A First Course on Kinetics and Reaction Engineering

Class 2 on Unit 2

Where We've Been

- Part I - Chemical Reactions
  - 1. Stoichiometry and Reaction Progress
  - 2. Reaction Thermochemistry
    - Numerical Solution of Non-Linear Equations (Supplemental Unit S2)
  - 3. Reaction Equilibrium
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors

Reaction Thermochemistry

- Heat of reaction at 298 K
  - Using heats of formation at 298 K
    - $\Delta H_j^0(298\ \mathrm{K}) = \sum_{\substack{i=\text{ all}\\ \text{species}}} \nu_{i,j} \Delta H_{f,i}^0(298\ \mathrm{K})$
  - Using heats of combustion at 298 K
    - $\Delta H_j^0(298\ \mathrm{K}) = \sum_{\substack{i=\text{ all}\\ \text{species}}} \nu_{i,j} \left(-\Delta H_{c,i}^0(298\ \mathrm{K})\right)$
- Heat of reaction at other temperatures
  - If there are no phase changes between 298 K and the temperature of interest
    - $\Delta H_j^0(T) = \Delta H_j^0(298\ \mathrm{K}) + \sum_{\substack{i=\text{ all}\\ \text{species}}} \left(\nu_{i,j} \int_{298\,K}^{T} \hat{C}_{p,i}\, dT \right)$
- Gibbs free energy change for reaction at 298 K
  - $\Delta G_j^0(298\ \mathrm{K}) = \sum_{\substack{i=\text{all}\\ \text{species}}} \nu_{i,j} \Delta G_{f,i}^0(298\ \mathrm{K})$
- Adiabatic temperature change
  - If there are no phase changes between initial and final temperatures, T_1 and T_2
    - $\sum_{j=1}^{N_{ind}} \xi_j \left(-\Delta H_j(T_1)\right) = \sum_{\substack{i=all\\ species}} \int_{T_1}^{T_2} \hat{C}_{p,i} \left(n_i^0 + \nu_{i,j}\xi_j\right) dT$

Questions?

Calculation of Heats of Reaction

- This activity will use the 02_Activity_1_Handout.pdf file; please take it out
- The handout is a solution to a problem
  - It presents the calculation of the heat of the water-gas shift reaction at 250 °C
  - It contains one or more mistakes
- Identify as many errors as you can in the next ~5 minutes

Calculation of Heats of Reaction

- This activity will use the 02_Activity_1_Handout.pdf file; please take it out
- The handout is a solution to a problem
  - It presents the calculation of the heat of the water-gas shift reaction at 250 °C
  - It contains one or more mistakes
- Identify as many errors as you can in the next ~5 minutes
  - You can't arbitrarily mix heats of formation and combustion; the calculated heat at 298K is wrong.
    - The heat calculated in the solution is for $C + CO + O_2 + H_2O \rightarrow 2\ CO_2 + H_2$ (if the correct values of the stoichiometric coefficients are used)
  - While the proper sign convention was used, the calculation used the starting moles of reactants and final moles of products where it should have used stoichiometric coefficients.
  - The calculation failed to account for the latent heat of vaporization of water upon heating from 298 to 543 K
  - There may be a problem with the heat capacities: it seems odd that hydrogen is nearly equal to the carbon oxides
    - Actually, the values are bad because the calculation took the first term of a polynomial expression and ignored the temperature dependent terms (you wouldn't be expected to catch this just by looking at the calculation)
- Consider how to correct the solution
  - What equations would you use?
  - What additional data would you need, beyond what was provided?

Common Ways to Correct the Mistakes

- Calculation of the heat of reaction at 298 K
  - Use heats of combustion
    - with liquid water as the product
    - with hypothetical ideal gas water as the product

$$\Delta H_1^0(298\text{ K}) = \nu_{CO,1}\left(-\Delta H_{c,CO}^0(298\text{ K})\right) + \nu_{CO_2,1}\left(-\Delta H_{c,CO_2}^0(298\text{ K})\right)$$
$$+\nu_{H_2O,1}\left(-\Delta H_{c,H_2O_{(l)}}^0(298\text{ K})\right) + \nu_{H_2,1}\left(-\Delta H_{c,H_2}^0(298\text{ K})\right)$$

  - Use heat of formation
    - with same two standard states

$$\Delta H_1^0(298\text{ K}) = \nu_{CO,1}\left(\Delta H_{f,CO}^0(298\text{ K})\right) + \nu_{CO_2,1}\left(\Delta H_{f,CO_2}^0(298\text{ K})\right)$$
$$+\nu_{H_2O,1}\left(\Delta H_{f,H_2O_{(l)}}^0(298\text{ K})\right) + \nu_{H_2,1}\left(\Delta H_{f,H_2}^0(298\text{ K})\right)$$

- Calculation of the heat of reaction at 543 K

$$\Delta H_1^0(543\text{ K}) = \Delta H_1^0(298\text{ K}) + \nu_{CO,1}\int_{298\text{ K}}^{543\text{ K}} \hat{C}_{p,CO}\,dT + \nu_{CO_2,1}\int_{298\text{ K}}^{543\text{ K}} \hat{C}_{p,CO_2}\,dT + \nu_{H_2,1}\int_{298\text{ K}}^{543\text{ K}} \hat{C}_{p,H_2}\,dT +$$

  - If liquid water was the standard state

$$\nu_{H_2O,1}\left[\int_{298\text{ K}}^{373\text{ K}} \hat{C}_{p,H_2O_{(l)}}\,dT + \Delta H_{v,H_2O}^0(373\text{ K}) + \int_{373\text{ K}}^{543\text{ K}} \hat{C}_{p,H_2O_{(v)}}\,dT\right]$$

  - If ideal gas water was the standard state

$$\nu_{H_2O,1}\int_{298\text{ K}}^{543\text{ K}} \hat{C}_{p,H_2O_{(v)}}\,dT$$

- It is essential to identify one standard state for each species and then to use that standard state consistently throughout the problem solution

Solving Algebraic Equations

- Representation of the equations: $\begin{cases} 0 = f_1(z_1, z_2, \cdots, z_n) \\ 0 = f_2(z_1, z_2, \cdots, z_n) \\ \vdots \\ 0 = f_n(z_1, z_2, \cdots, z_n) \end{cases}$
  - or in vector form: $0 = \underline{f}(\underline{z})$
- General approach
  - Guess the solution, $\underline{z}_0$, use the guess to generate approximate linear equations, solve the approximate linear equations to obtain an improved guess
  - Repeat that process until
    - A specified number of iterations have occurred
    - A specified number of function evaluations have occurred
    - The values of the functions less than some specified tolerance
    - The values of the unknowns are changing by less than some specified tolerance
- The equations can be linearized by truncating a Taylor series expansion
  - $f_1(z_1, z_2, \cdots, z_n) \simeq f_1(\underline{z}_0) + \left.\frac{\partial f_1}{\partial z_1}\right|_{\underline{z}_0} \left(z_1 - (z_1)_0\right) + \left.\frac{\partial f_1}{\partial z_2}\right|_{\underline{z}_0} \left(z_2 - (z_2)_0\right) + \cdots + \left.\frac{\partial f_1}{\partial z_n}\right|_{\underline{z}_0} \left(z_n - (z_n)_0\right)$
  - The derivatives in the linearized equation can be approximated numerically
    - $\left.\frac{\partial f_i}{\partial z_j}\right|_{\underline{z}_0} \simeq \frac{f_i\left((z_1)_0, \cdots, \left((z_j)_0 + \delta z_j\right), \cdots, (z_n)_0\right) -_i \left((z_1)_0, \cdots, (z_j)_0, \cdots, (z_n)_0\right)}{\delta z_j}$

Solving Algebraic Equations Using MATLAB

- The built-in MATLAB function fsolve performs the tasks just described
  - The user provides
    - a guess for the solution, $\underline{z}_0$
    - a function that fsolve can call
      - this function takes values of the unknowns, $\underline{z}$, as its only argument
      - it returns the values of the functions, $\underline{f}$, calculated using the values of $\underline{z}$ passed to it
- A MATLAB template file named SolvNonDif.m is provided for your use
  - It requires four modifications
    - Enter the values of any constants that appear in the problem being solved
    - Enter expressions to evaluate the functions, $\underline{f}$, given the values of the variables, $\underline{z}$
    - Enter the values to be used as the guess for the solution, $\underline{z}_0$
    - Enter code to calculate any additional quantities that are desired using the solution to the equations
  - It produces
    - A message stating whether a valid solution was obtained
    - A solution, $\underline{z}$, to the equations
    - The values of the functions, $\underline{f}$, evaluated using the returned solution, $\underline{z}$
    - A listing of the values of any additional quantities you entered code for
  - Step-by-step instructions for using it are provided
  - Example 1 illustrates its use

Problem Statement

In equations (1) through (4) A, B and C are constants with values of 0.2083 mol/min, 5.472 min/mol and 0.4164 mol/min, respectively. Solve the equations for z_1, z_2, z_3 and z_4, and then compute the ratio of z_1 to z_2.

$$f_1\left(\underline{z}\right) = A - B z_1^{1.5} z_2^{0.5} - z_1 = 0 \qquad (1)$$

$$f_2\left(\underline{z}\right) = C - B z_1^{1.5} z_2^{0.5} - z_2 = 0 \qquad (2)$$

$$f_3\left(\underline{z}\right) = B z_1^{1.5} z_2^{0.5} - z_3 = 0 \qquad (3)$$

$$f_4\left(\underline{z}\right) = B z_1^{1.5} z_2^{0.5} - z_4 = 0 \qquad (4)$$

- The equations do not contain derivatives or integrals, only algebraic terms
  - SolvNonDif.m can be used to solve the equations
  - Follow the step-by-step instructions provided with this supplemental unit
- Save a copy of SolvNonDif.m as S2_Example_1.m
  - Modify the initial comment
  - Change the function declaration statement
  - It will require four modifications before it can be used
  - A copy of the fully-modified file is included with this supplemental unit

First Modification of SolvNonDif.m

- First required modification: define variables to hold the values of all constants that appear in the problem being solved
  - Here there are three: A, B and C
  - Results of modification

```
% Modified version of the MATLAB template file SolvNonDif.m used to solve
% Example 1 of Supplemental Unit S2 of "A First Course on Kinetics and
% Reaction Engineering."
%
function z = S2_Example_1
    % Known quantities and constants (in units of mol and min)
    A = 0.2083;
    B = 5.472;
    C = 0.4167;
```

Second Modification of SolvNonDif.m

- Provide code to evaluate the functions, f, within the internal function evalEqns

$$f_1(\underline{z}) = A - Bz_1^{1.5} z_2^{0.5} - z_1 = 0$$

$$f_2(\underline{z}) = C - Bz_1^{1.5} z_2^{0.5} - z_2 = 0$$

$$f_3(\underline{z}) = Bz_1^{1.5} z_2^{0.5} - z_3 = 0$$

$$f_4(\underline{z}) = Bz_1^{1.5} z_2^{0.5} - z_4 = 0$$

  - Resulting modification

```
% Function that evaluates the equations
function f = evalEqns(z)
    term1 = z(1)^1.5*z(2)^0.5;
    f = [
        A - B*term1 - z(1);
        C - B*term1 - z(2);
        B*term1 - z(3);
        B*term1 - z(4);
    ];
end % of internal function evalEqns
```

Third and Fourth Modifications of SolvNonDif.m

- Third modification is to provide guesses for the solution
- Fourth (and final modification) is to calculate additional desired or requested quantities using the solution
  - Here we are asked for the ratio of z_1 to z_2

```
% guesses for the solution
z_guess = [
    1
    1
    1
    1
];

% Solve the set of algebraic equations
z = fsolve(@evalEqns, z_guess);
display('The solver found the following values for the unknowns:');
z
display('The corresponding values of the functions being solved are as follows:');
f = evalEqns(z)

% compute the requested ratio
ratio = z(1)/z(2)
```

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