

Ch.E. 375, W, '09 - Assignment Ten

Computer Tools/Skills in Chemical Engineering

Course web site: <http://courses.washington.edu/checomp/>

Course mailman (send e-mail to entire class): cheme375a_wi09@u.washington.edu

e-book: <http://faculty.washington.edu/finlayso/ebook/>

Reading: Ch. 11, Convection and Diffusion, pp. 209-211, Table 11.2, 214-217

Class: Review homework

Convective diffusion equation, added in Comsol; example

Flow past a sphere

Fluid mechanics and its impact on baseball

Assignment Ten

Consider the device used in Assignment Nine. The flow will be reversed, though, coming in the right and going out on the left-hand side. Change your model to do this. Use a constant velocity of -0.1 cm/sec on each boundary on the right-hand side and $p = 0$ on the left-hand side. For each of the steps below, note the number of elements and the degrees of freedom used in each calculation.

1. Create the mesh from scratch; then refine it once. Solve the flow problem
2. Add the convective diffusion equation to your model. Set the diffusivity to 10^{-4} cm^2/sec . Put in u and v into the boxes for velocity. Set the concentration to 1, 0, 1, 0 from top to bottom on the right-hand side.
3. Go to Solver/Solver Manager. Click on Store solution (to save the flow solution). Then click both the Use Stored Solution buttons; change to Solve For and select only the convective diffusion equation.
4. Solve and plot the concentration at the exit (left-hand side).
5. Use Physics/Subdomain and click on Artificial Diffusion/Petrov-Galerkin
6. Resolve; plot the concentration at the exit.
7. Change the diffusivity to 10^{-5} cm^2/sec and solve; plot the exit concentration. If it isn't smooth, refine the mesh once and resolve. Continue thus until the solution is smooth or you reach 'out of memory' error.

Questions to answer:

1. Is the output well mixed?
2. How does this change when the diffusivity changes from 10^{-4} cm^2/sec to 10^{-5} cm^2/sec ?
3. What is the Peclet number at the exit, defined as the average velocity times height divided by the diffusivity. Remember Peclet numbers below 1000 are manageable, those above 1000 are difficult and require small finite elements, i.e. a large number of elements.
4. Describe in words what happens to the concentration at the outlet when you refine the mesh; when the Peclet number increases.
5. If you wanted better mixing, what would you do?

Ch.E. 375, W, '09 - Assignment Nine
Computer Tools/Skills in Chemical Engineering

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Reading: Ch. 9 and 10, Fluid Flow; pp. 147-151, 156-161, 175-179

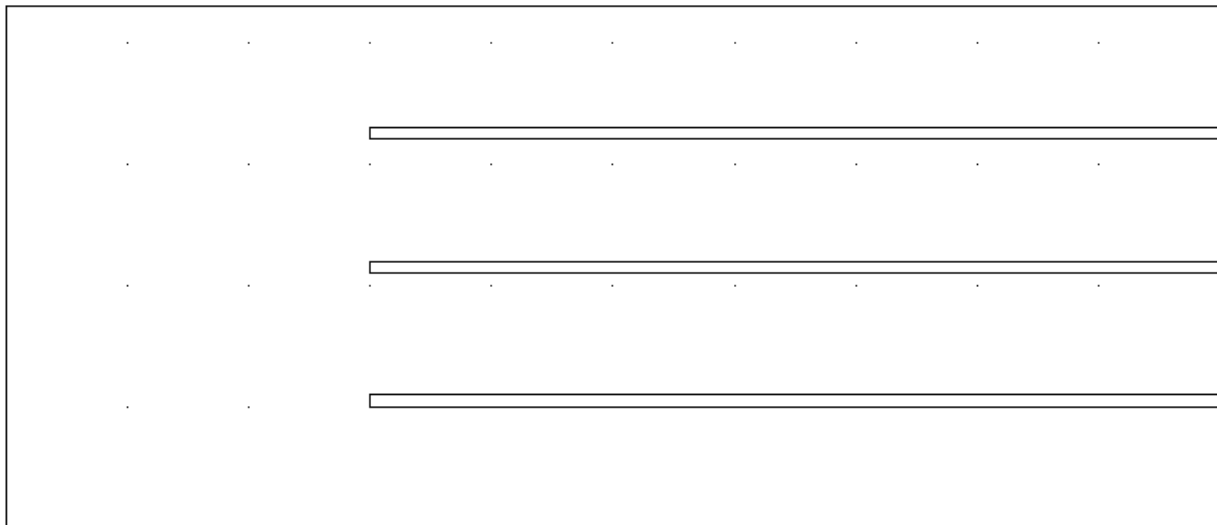
Class: Review of homework: startup of a chemical reactor
Solution of two-point boundary value problems
Solution of 2D and 3D Navier-Stokes equations

Laboratory problem
Problem 9.15.

