A First Course on Kinetics and Reaction Engineering

Class 16 on Unit 16

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
  - A. Rate Expressions
  - B. Kinetics Experiments
  - C. Analysis of Kinetics Data
    - 13. CSTR Data Analysis
    - 14. Differential Data Analysis
    - 15. Integral Data Analysis
    - 16. Numerical Data Analysis
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors

Numerical Least Squares

- When a single-response model equation cannot be linearized, numerical least squares may offer a solution
  - You'll need to provide the experimental set and response variable data, a guess for each model parameter and code that calculates the model predicted response for a data point, given the model parameters and the set variable values for that data point
- When a single-response model equation cannot be analytically integrated or explicitly solved for the response variable, numerical least squares may offer a solution
  - Also if the model is a set of algebraic equations or a set of initial value, ordinary differential equations
  - The model equation(s) will need to be solved numerically
    - In the code above, you will need to call an appropriate equation solver
    - You will need to provide additional input items
      - guesses for the solution (algebraic equations) or initial/final values (ODEs)
      - code to evaluate the equations being solved
  - The code you provide above must use these results to calculate the model predicted response
- Trade-offs
  - Linear least squares requires analytical integration (for ODE models), linearization and calculation of re-defined set and response variables, but the parameters are calculated directly
  - Numerical least squares eliminates the need to integrate ODEs, linearize equations and calculate re-defined variables, but finding the parameters requires a guess
    - If the guess is not close enough, the method may fail to find values for the parameters

Analyzing Multiple Response Data

- When multiple response data are involved
  - You can't use numerical least squares fitting routines provided by common mathematics software packages
    - they are written to minimize the sum of the squares of the errors in a single response variable
  - Instead, you will need to
    - decide what objective function is an appropriate replacement for the sum of the squares of the errors and provide code to calculate it, given the experimental and model-predicted responses
    - use a numerical minimization routine instead of a numerical least squares routine
      - most mathematics software packages provide several
    - calculate statistical quantities such as correlation coefficients and 95% confidence intervals yourself
- The solution of the model equations and calculation of the model-predicted response can be done numerically as described on the last slide.
- A simple sum of the squares of the errors of all responses is ***almost never the appropriate objective*** function to minimize when finding the best values for the parameters
  - i. e. do not use $$\Phi = \sum_{\substack{j=\text{ all}\\\text{data}\\\text{points}}} \left[\left(y_{1,\text{model}} - y_{1,\text{expt.}} \right)_j^2 + \left(y_{2,\text{model}} - y_{2,\text{expt.}} \right)_j^2 \right]$$
- If every response has been measured in every experiment (dense response matrix) and the errors can be assumed to be Normally distributed, minimize this determinant

$$\Phi = \begin{vmatrix} \sum\limits_{\text{all j}} \left(\varepsilon_{1j}\right)^2 & \sum\limits_{\text{all j}} \varepsilon_{1j}\varepsilon_{2j} & \cdots & \sum\limits_{\text{all j}} \varepsilon_{1j}\varepsilon_{nj} \\ \sum\limits_{\text{all j}} \varepsilon_{1j}\varepsilon_{2j} & \sum\limits_{\text{all j}} \left(\varepsilon_{2j}\right)^2 & \cdots & \sum\limits_{\text{all j}} \varepsilon_{2j}\varepsilon_{nj} \\ \vdots & \vdots & \ddots & \vdots \\ \sum\limits_{\text{all j}} \varepsilon_{1j}\varepsilon_{nj} & \sum\limits_{\text{all j}} \varepsilon_{2j}\varepsilon_{nj} & \cdots & \sum\limits_{\text{all j}} \left(\varepsilon_{nj}\right)^2 \end{vmatrix}$$

$$\varepsilon_{ij} = \left(y_{i,\text{model}} - y_{i,\text{expt.}} \right)_j$$

Questions?

Activity 15.2

The gas phase, isothermal decomposition shown in reaction (1), was studied at 1150 K and 1 atm pressure using a PFR.

$$2\,A \rightarrow 2\,Y + Z \qquad (1)$$

The feed was pure A, and the tubular reactor had a volume of 150 cm^3. The inlet flow rate was varied and the outlet partial pressure of Z was measured. The data are tabulated in the table to the right.

