors



$$C_6H_{12} \rightleftarrows 3H_2 + C_6H_6$$

$$A \rightleftarrows 3B + C$$

- Mole balances: $\dfrac{dF_A}{dV} = r_A$ $\qquad \dfrac{dF_C}{dV} = r_C$

$$F_{B|_V} - F_{B|_{V+\Delta V}} - R_B \Delta V + r_B \Delta V = 0$$

generation

IN by flow

OUT by diffusion

OUT by flow

no accumulation

$$\frac{dF_B}{dV} = r_B - R_B$$

Membrane reactors

$$\frac{dF_B}{dV} = r_B - R_B$$

$$R_B = W_B a = k_c' a (C_B - C_{BS})$$

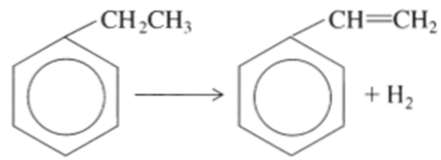
- Diffusion flux → W_B
- area per volume → a
- mass transfer coefficient → k_c'
- concentration in the sweep gas channel → C_{BS}

$$a = \frac{\pi DL}{\pi LD^2/4} = \frac{4}{D}$$

- Assuming C_{BS}=*0* and introducing $k_c = k_c' a \Longrightarrow R_B = k_c C_B$

Example: Dehydrogenation reaction

- Typical reactions:
  - dehydrogenation of ethylbenzene to styrene;
  - dehydrogenation of butane to butene
  - dehydrogenation of propane to propene



$$C_4H_{10} \longrightarrow C_4H_8 + H_2$$

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$

- Problem: for a reaction of type $A \rightleftarrows B + C$ where an equilibrium constant Kc=0.05 mol/dm^3; temperature 227ºC, pure A enters chamber at 8.2 atm and 227ºC at a rate of 10 mol/min
  - write differential mole balance for A, B, C
  - plot the molar flow rate as a function of space and time
  - calculate conversion at V=400 dm^3.
- Assume that the membrane is permeable for B only, catalyst density is ρ_b=1.5 g/cm^3, tube inside diameter 2cm, reaction rate k=0.7 min^{-1} and transport coefficient k_c=0.2 min^{-1}.

Example

- Mole balance:

$$\frac{dF_A}{dV} = r_A \qquad \frac{dF_B}{dV} = r_B - R_B \qquad \frac{dF_C}{dV} = r_C$$

- Rate law

$$-r_A = k\left(C_A - \frac{C_B C_C}{K_C}\right)$$

- Transport out of the reactor

$$R_B = k_c C_B$$

- Stoichiometry

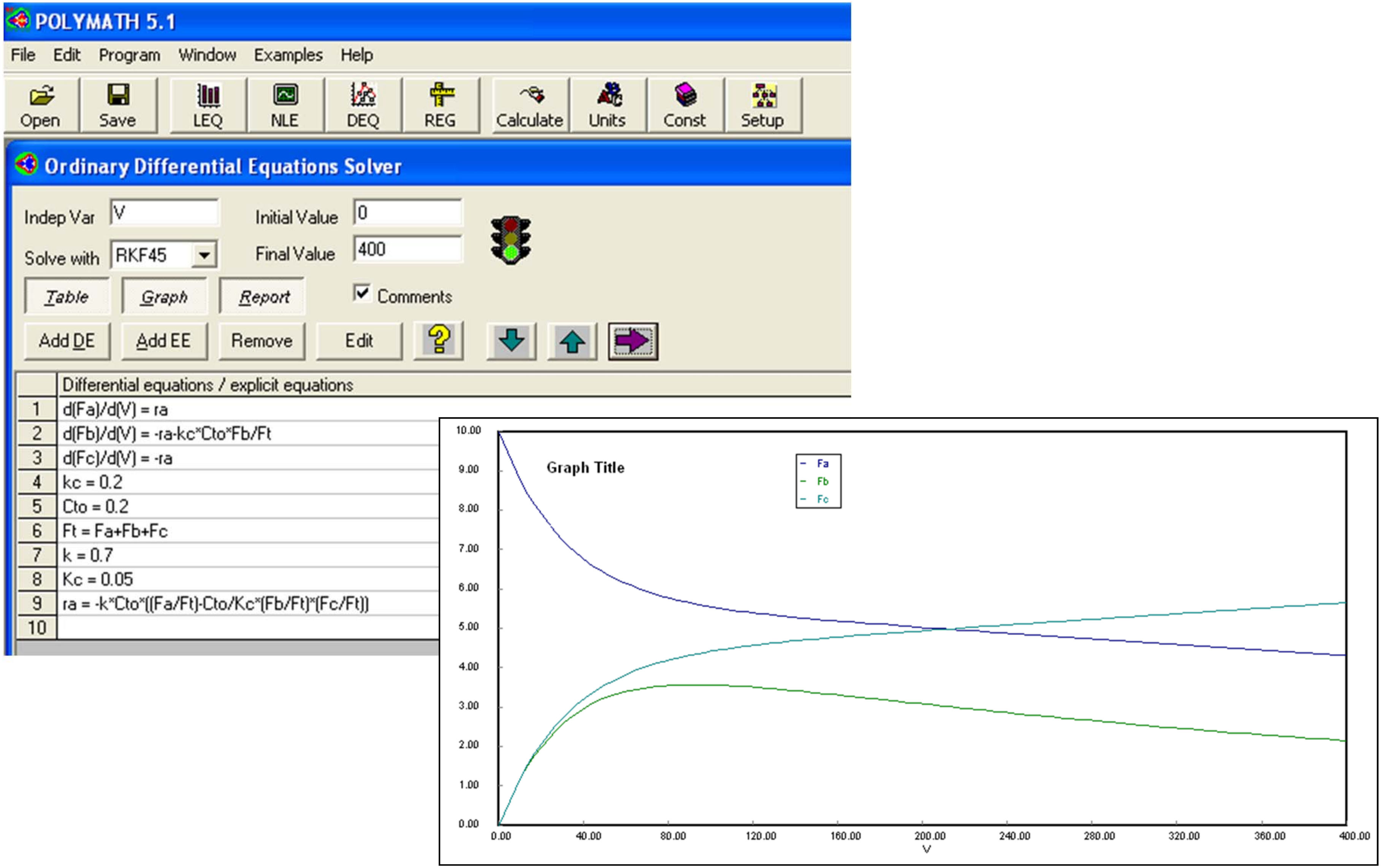
$$C_A = C_{T0}\frac{F_A}{F_T} \qquad C_B = C_{T0}\frac{F_B}{F_T} \qquad C_C = C_{T0}\frac{F_C}{F_T}$$