Assignment Eight

Consider the 2D device shown. Water (density 1 g/cm^3 , viscosity 0.01 g/cm sec) comes in on the left-hand side with an average velocity of 1 cm/sec . The device is 1 cm long and 0.43 cm high. The slits removed are 0.01 cm high and 0.7 cm long. If the lower, left corner is at $x = 0, y = 0$ the inlet velocity is (in cm/sec) $13.95y - 32.45 y^2$. Use the 2D version of Comsol to solve the Navier-Stokes equation in this situation.

- Find the pressure drop needed to achieve this flow.
- Plot the results showing the streamlines and pressure (in color).
- Where is the flow fully developed as between two flat plates?
- What is the Reynolds number at the inlet? in each channel? Is the flow laminar?
- What fraction of flow goes through each channel?
- If the flow is not identical in the different channels, what design changes do you suggest to make them identical? (Just describe the trends, you don't have to produce the design.)



Ch.E. 375, W, '09 - Assignment Eight
Computer Tools/Skills in Chemical Engineering

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Reading: Ch. 8, Chemical Reactions, pp. 111-141, especially pp. 114-116, 134-141

Class: Review of homework: discussion of trends

Types of chemical reactors (this is where the money is made)

Numerical solution of ordinary differential equations

Laboratory problem

Problem 8.5. Biological stirred tank reactor.

Assignment Eight

Problem 8.13. The initial concentration is σ_0 not c_0 . Transient version of 8.5.

Ch.E. 375, W, '09 - Assignment Seven

Computer Tools/Skills in Chemical Engineering

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e-book: <http://faculty.washington.edu/finlayso/ebook/>

Reading: Chemical Reaction Equilibria from Molecular Considerations
www.etomica.org, Applications/Modules, Reaction Equilibrium

Class: Review of homework
Demonstration of molecular motion and coming to equilibrium
Derivation of equations to be solved in MATLAB

Laboratory problem and Assignment Seven

Chemical Reaction Equilibria from Molecular Considerations

This assignment studies chemical reaction equilibria from a molecular engineering perspective. We are going to use a program on the internet to perform molecular dynamics calculations; the equilibrium results will also be compared to the solution from continuum equations (based on molecular parameters) solved in MATLAB. Acknowledgement is given to Prof. David Kofke, University at Buffalo, State University of New York. His project is on the internet site www.etomica.org, that was developed with support from the National Science Foundation.

The internet reference is:

www.etomica.org.

Choose Applications/Modules, Choose the Reaction Equilibrium module. There you can read about the model to see the molecular considerations. After reading the background, choose Simulator to get the program. You can run it on-line, or you can download it and run it locally. I've done so on both the PCs in BNS 125 and on a Mac. The MATLAB code is given below, but it is available on the class website, too:

<http://courses.washington.edu/checomp>.

1. Read the material on the website. We have a system with two types of molecules, called red (R) and blue (B). They can react to form dimers according to the following reactions:



The attractive/repulsive potential energy is a short range square well potential. For a molecular separation distance greater than σ , the diameter of interaction, the potential energy is zero. For distances between $\kappa\sigma$ and σ the potential energy of attraction is $-\epsilon$. Thus κ is a fraction, less than 1. (ϵ/k_B is used in the programs, with dimensions of temperature, where k_B is Boltzmann's

constant.) For distances between 0 and $\kappa\sigma$ the repulsive potential is infinite. In addition, we need the number density, ρ , which has units of number of molecules per \AA^2 (angstrom squared).

2. Try the program on the internet site. It has pre-set the parameters to

$$\varepsilon / k_B = 200 \text{ K}, T = 300 \text{ K}, \kappa = 0.65, \sigma = 3 \text{ \AA} \text{ with } 30 \text{ R and } 30 \text{ B initially.}$$

Begin the simulation and look at (a) the molecular motion; (b) composition; (c) fraction. As the calculation proceeds, there are wild fluctuations but the average values settle down. (If more molecules were used, the fluctuations would not be as wild.) Note the mole fractions of the 5 species after some time.

3. Run the MATLAB code for the same set of parameters. (Use 0.88 for the initial density.) The results should be close. The theory for the MATLAB code is provided on page 2, and the code depends on the same molecular parameters.

4. Your assignment is to vary parameters and deduce their effect.

(a) changing T (b) changing σ (c) your choice

For each case report on the effect of changing that parameter and the values you used.

Development of equations

The equations that must be solved for chemical equilibrium are described on the internet page. Here they are summarized. For chemical equilibrium of the three reactions, we have the following balances of chemical potential

$$\mu_{RR} - 2\mu_R = 0$$

$$\mu_{RB} - \mu_R - \mu_B = 0$$

$$\mu_{BB} - 2\mu_B = 0$$

The chemical potentials are given by

$$\mu_i = \mu_i^0 + k_B T \ln \rho + k_B T \ln x_i = \mu_i^0 + k_B T \ln(\rho x_i)$$

For an ideal gas we have taken $\phi_i = 1$. The standard state of each species is a pure component at unit density. For R and B there is only one state possible and the standard states have zero chemical potential. For RR, RB, and BB, the standard states are (molecular arguments are not shown) (here ε is not ε/k_B)

$$\mu_i^0 = \varepsilon - k_B T \ln[\pi\sigma^2(1 - \kappa^2) / \Sigma]$$

In addition, $\Sigma = 1$ for RB and 2 for RR and BB since there is no difference if the 2R atoms are exchanged in the RR molecule.

Thus we must satisfy the following equations (all $f(i) = 0$).

$$\text{RR} : f(1) = \varepsilon - k_B T \ln[\pi\sigma^2(1 - \kappa^2) / 2] + k_B T \ln \rho + k_B T \ln x_{RR} - 2k_B T \ln \rho - 2k_B T \ln x_R$$

$$\text{RB} : f(2) = \varepsilon - k_B T \ln[\pi\sigma^2(1 - \kappa^2) / 1] + k_B T \ln \rho + k_B T \ln x_{RB} - 2k_B T \ln \rho - k_B T \ln x_R - k_B T \ln x_B$$

$$\text{BB} : f(3) = \varepsilon - k_B T \ln[\pi\sigma^2(1 - \kappa^2) / 2] + k_B T \ln \rho + k_B T \ln x_{BB} - 2k_B T \ln \rho - 2k_B T \ln x_B$$

In addition the total number of R atoms and B atoms cannot change.

$$f(4) = [\rho(x_R + 2x_{RR} + x_{RB})]_0 - [\rho(x_R + 2x_{RR} + x_{RB})]$$

$$f(5) = [\rho(x_B + 2x_{BB} + x_{RB})]_0 - [\rho(x_B + 2x_{BB} + x_{RB})]$$

Finally the sum of mole fractions is 1.0

$$f(6) = 1 - x_R - x_B - x_{RR} - x_{RB} - x_{BB}$$

These are the equations solved in the MATLAB code. The molecular parameters are the same ones used in the molecular dynamics calculations. (There is a discrepancy with respect to the density – ignore that and use the value given in the MATLAB code.)

The equations can be rearranged into the form of the usual equilibrium constant for a reaction.

$$k_B T \ln K_{\rho RR} = k_B T \ln x_{RR} - 2k_B T \ln x_R - k_B T \ln \rho$$

$$k_B T \ln K_{\rho RB} = k_B T \ln x_{RB} - k_B T \ln x_R - k_B T \ln x_B - k_B T \ln \rho$$

$$k_B T \ln K_{\rho BB} = k_B T \ln x_{BB} - 2k_B T \ln x_B - k_B T \ln \rho$$

Here the equilibrium constants are given by

$$\ln K_{\rho RR} = -\frac{\varepsilon}{k_B T} + \ln \frac{\pi \sigma^2 (1 - \kappa^2)}{\Sigma (= 2)}, \quad \ln K_{\rho RB} = -\frac{\varepsilon}{k_B T} + \ln \frac{\pi \sigma^2 (1 - \kappa^2)}{\Sigma (= 1)},$$

$$\ln K_{\rho BB} = -\frac{\varepsilon}{k_B T} + \ln \frac{\pi \sigma^2 (1 - \kappa^2)}{\Sigma (= 2)}$$

The subscript ρ indicates that this equilibrium constant depends on the number density, not the pressure. Then the equations governing equilibrium are

$$\ln K_{\rho RR} = \ln x_{RR} - 2 \ln x_R - \ln \rho \quad \text{or} \quad K_{\rho RR} = \frac{x_{RR}}{x_R^2 \rho}$$

$$K_{\rho RB} = \frac{x_{RB}}{x_B x_R \rho} \quad \text{and} \quad \ln K_{\rho BB} = \frac{x_{BB}}{x_B^2 \rho}$$

Note that the number density takes the place of pressure in the earlier formulations of chemical equilibrium. Thus, it would be possible to calculate the equilibrium constant for chemical equilibrium in the form

$$K_{RR} = \frac{x_{RR}}{x_R^2 p}, \quad K_{RB} = \frac{x_{RB}}{x_B x_R p}, \quad \text{and} \quad K_{BB} = \frac{x_{BB}}{x_B^2 p}$$

from the molecular value. The molecular calculations can be compared with experiment by comparing the equilibrium compositions.

MATLAB code:

```
% run_dimer.m
global eps sigma kappa kT initial energy term1 term2
eps_k = 200; % (negative) energy of attraction/Boltzmann
constant (K)
sigma = 3; % Angstroms, diameter on interaction
kappa = 0.65; % fraction of sigma that is repulsion
T = 300;% temperature (K)
energy = eps_k/T
term2 = log(pi*sigma^2*(1-kappa^2)/2)
term1 = log(pi*sigma^2*(1-kappa^2))
energy-term2
energy-term1
initial = [.5 .5 .88];%start at xR xB density(number/area)
x0 = [0.37 .37 .1 .06 .1 .04];
%OPTIONS = OPTIMSET('MaxFunEvals',1000)
%x=fsolve('dimer',x0,OPTIONS)
x=fsolve('dimer',x0)
feval('dimer',x)

% dimer.m
function f=dimer(x)
global eps sigma kappa kT initial energy term1 term2
xR = x(1);
xB = x(2);
xRR = x(3);
xRB = x(4);
xBB = x(5);
rho = x(6);
f(1) = energy - term2 + log(xRR)-log(rho)-2*log(xR);
f(2) = energy - term1 + log(xRB)-log(rho)-log(xR)-log(xB);
f(3) = energy - term2 + log(xBB)-log(rho)-2*log(xB);
f(4) = initial(3)*initial(1)-rho*(xR+2*xRR+xRB);
f(5) = initial(3)*initial(2)-rho*(xB+2*xBB+xRB);
f(6)=1-xR-xB-xRR-xRB-xBB;
```

Ch.E. 375, W, '09 - Assignment Six
Computer Tools/Skills in Chemical Engineering

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e-book: <http://faculty.washington.edu/finlayso/ebook/>

Reading: Using AspenPlus –Read Ch. 7, pp. 89-108, especially 89-97.

Class: Review of homework
Process Simulation using AspenPlus: What is different?
Convergence: will it or won't it – work smart!

Laboratory problem

Prepare the flowsheet for the process in Assignment Six.

Assignment Six

This assignment is a combination of problems 5.6 and 7.5. The full description is given below, but you are advised to read the material in the original problem statement for clarification.

Synthetic ethanol is made by vapor-phase hydration of ethylene as shown in Fig. 5-15.

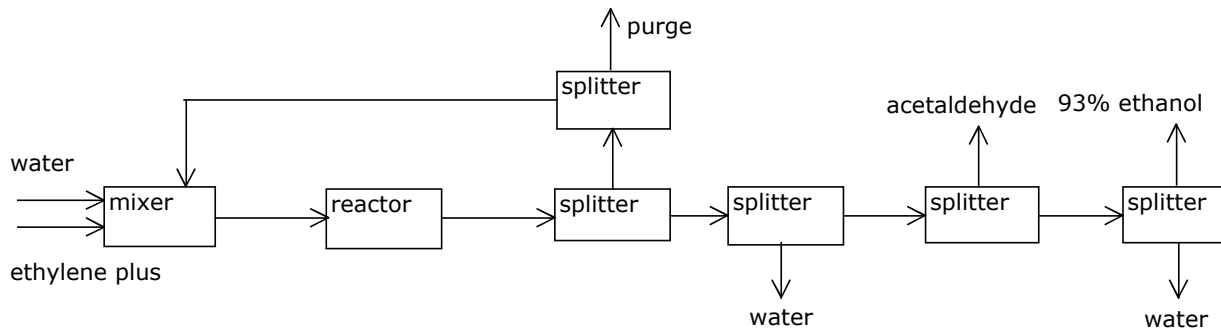


Figure 5-15. Ethanol process (Schematic only)



Water and ethylene is mixed with a recycle stream and sent to a reactor where the reaction in Eq. (5.21) takes place (5% conversion per pass). The ethylene feed is 97% ethylene but also contains acetylene (2.9%) and inert gases (0.1%) and the total stream is 100 lb.mol/hr. The acetylene reacts with water, too, forming acetaldehyde (50% conversion per pass).



The reactor effluent is cooled to remove the liquids (ethanol, acetaldehyde, water). The gases (ethylene, acetylene, and inert gases) are recycled, but a purge stream is needed to remove the inert gases. *Note: This is a schematic diagram only. Your process is much more sophisticated.*

The feed streams are at one atmosphere and room temperature. Since only 5% of the ethylene reacts each pass, the amount of ethylene in the recycle stream must be large. Also, it is desirable to have the water molar flow rate going into the reactor at 60% of the ethylene molar flow rate, and to keep the concentration of inert into the reactor at a few percent of the total flow rate into the reactor. The first of these requirements is met by making sure there is enough water in the recycle stream; you may also use a controller. The second of these requirements is determined by the fraction of the recycle stream that is purged. The reactor operates at 960 psia and 570 °F. Thus, you must heat the reactor feed, and after the reaction occurs you must cool the product. All the separation units can be modeled using simple splitters, even though in the real process vapor-liquid separators and distillation towers are used. The first splitter, modeling the vapor-liquid separator, runs at 100 psia and 130 °F; all the light gases go to the vapor: acetylene, ethylene, carbon dioxide. The vapor stream has 5% of the acetaldehyde, ethanol, and water; the rest goes out as liquid to the next splitter. The next splitter removes 60% of the water, and all the other components go out the top. The next splitter removes 80% of the acetaldehyde, all the lighter components, and 0.1% of the water and ethanol. The final splitter splits the streams into an overhead that is about 90% ethanol, all the acetaldehyde, and the rest water. If you lower the pressure anywhere, you need to supply compressors.

Use either the WILSON–RK (Wilson equation) or UNIQUAC–RK thermodynamics. We've tested both of those for the ethanol-water system by comparison with experimental data and they gave good results.

Convergence can be done first with Wegstein (the default choice), but it might require Broyden to finish the convergence. (see pages 100-105)

Your report should include a process flow-sheet, a table of stream flow-rates, temperatures, and pressures. In addition, list the operating parameters for any pumps and compressors and the heat duties of heat exchangers and the reactor. Also provide an overall balance: what fraction of the ethylene fed to your process ends up in the ethanol product stream?

Ch.E. 375, W, '09 - Assignment Five
Computer Tools/Skills in Chemical Engineering

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Reading: Using AspenPlus – Review pp. 35-37, Read Ch. 6, pp. 73-87

Class: Review of homework

Testing Thermodynamics using Vapor-liquid equilibria

Distillation using AspenPlus; DSTWU and RADFRAC

Laboratory problem

Find a y-x diagram for ethanol-water system at 14.7 psia. Use the UNIQUAC-RK thermodynamics and compare with Figure 3.7.

Assignment Five

Solve Problem 6.1 and 6.2 using the UNIQUAC-RK thermodynamics. The input stream is stream 2 in Figure 6.9, as listed in Table 6.6, except at 51 psia. Compare the results you obtained with the shortcut method with those obtained with RADFRAC.

Assignment Five. Ch.E. 375, W, '09 - Assignment Four
Computer Tools/Skills in Chemical Engineering

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Reading: Using AspenPlus

Ch. 2, pp. 16-22; Ch. 3, pp. 31-37; Ch. 4, p. 52

Class: Review of homework

Solving vapor-liquid equilibrium problems using AspenPlus

Solving chemical reaction equilibrium problems using AspenPlus

Laboratory problem

Do the examples on pages 16-22.

Assignment Four

Part 1. Using Aspen, solve problem 3.3 using the Flash2 module. Present results for the vapor fraction and composition of both phases. What evidence can you cite that validates your solution? What thermodynamic choice did you make and why?

Part 2. Using Aspen, solve problem 4.7, part 1, using the RGibbs module. Note that you do not need to specify the reactions: all possible reactions among those components will be included. How do your results compare to those in Assignment Three? What thermodynamic option did you use and why?

Ch.E. 375, W, '09 - Assignment Three
Computer Tools/Skills in Chemical Engineering

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Reading: Ch. 4, pp. 41-49, Chemical Reaction Equilibrium with Excel, MATLAB

Class: Theory of chemical equilibrium
Solving chemical equilibrium with Excel
Solving chemical equilibrium with MATLAB

Laboratory problem

4.2. Find the molar flow rates of all species out of an equilibrium reactor when the inlet values of nitrogen, hydrogen, and ammonia are 1.1, 3, and 0.2. The equilibrium constant is 0.05 at 589 °K.

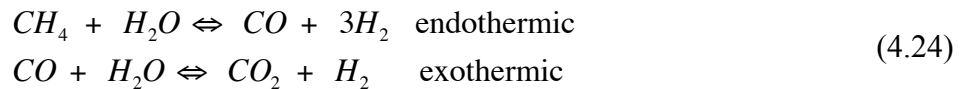
$$K_p = \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} = \frac{y_{NH_3}}{y_{N_2}^{1/2} y_{H_2}^{3/2}} \frac{1}{P} \quad (4.20)$$

for the reaction written as: $\frac{1}{2}N_2 + \frac{3}{2}H_2 \leftrightarrow NH_3$. Use 220 atm for the pressure. First, (a) use Excel; then, (b) use MATLAB. (Hint: you will have to derive some equations.)

Assignment Three

Solve problem 4.7 (modified and restated below) using MATLAB.

4.7. In a steam reformer, steam is added to methane and two (or more) reactions take place.



The composition out of the reformer is based mainly on chemical equilibrium (Marsh, *et al.*, 1994, p. 165). Determine the equilibrium composition when the steam/methane ratio of the inlet stream is 3, the pressure is 14 atm, and the equilibrium constants for the two reactions are, $K_p = 49.0$ and 1.31, respectively.

Ch.E. 375, W, '09 - Assignment Two Computer Tools/Skills in Chemical Engineering

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e-book: <http://faculty.washington.edu/finlayso/ebook/>

Reading:

pp. 11-15, 25-29

Class:

Errors made in homework – how to find

MATLAB: function, feval, fzero, loops, plotting, transfer data, global

Problem: Find the specific volume of n-butane at 500 K and 18 atm using the Redlich-Kwong equation of state in MATLAB

Phase equilibria problems

Solution using Excel

Laboratory problem

Do pp. 11-13 in the book

Assignment Two

Part 1: Using MATLAB and the Redlich-Kwong-Soave equation, plot the compressibility factor for the problem solved in Assignment One: 2.4. Consider a mixture of 25% ammonia, the rest nitrogen and hydrogen in a 1:3 ratio. The gas is 550 °K and compute the compressibility factor for pressures from 10 to 500 atm. The acentric factors for the RK-Soave method are: ammonia, 0.250; H₂, -0.22; nitrogen, 0.040. How do you check your work?

Part 2: (From problem 3.3) Use Excel to solve for the fraction vapor and the composition of vapor and liquid when the vapor-liquid mixture is separated at 51 psia and 130 °F. The z_i values are obtained from the flow rates given in Problem 3.3. The K -values at these conditions are: 4.57, 1.98, 1.60, 0.696, 0.564, respectively.

Ch.E. 375, W, '09 - Assignment One
Computer Tools/Skills in Chemical Engineering

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Class:

Introduction
Summary of equations of state; molecular basis
Single nonlinear equations in Excel
Excel hints – Appendix A
Problem: Find the specific volume of n-butane at 500 K and 18 atm using the Redlich-Kwong equation of state.

Laboratory problems

Part 1. Access the class website.

Part 2. Access the e-book, <http://faculty.washington.edu/finlayso/ebook>

Part 3. 2.5. Find the molar volume of methanol gas at 100 atm and 300 °C using the Redlich-Kwong equation of state, $T_c = 512.6$ K, $p_c = 79.9$ atm, $a = 8.96$ (note error in book), $b = 0.04561$; units of a and b correspond to v in liter / g mol. Use Excel.

Assignment One

2.4. Consider a mixture of 25% ammonia, the rest nitrogen and hydrogen in a 1:3 ratio. The gas is at 270 atm and 550 °K. Use Excel to compute the specific volume using:

- (a) ideal gas law;
- (b) Redlich-Kwong equation of state;
- (c) Redlich-Kwong- Soave equation of state.

The acentric factors for the RK-Soave method are: ammonia, 0.250; H₂, -0.22; nitrogen, 0.040. Where did you get the data you needed? How do the three answers compare? Is the gas ideal or not? Comment.