Group 1: Test the adequacy of $r_A = -k \cdot C_A$ as a rate expression.

Group 2: Test the adequacy of $r_A = -k \cdot C_A^2$ as a rate expression.

Inlet Feed Rate ($cm^3\ min^{-1}$)	Outlet Mole Fraction of Z
2.26	0.088
1.23	0.131
0.73	0.166
0.51	0.195
0.29	0.228
0.17	0.260
0.09	0.287

Recall the Solution Process from Class 15

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable
- Write the mole balance design equation for the reactor used in the experiments
- Substitute the rate expression to be tested into the design equation
- Integrate the mole balance
  - Identify the dependent and independent variables
  - Identify any other variable quantities appearing in the mole balance
  - Express the other variables in terms of the dependent variable and the independent variable
  - Substitute for the other variables in the design equation so only the dependent and independent variables remain
  - Separate the variables
  - Integrate the design equation
- Linearize the integrated design equation
- Calculate the values of y and x for each experimental data point
- Fit the linear model to the corresponding x-y data
- Decide if the fit is acceptable and report the values and uncertainties for the kinetic parameters

Mole Balance Design Equation

- Mole balance on A: $\frac{d\dot{n}_A}{dz} = \frac{\pi D^2}{4} r_A$
- Substitute the rate expressions

$$\frac{d\dot{n}_A}{dz} = \frac{-\pi D^2}{4} kC_A \qquad\qquad \frac{d\dot{n}_A}{dz} = \frac{-\pi D^2}{4} kC_A^2$$

- Prepare for integration
  - Definition of concentration and ideal gas law: $C_A = \frac{\dot{n}_A}{\dot{V}} = \frac{\dot{n}_A P}{\dot{n}_{tot} RT}$
  - Mole table or definition of extent of reaction
    - $\dot{n}_A = \dot{n}_A^0 - 2\xi \quad \Rightarrow \quad \xi = \frac{\dot{n}_A^0 - \dot{n}_A}{2}$
    - $\dot{n}_{tot} = \dot{n}_A^0 + \xi \quad \Rightarrow \quad \dot{n}_{tot} = \frac{3\dot{n}_A^0 - \dot{n}_A}{2}$
  - Substituting

$$\frac{d\dot{n}_A}{dz} = \frac{-\pi D^2 kP}{2RT} \frac{\dot{n}_A}{3\dot{n}_A^0 - \dot{n}_A} \qquad\qquad \frac{d\dot{n}_A}{dz} = \frac{-\pi D^2 kP^2}{R^2 T^2} \frac{\dot{n}_A^2}{\left(3\dot{n}_A^0 - \dot{n}_A\right)^2}$$

- Separate the variables and integrate

$$\int_{n_A^0}^{n_A} \frac{3\dot{n}_A^0 - \dot{n}_A}{\dot{n}_A} d\dot{n}_A = \frac{-\pi D^2 kP}{2RT} \int_0^L dz \qquad\qquad \int_{n_A^0}^{n_A} \left(\frac{3\dot{n}_A^0 - \dot{n}_A}{\dot{n}_A}\right)^2 d\dot{n}_A = \frac{-\pi k}{2}\left(\frac{DP}{RT}\right)^2 \int_0^L dz$$

$$\left(\dot{n}_A - \dot{n}_A^0\right) - 3\dot{n}_A^0 \ln\left(\frac{\dot{n}_A}{\dot{n}_A^0}\right) = \frac{\pi D^2 kPL}{2RT}$$

$$9\left(\dot{n}_A^0\right)^2 \left(\frac{1}{\dot{n}_A} - \frac{1}{\dot{n}_A^0}\right) + 6\dot{n}_A^0 \ln\left(\frac{\dot{n}_A}{\dot{n}_A^0}\right) - \left(\dot{n}_A - \dot{n}_A^0\right) = \frac{-\pi kL}{2}\left(\frac{DP}{RT}\right)^2$$

$$\left(\dot{n}_A - \dot{n}_A^0\right) - 3\dot{n}_A^0 \ln\left(\frac{\dot{n}_A}{\dot{n}_A^0}\right) = \frac{\pi D^2 kPL}{2RT} \qquad 9\left(\dot{n}_A^0\right)^2\left(\frac{1}{\dot{n}_A} - \frac{1}{\dot{n}_A^0}\right) + 6\dot{n}_A^0 \ln\left(\frac{\dot{n}_A}{\dot{n}_A^0}\right) - \left(\dot{n}_A - \dot{n}_A^0\right) = \frac{-\pi kL}{2}\left(\frac{DP}{RT}\right)^2$$