$$C_{A0} = C_{T0} = \frac{P_0}{RT_0} = 0.2 \text{ mol/dm}^3$$

$$r_B = r_C = -r_A$$

Example

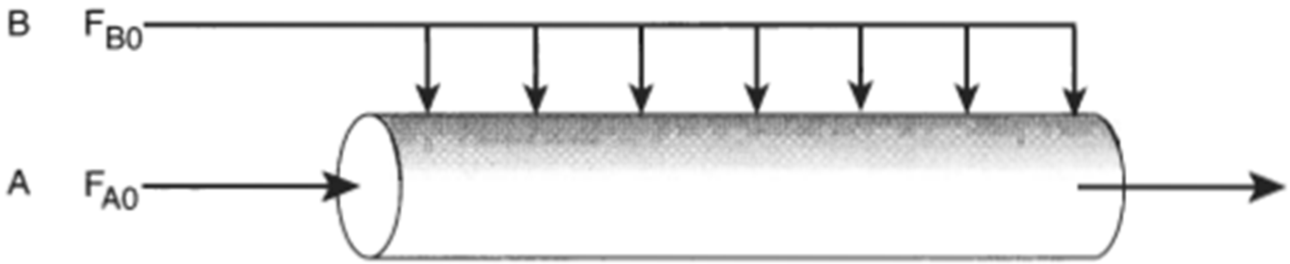
- POLYMATH solution



Use of Membrane reactors to enhance selectivity

$$A + B \rightarrow C + D$$

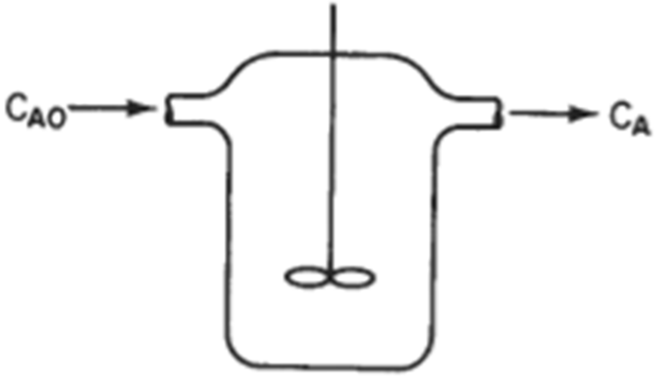
- **B** is fed uniformly through the membrane



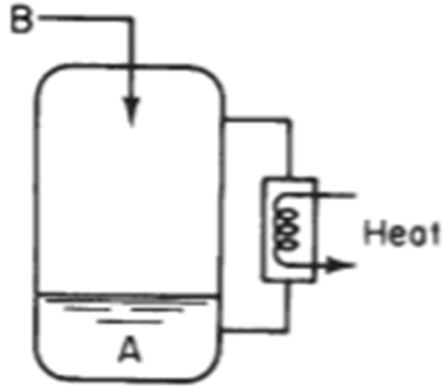
$$\frac{dF_B}{dV} = r_B + R_B$$

Unsteady state operation of stirred reactors

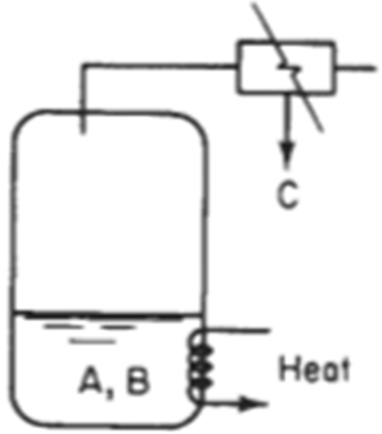
$$A + B \rightarrow C + D$$



reactor start-up



semibatch w. cooling



reactive distillation

- during the start up of a reactor:
- slow addition of component **B** to a large quantity of **A** e.g. when reaction is highly exothermic or unwanted side reaction can occur at high concentration of **B**
- one of the products (**C**) is vaporized and withdrawn continuously.

Startup of CSTR

- Conversion doesn't have any meaning in startup so we have to use concentrations

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt}$$

- For liquid phase with constant overflow
  $v = v_0; V = V_0$

$$C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt}, \quad \tau = \frac{V_0}{v_0}$$

- For the 1st order reactions

$$-r_A = kC_A, \quad \frac{dC_A}{dt} + \frac{1+\tau k}{\tau} C_A = \frac{C_{A0}}{\tau}$$

$$C_A = \frac{C_{A0}}{1+\tau k}\left\{1 - \exp\left[-(1+\tau k)\frac{t}{\tau}\right]\right\}$$

- e.g. to reach 99% steady state concentration

$$C_{AS} = \frac{C_{A0}}{1+\tau k}, \quad t_s = 4.6\frac{\tau}{1+\tau k}$$

for small k:

$$t_s = 4.6\tau$$

for large k:

$$t_s = 4.6/k$$

Semibatch reactors

- semibatch reactors could be used e.g. to improve selectivity

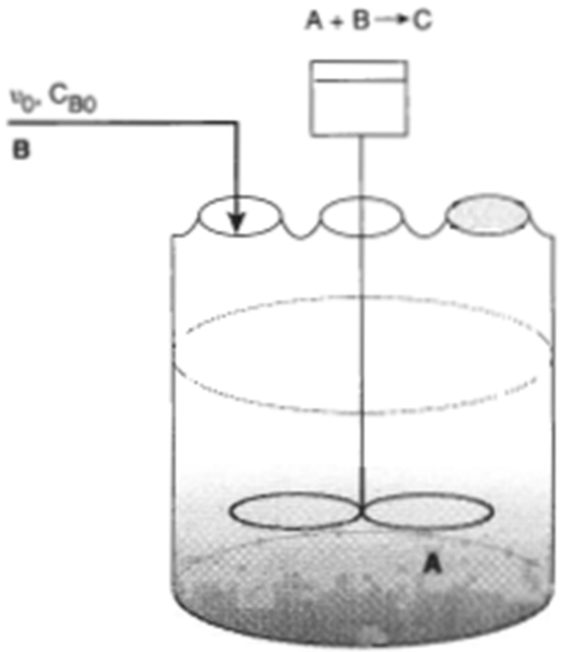
$$A + B \xrightarrow{k_D} D \qquad r_D = kC_A^2 C_B$$

$$A + B \xrightarrow{k_U} U \qquad r_U = kC_A C_B^2$$

- selectivity: $$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U}\frac{C_A}{C_B}$$

Selectivity can be increased by keeping concentration A high and concentration B low

Semibatch equations



- For component **A**: no flow in/out

$$r_A V = \frac{dN_A}{dt} = \frac{d\left(C_A V\right)}{dt} = \frac{VdC_A}{dt} + \frac{C_A dV}{dt}$$

$$V = V_0 + v_0 t$$

$$-v_0 C_A + r_A V = \frac{VdC_A}{dt} \Rightarrow \frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A$$

- For component **B**:

$$\frac{dN_B}{dt} = r_B V + F_{B0}$$

$$\frac{VdC_B}{dt} + \frac{C_B dV}{dt} = r_B V + v_0 C_{B0}$$

$$\frac{dC_B}{dt} = r_B + \frac{v_0}{V}\left(C_{B0} - C_B\right)$$

Example 4.9

- Production of methyl bromide is carried as an irreversible liquid phase reaction in isothermal semibatch reactor. Consider reaction to be elementary.

$$CNBr + CH_3NH_2 \rightarrow CH_3Br + NCNH_2$$

initial volume of fluid	$V_0 = 5dm^3$
initial concentration CNBr	$C_0(CNBr) = 0.05\, mol / dm^3$
flow of CH_3NH_2 solution	$v_0 = 0.05\, dm^3 / s$
concentration CH_3NH_2	$C_0(CH_3NH_2) = 0.025 mol / dm^3$
rate constant	$k = 2.2 dm^3 / s \cdot mol$

Solution

- mole balance:

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A; \qquad \frac{dC_B}{dt} = r_B + \frac{v_0 (C_{B0} - C_B)}{V}$$

- rate law:

$$r_A = -kC_A C_B$$

- combining

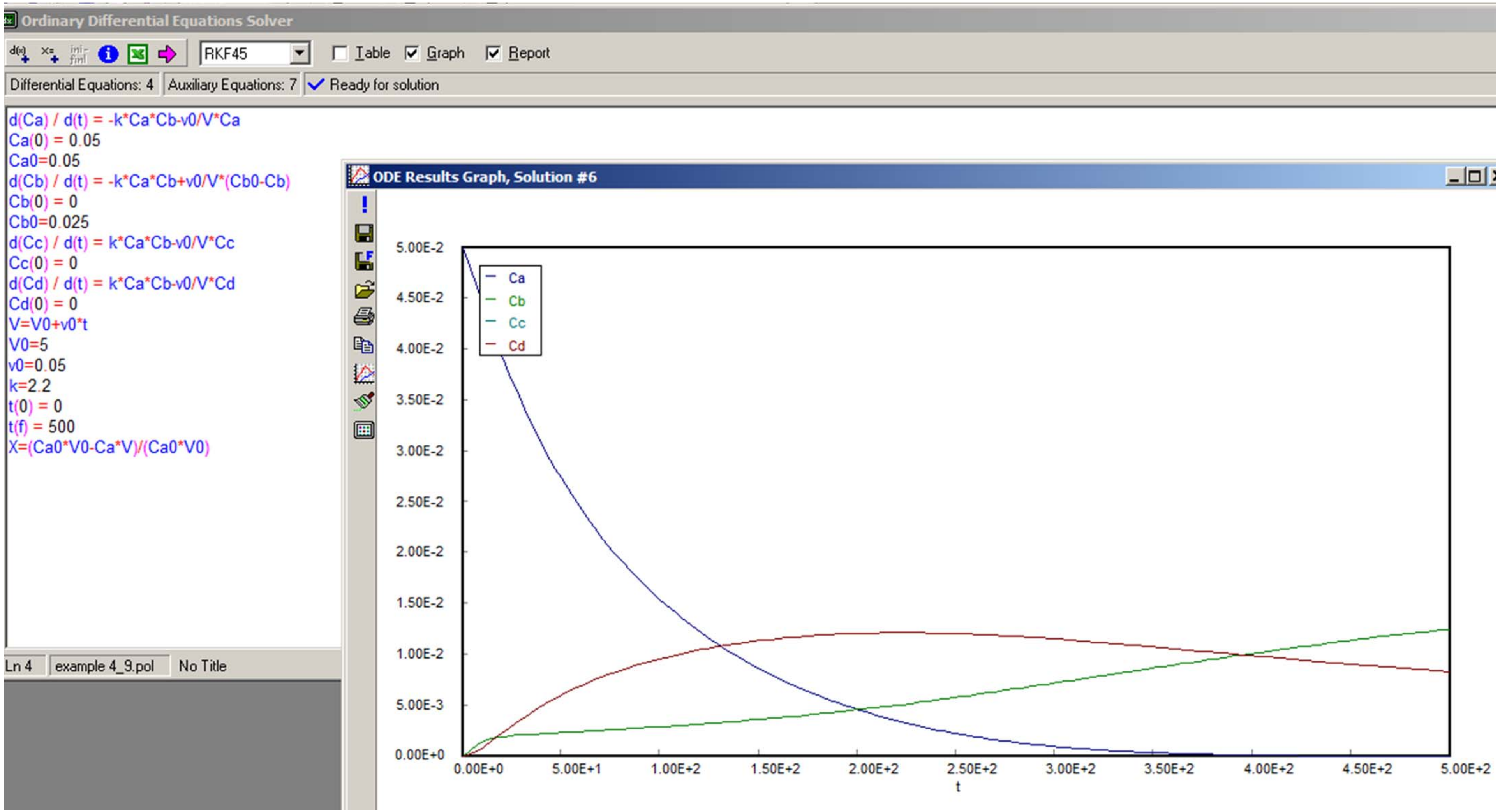
$$\frac{dC_A}{dt} = -kC_A C_B - \frac{v_0}{V} C_A; \qquad \frac{dC_B}{dt} = -kC_A C_B + \frac{v_0 (C_{B0} - C_B)}{V}$$

$$\frac{dC_C}{dt} = -kC_A C_B - \frac{v_0}{V} C_C; \qquad \frac{dC_D}{dt} = -kC_A C_B - \frac{v_0}{V} C_D;$$

$$V = V_0 + v_0 t$$

$$X = \frac{N_{A0} - N_A}{N_{A0}} = \frac{C_{A0} V_0 - C_A V}{C_{A0} V_0}$$

Polymath calculation



Analysis of rate data

- Main question: How to collect rate data and deduce the reaction rate law?

- The Algorithm:
  1. Postulate a rate law
  2. Select appropriate reactor type and mole balance
  3. Determine the variables and process the experimental data. Apply simplification and create a model
  4. Fit model to the data and find the coefficients.
  5. Analyze your rate model for ”goodness of fit”.

Batch reactor data

- For **irreversible** reactions, it is possible to determine reaction order α and ratee constant k by either non-linear regression or differentiating concentration vs time data
- Differential method is most applicable when:
  - rate is function of one concentration only:

$$A \rightarrow \text{Products}$$

$$-r_A = k_A C_A{}^{\alpha}$$

  - method of excess is used

$$A + B \rightarrow \text{Products}$$

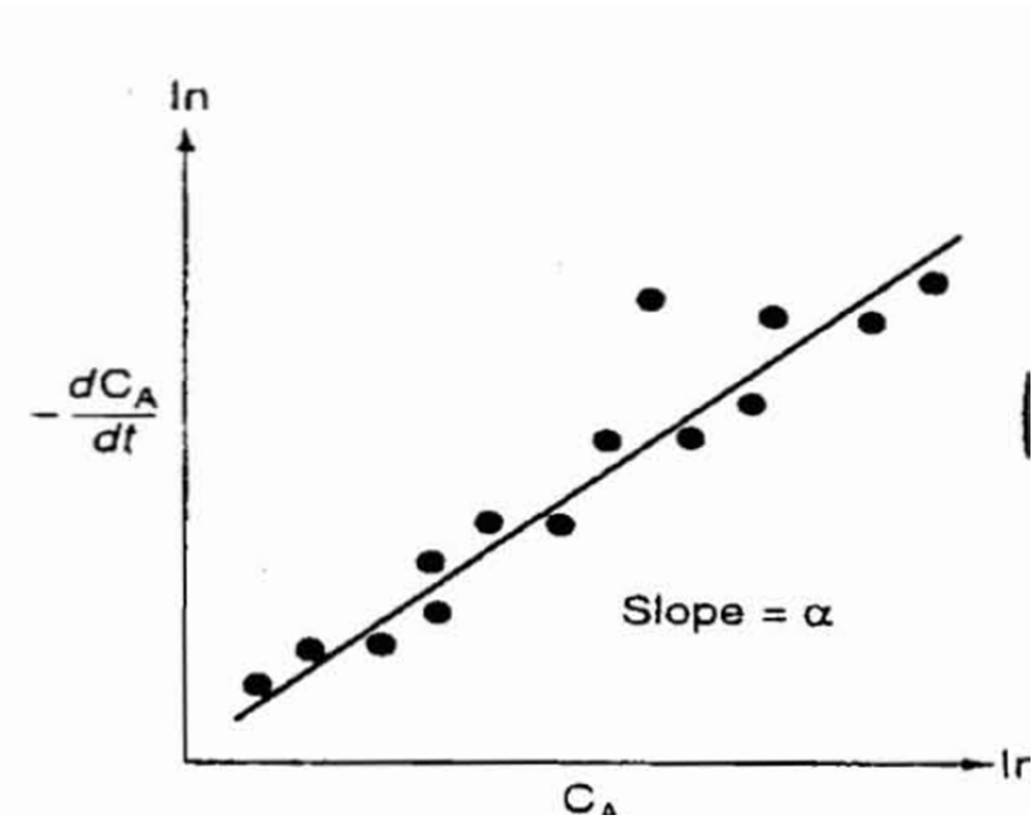
$$-r_A = k_A C_A{}^{\alpha} C_b{}^{\beta}$$

Batch reactor: differential method

- Combing mole balance and rate law:

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

$$\ln\left[-\frac{dC_A}{dt}\right] = \ln k_A + \alpha \ln C_A$$

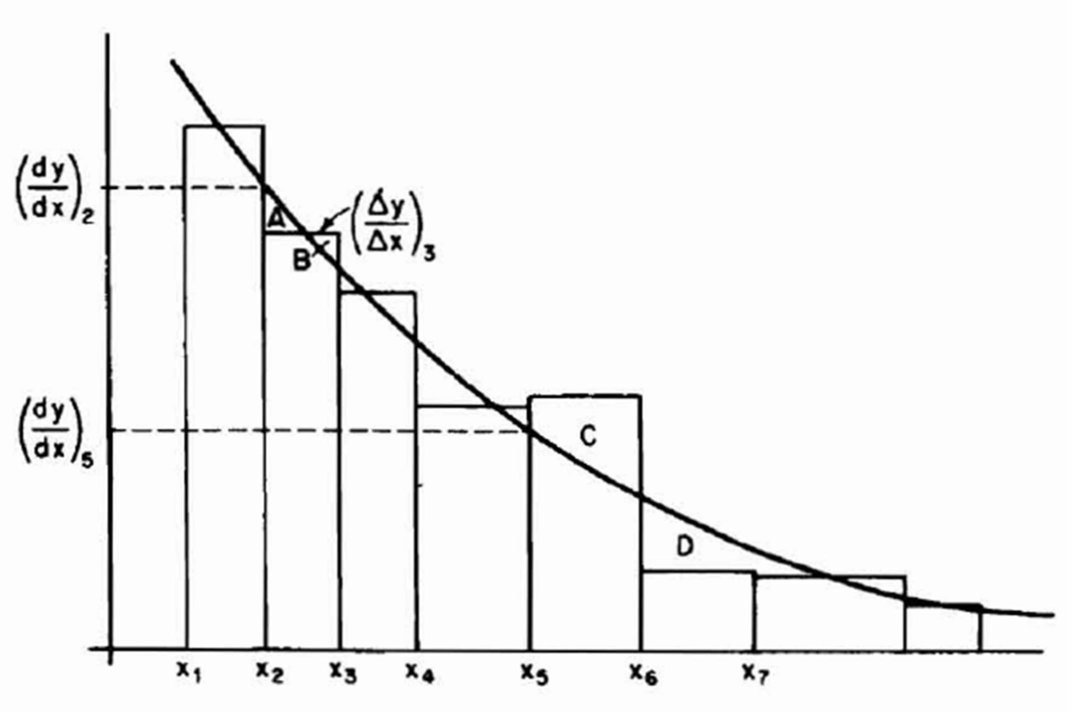


$$k_A = \frac{-(dC_A/dt)}{\left(C_{Ap}\right)^{\alpha}}$$

Batch reactor: differential method

- Techniques to obtain dC/dt from the data:
  - Graphical
  - Numerical
  - Differentiation of polinomial fit.

- Graphical:
  - $\frac{\Delta C}{\Delta t}$ plotted vs. t,
  - smooth curve plotted to appoximate the area under the histogramm



Batch reactor: differential method

- Numerical method:
  - three-point differentiation formulas

first point
$$\left(\frac{dC_A}{dt}\right)_{t0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t}$$

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

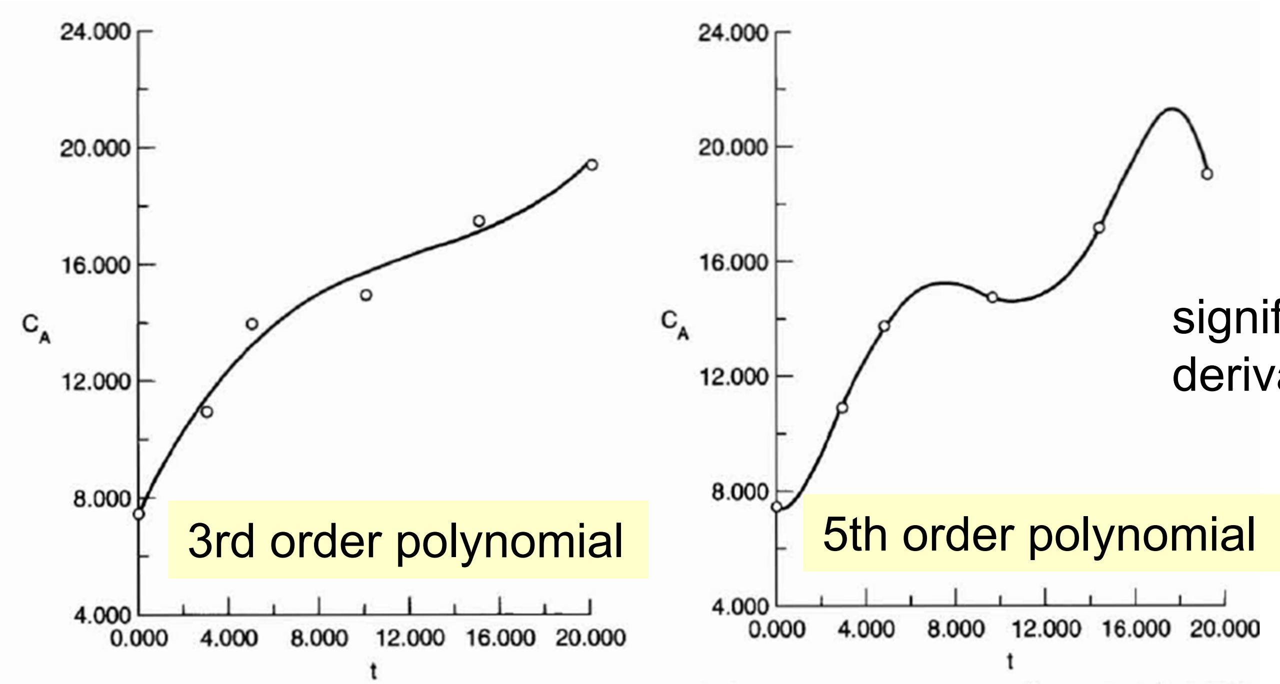
last point
$$\left(\frac{dC_A}{dt}\right)_{tf} = \frac{C_{A(f-2)} - 4C_{A(f-1)} + 3C_{Af}}{2\Delta t}$$

Batch reactor: differential method

- Polynomial fit:
  - fit C_A with a polynomial and differentiate

$$C_A = a_0 + a_1 t + a_2 t^2 + \ldots + a_n t^n$$

$$\left(\frac{dC_A}{dt}\right) = a_1 + 2a_2 t + 3a_3 t^2 + \ldots + n a_n t^{n-1}$$



significant error in derivative

Batch reactor: integral method

- Used when reaction order is known to evaluate the rate constant. The procedure:
  - assume the reaction order
  - integrate the model equation
  - plot the data in appropriate coordinates and fit the data
- Example $A \rightarrow \text{Products}$

0th order	1st order	2nd order
$\frac{dC_A}{dt} = r_A;$	$\frac{dC_A}{dt} = r_A;$	$\frac{dC_A}{dt} = r_A;$
$\frac{dC_A}{dt} = -k$	$\frac{dC_A}{dt} = -kC_A$	$\frac{dC_A}{dt} = -kC_A{}^2$
$C_A = C_{A0} - kt$	$\ln \frac{C_{A0}}{C_A} = kt$	$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$

Batch reactor: integral method

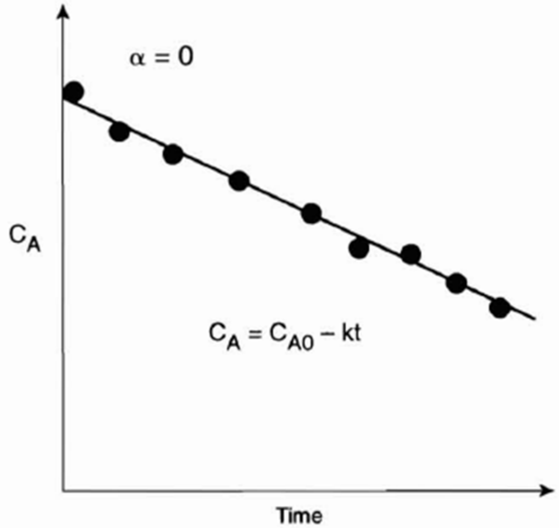


Figure 5-3 Zero-order reaction.

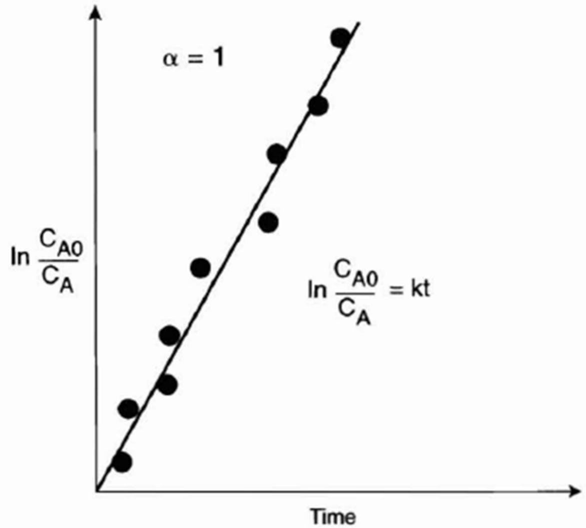


Figure 5-4 First-order reaction.

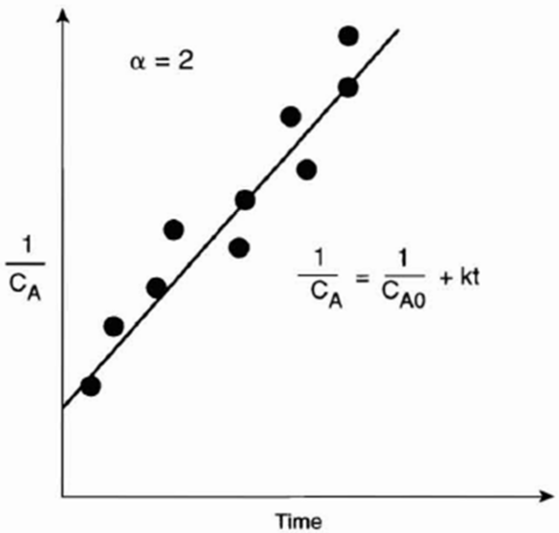


Figure 5-5 Second-order reaction.

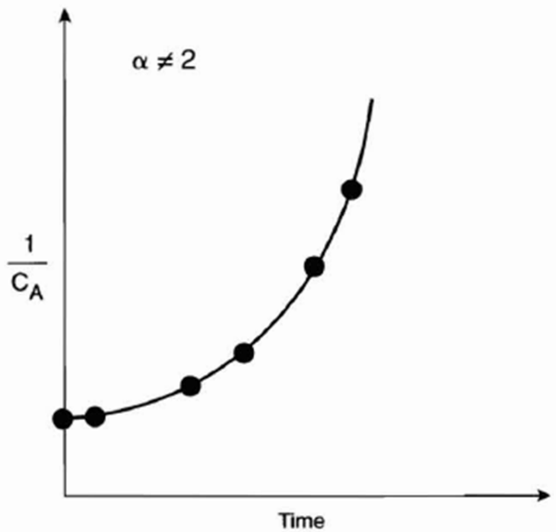


Figure 5-6 Plot of reciprocal concentration as a function of time.

Batch reactor: non-linear regression

- parameters in the non-linear equation (e.g. reaction order and rate constant) are varied to minimize the sum of squares:

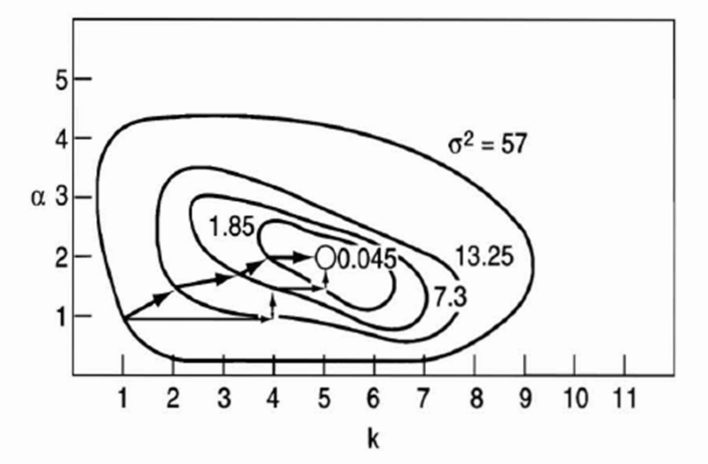
$$\sigma^2 = \frac{s^2}{N-K} = \frac{1}{N-K}\sum_i^N (r_{im} - r_{ic})^2$$

measured value

experimental value

number of parameters to be determined

number of runs



steepest gradient descent trajectory to find α and k

Example 5-3

$$\left(C_6H_5\right)_3 CCl + CH_3OH \rightarrow \left(C_6H_5\right)_3 COCH_3 + HCl$$

$$A \quad + \quad B \quad \rightarrow \quad C \quad + \quad D$$

- The reaction of trityl and methanol is carried out in a solution of benzene and pyridine. Pyridine reacts with HCl and precipitate so the reaction is irreversible. Initial concentration of methanol 0.5 mol/dm^3. and trityl 0.05 mol/dm^3. Determine reaction order with trityl.

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

$$t = \frac{1}{k'} \frac{C_{A0}{}^{1-\alpha} - C_A{}^{1-\alpha}}{1-\alpha}$$

Method of initial rates

- Differential method might be problematic if backward reaction rate is significant. In this case method of initial rates should be used instead
- Series of experiments are carried out at different initial concentrations C_{A0} and initial rate $-r_{A0}$ is determined
- rate dependence is plotted to determine the reaction order, e.g.

$$-r_{A0} = kC_{A0}{}^{\alpha}$$

Method of half-lives

- Half-life time of the reaction (time for the concentration of the reactant to fall by half) is determined as function of initial concentration

$$A \rightarrow \text{Products}$$

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

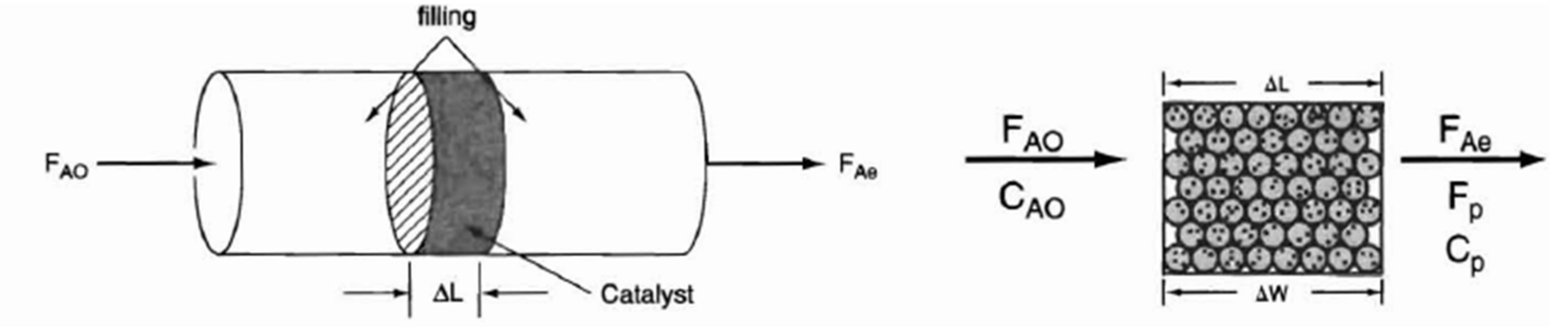
$$t = \frac{1}{k(\alpha - 1)}\left[\frac{1}{C_A{}^{\alpha-1}} - \frac{1}{C_{A0}{}^{\alpha-1}}\right]$$

$t = t_{1/2} \;\; at \;\; C_A = \frac{1}{2}C_{A0}$

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

Differential reactor

- consist of a tube with a thin catalyst disk (wafer)
- conversion of the reactants, concentration and temperature should be small
- most commonly used catalytic reactor to obtain experimental data



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

$$-r'_A = -r'_A(C_{A0})$$

bed concentration is equal to the inlet

Problems

- **P4-26:** A large component in the processing train for fuel cell technology is the water gas shift membrane reactor, where H_2 can diffuse out the sides of the membrane while the other gases cannot.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

- Based on the following information plot the concentration and molar flow rates of each of the reacting species down the length of the membrane reactor. Assume: the volumetric feed is 10dm^3/min at 10atm; equil molar feed of CO and water vapour with C_{T0}=0.4mol/dm^3, equilibrium constant K_e=1.44, reaction rate k=1.37 dm^6/mol·kg cat·min, mass transfer coefficient for H_2 kc=0.1dm^3/mol·kg cat·min.Compare with PFR.
- **P5-13**