- Neither equation can be properly linearized for fitting by linear least squares
- Each equation has only one parameter, *k*
  - Rearrange to get expression for *k*
  - Calculate value of *k* for each data point
  - Find average *k* and its standard deviation
  - Check that standard deviation is small compared to average and there are no trends in the differences between individual *k* values and the average
- To calculate *k*
  - *P* and *T* are given, *R* is a known universal constant
  - Note that $\pi \cdot D^2 \cdot L = 4 \cdot V$, and *V* is given
  - Feed is pure A, so $\dot{n}_A^0 = \dfrac{P\dot{V}^0}{RT}$
  - From mole table or definition of extent of reaction
    - $\xi = \dfrac{\dot{n}_A^0 - \dot{n}_A}{2}$ (previous slide)
    - $y_Z = \dfrac{\dot{n}_Z}{\dot{n}_{tot}} = \dfrac{\xi}{\dot{n}_A^0 + \xi} = \dfrac{\dot{n}_A^0 - \dot{n}_A}{2\dot{n}_A^0 + \dot{n}_A^0 - \dot{n}_A} = \dfrac{\dot{n}_A^0 - \dot{n}_A}{3\dot{n}_A^0 - \dot{n}_A} \quad \Rightarrow \quad \dot{n}_A = \dot{n}_A^0 \dfrac{1 - 3y_Z}{1 - y_Z}$

Results

Inlet Feed Rate (cm^3 min^{-1})	Outlet Mole Fraction of Z	First Order *k* (min^{-1})	Second Order *k* (cm^3 mol^{-1} min^{-1})
2.26	0.088	0.0034	753
1.23	0.131	0.0032	787
0.73	0.166	0.0027	759
0.51	0.195	0.0026	797
0.29	0.228	0.0020	750
0.17	0.260	0.0017	786
0.09	0.287	0.0012	797
	Average:	0.0024	775
	Standard Deviation:	0.0008	21

- First order standard deviation is 33% of average and values show a trend
- Second order standard deviation is 3% of average and there does not appear to be a trend
- The second order rate expression is acceptable

Numerical Solution of Initial Value ODEs

- Sets of initial value ODEs

$$\frac{dz_1}{dt} = f_1(t, z_1, z_2, \cdots, z_n); \quad z_1(t_0) = z_1^0$$

$$\frac{dz_2}{dt} = f_2(t, z_1, z_2, \cdots, z_n); \quad z_2(t_0) = z_2^0$$

$$\vdots$$

$$\frac{dz_n}{dt} = f_n(t, z_1, z_2, \cdots, z_n); \quad z_n(t_0) = z_n^0$$

  - Critical distinction - value of every dependent variable is known at the same value of the independent variable (t_0)
  - Also know the "final" value of t or one of the z_i; solve for the corresponding unknown values of all the other variables
- Approach
  - Approximate the z_i over a small range of t from t_0 to $t_0 + h$ using a convenient mathematical function (e. g. linear)
  - Approximate constants in the chosen mathematical function (e. g. slope in a linear function) using the equations being solved
  - Calculate the values of the z_i at $t = t_0 + h$ using the approximate equations
  - Use the result as the new value of t_0 and repeat many times until t or z_i reaches its known "final" value

Numerical Solution of Initial Value ODEs

- Known Issues
  - Generally the smaller the “step size,” h, the greater the accuracy
    - but if h becomes too small, numerical roundoff will introduce significant errors
  - Stiff ODEs
    - One dependent variable changes very abruptly over a very small range of the independent variable
    - The changes in that variable affect the changes in other dependent variables over a much larger range of the independent variable
- Many different variations on the approach
  - Runge-Kutta is arguably the most popular for non-stiff equations
  - Special methods are required when solving stiff equations
- MATLAB provides several different built in functions
  - ode45 can be used for non-stiff equations; it implements the Runge-Kutta method
  - ode15s can be used of stiff equations
  - By default the built in solvers assume that the final value of t is known
    - An additional termination criterion can be specified where the equations are solved until one of the z_i reaches a known final value
      - A final value of t still must be specified
      - zi must reach its final value before t reaches the final value specified for it
- Template files named SolvIVDifI.m and SolvIVDifD.m are provided with instructions for their use
  - SolvIVDifI.m when the final value of independent variable is known
  - SolvIVDifD.m when the final value of one of the dependent variables is known

Problem Statement

In equations (1) and (2), A is a constant with a value of 0.1597. Calculate the value of t at which z_1 equals half its initial value and the ratio of z_1 to z_2 at this t.

$$\frac{dz_1}{dt} = -A\frac{z_1}{z_1 + z_2} \quad ; \quad z_1(0) = 0.103 \qquad (1)$$

$$\frac{dz_2}{dt} = 0.5A\frac{z_1}{z_1 + z_2} \quad ; \quad z_2(0) = 0.0 \qquad (2)$$

- The equations are ordinary differential equations; both boundary conditions are specified at t = 0, making them initial value ODEs
- The MATLAB template file, SolvIVDifD.m can be used to solve the equations because the final value of a dependent variable is known
  - Follow the step-by-step instructions for the modification and use of SolvIVDifD.m
  - Save a copy of the template file as S5_Example_2
    - Change the introductory comment to reflect the purpose of this modified file
    - Change the function statement to match the filename
- First required modification
  - Enter values of all constants involved in the problem
  - Here only one constant, A = 0.1597

Required Modifications

```
%
% This file requires six modifications before each use; the locations
% where editing is required are indicated by the comment "% EDIT HERE"
%
function [t_f,z] = SolvIVDifD
    % Known quantities and constants (in consistent units)
% EDIT HERE (Required modification 1 of 6):
    % define universal and problem-specific constants here
```

- Modify internal function odeqns so it evaluates the functions, f

$$\frac{dz_1}{dt} = f_1\left(t, z_1, z_2\right) = -A\frac{z_1}{z_1 + z_2}$$

$$\frac{dz_2}{dt} = f_2\left(t, z_1, z_2\right) = 0.5A\frac{z_1}{z_1 + z_2}$$

```
    % Function that evaluates the ODEs
    function dzdt = odeqns(t,z)
% EDIT HERE (Required modification 2 of 6):
        dzdt = [
            % Evaluate dz1/dt = f1(t, z1, z2, z3, ..., zn) here
            % Evaluate dz2/dt = f2(t, z1, z2, z3, ..., zn) here
            % and so on through fn, one per line
        ];
    end % of internal function odeqns
```

Required Modifications

- Provide the initial conditions: $z_1(0) = 0.103 \quad z_2(0) = 0.0$

```
% Initial values
t0 = 0.0;
z0 = [
    0.103
    0.0
];
```

- Provide the termination conditions
  - Want to stop because z_1 reaches one half of $z_1(0)$ so set tf to a very large number

```
tf = 1000.0;
```

Required Modifications

- Enter and expression that will cause stop_when to equal zero when z1 reaches its final value: $z_1 - \frac{z_1(0)}{2}$

```
% Function that provides the integration stopping criterion
function [stop_when, isterminal, direction] = stop(t,z)
    isterminal = 1;
    direction = 0;

    % The variable stop_when should equal zero when the desired
    % stopping criterion is reached
    stop_when = z(1)-z0(1)/2.0;
end % of internal function stop
```

- Final required modification
  - Perform any additional calculations using the results of solving the ODEs
  - Here asked to calculate the ratio of z_2 to z_1

```
% calculate the ratio of z2 to z1
ratio = z(2)/z(1)
```

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
  - A. Rate Expressions
  - B. Kinetics Experiments
  - C. Analysis of Kinetics Data
    - 13. CSTR Data Analysis
    - 14. Differential Data Analysis
    - 15. Integral Data Analysis
    - 16. Numerical Data Analysis
- Part III - Chemical Reaction Engineering
  - A. Ideal Reactors
    - 17. Reactor Models and Reaction Types
  - B. Perfectly Mixed Batch Reactors
  - C. Continuous Flow Stirred Tank Reactors
  - D. Plug Flow Reactors
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors