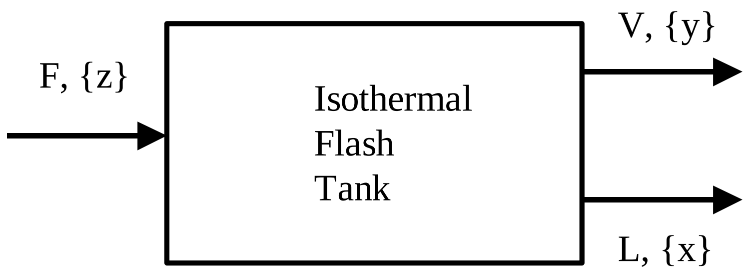
Midterm Examination Number Three
Administered: Friday-Monday, April 9-12, 1999

Problem 1.

Consider an isothermal flash tank:



This unit takes a pressurized liquid, three-component feed stream and exposes it to a low pressure vessel maintained under isothermal conditions. The net result is that some of the fluid is vaporized, while some fluid remains liquid. The compositions of the liquid and vapor phase are determined by the combined analysis of mass balances and Raoult's Law for vapor-liquid equilibrium.

The temperature in the flash tank is $T = 298K$ and the pressure in the tank is $P = 101kPa$.

Raoult's Law states that the product of the liquid mole fraction of component i and the vapor pressure of component i is equal to the partial pressure of component i in the vapor phase:

$$x_i P_i^{vap} = y_i P$$

For Problem 1, Use the following data for the temperature given above

$$P_A^{vap} = 0.6 bar \ @ \ T = 298K$$
$$P_B^{vap} = 1.0 bar \ @ \ T = 298K$$
$$P_C^{vap} = 2.0 bar \ @ \ T = 298K$$

$$F = 100 \ mol/hr \quad V = 44.738 mol/hr \quad L = F - V \ mol/hr$$
$$z_A = 0.4 \quad y_A = ? \quad x_A = ?$$
$$z_B = 0.3 \quad y_B = ? \quad x_B = ?$$
$$z_C = 0.3 \quad y_C = ? \quad x_C = ?$$

Then you have six unknowns, the compositions of the liquid stream and the composition of the vapor stream.

(a) Write equations which will yield the unknowns. Clearly identify the origin of each equation (mass balance, constraint, Raoult's Law)

(b) Convert these equations to a linear form with unknown terms on the left hand side and constants on the right hand side, if they are not already in that form.

(c) Convert the equations to matrices and vectors.

(d) Compute the determinant and rank of the matrix, and list the random values of F and L used in the calculation.

(e) Using MATLAB linear algebra functions, solve for the steady-state values of the unknown compositions. Show MATLAB code.

(Hint: since you have 3 components, you will have three mass balances. You also have 2 streams with constraints that the sum of the mole fractions must be unity. You also have 3 Raoult's Law constraints Therefore, you have8 equations. However, you only have 6 unknowns. Not all of the 8 equations are independent. You must choose 8 independent equations. Part (d) should indicate to you whether you have selected 6 independent equations.)

Solution:

(a) Write equations

A mole balance: $0 = Fz_A - Lx_A - Vy_A$

B mole balance: $0 = Fz_B - Lx_B - Vy_B$ **(not used, dependent)**

C mole balance: $0 = Fz_C - Lx_C - Vy_C$ **(not used, dependent)**

liquid mole fraction constraint: $1 = x_A + x_B + x_C$

vapor mole fraction constraint: $1 = y_A + y_B + y_C$

A equilibrium constraint: $x_A P_A^{vap} = y_A P$

B equilibrium constraint: $x_B P_B^{vap} = y_B P$

C equilibrium constraint: $x_C P_C^{vap} = y_C P$

(b) Put equations in linear form

A mole balance: $Lx_A + Vy_A = Fz_A$

B mole balance: $Lx_B + Vy_B = Fz_B$ **(not used, dependent)**

C mole balance: $Lx_C + Vy_C = Fz_C$ **(not used, dependent)**

liquid mole fraction constraint: $x_A + x_B + x_C = 1$

vapor mole fraction constraint: $y_A + y_B + y_C = 1$

A equilibrium constraint: $x_A P_A^{vap} - y_A P = 0$

B equilibrium constraint: $x_B P_B^{vap} - y_B P = 0$

C equilibrium constraint: $x_C P_C^{vap} - y_C P = 0$

(c) Put equations in matrix form

matrix of coefficients, A (6 x 6)

eqn/var	x_A	x_B	x_C	y_A	y_B	y_C
1	L	0	0	V	0	0
2	0	L	0	0	V	0
3	0	0	L	0	0	V
4	1	1	1	0	0	0
5	0	0	0	1	1	1

6	P_A^{vap}	0	0	$-P$	0	0
7	0	P_B^{vap}	0	0	$-P$	0
8	0	0	P_C^{vap}	0	0	$-P$

vector of right hand sides, b (6x1)

eqn	b
1	Fz_A
2	Fz_B
3	Fz_C
4	1
5	1
6	0
7	0
8	0

(d) Compute the determinant and rank of the matrix.

The rank of the 8 x 6 matrix written above is 6. Therefore, we need only 6 equations. I knocked out 2 of the mass balances (the second and the third) and obtained the matrix below. The rank was still 6 so I knew that I had a set of independent equations.

```
A =
  [55.2620         0         0   44.7380         0         0
    1.0000    1.0000    1.0000         0         0         0
         0         0         0    1.0000    1.0000    1.0000
    0.6000         0         0   -1.0132         0         0
         0    1.0000         0         0   -1.0132         0
         0         0    2.0000         0         0   -1.0132]

b =[40;1;1;0;0;0]

rankA =6
detA =-83.9346
```

```
F = 100;
V = 44.738;
L = F - V;

zA = 0.4;
zB = 0.3;
zC = 0.3;

PvapA = 0.6;
PvapB = 1.0;
PvapC = 2.0;

P = 1.01325;
```

```
A = [L  0  0  V  0  0
%   0   L  0  0  V  0
%   0   0  L  0  0  V
   1 1  1  0  0  0
   0 0  0  1  1  1
   PvapA  0  0  -P 0  0
   0 PvapB   0  0  -P 0
   0 0  PvapC   0  0  -P]

%b =[F*zA; F*zB; F*zC; 1; 1; 0; 0; 0]
b =[F*zA; 1; 1; 0; 0; 0]

rankA = rank(A)

detA = det(A)

x = A\b

xA = x(1);
xB = x(2);
xC = x(3);
yA = x(4);
yB = x(5);
yC = x(6);

f(1) = L*xA + V*yA - F*zA;
f(2) = L*xB + V*yB - F*zB;
f(3) = L*xC + V*yC - F*zC;
f(4) = yA + yB + yC - 1.0;
f(5) = xA + xB +xC - 1.0;
f(6) = PvapA*xA -P*yA;
f(7) = PvapB*xB -P*yB;
f(8) = PvapC*xC -P*yC;
```

x = [0.4893
0.3018
0.2090
0.2897
0.2978
0.4125]

$x_A = 0.4893$ $x_B = 0.3018$ $x_C = 0.2090$

$y_A = 0.2897$ $y_B = 0.2978$ $y_C = 0.4125$

Problem 2.

Consider the same flash tank describe in Problem (1). Now consider that the L and V stream flowrates are also unknowns. This makes the problem a set of 8 non-linear equations. Use syseqn.m or the MATLAB program of your choice to solve for liquid and vapor stream compositions and flow-rates. Use an initial guess of

x_A =0.33 x_B =0.33 x_C =0.33

y_A =0.33 y_B =0.33 y_C =0.33

L =50 V =50

Show your input file, syseqninput.m. Show your answer. Clearly indicate which variables are which.

Solution:

```
syseqn([0.33,0.33,0.33,0.33,0.33,0.33,50,50])
VARIABLE    INPUT     OUTPUT
    1   3.3000000e-001  4.8927470e-001
    2   3.3000000e-001  3.0176542e-001
    3   3.3000000e-001  2.0895988e-001
    4   3.3000000e-001  2.8972595e-001
    5   3.3000000e-001  2.9781931e-001
    6   3.3000000e-001  4.1245473e-001
    7   5.0000000e+001  4.4738291e+001
    8   5.0000000e+001  5.5261709e+001
```

x_A =0.4893 x_B =0.3018 x_C =0.2090

y_A =0.2897 y_B =0.2978 y_C =0.4125

V =44.738 mol/hr L =55.262 mol/hr

Problem 3.

In an isothermal batch reactor, the following reaction occurs:

$$A + 2B \rightarrow C$$

You know the initial concentrations of A, B, and C: A_o, B_o, and C_o.

You record the concentration of C, $C(t)$, as a function of time, t.

You repeat the experiment for several different temperatures, T.
(Thus you have the concentration as a function of time and temperature.)

From kinetics, you know the rate of production of C is given by:

$$rate(t) = \frac{dC(t)}{dt} = A \cdot B^2 \cdot k_o \exp^{\frac{-Ea}{RT}} = (A_o - C) \cdot (B_o - 2C)^2 \cdot k_o \exp^{\frac{-Ea}{RT}}$$

You want to perform a regression to obtain the reaction rate constant, k_o and the activation energy, E_a but you couldn't measure the rate, $\frac{dC(t)}{dt}$, only the concentration $C(t)$. (This is how the process usually works). To handle this, you can rearrange and analytically integrate this differential equation to yield:

$$k_o \exp^{\frac{-Ea}{RT}} t = \left(\frac{-2}{(B_o - 2A_o)^2}\right)\left[\begin{array}{l} 2(B_o - 2A_o)\left(\frac{1}{B_o - 2C} - \frac{1}{B_o - 2C_o}\right) \\ -2\ln\left(\frac{B_o - 2C}{B_o - 2C_o}\right) + \frac{1}{2}\ln\left(\frac{A_o - C}{A_o - C_o}\right) \end{array}\right]$$

(a) Put this equation in a form like $y = b_o + b_1 x$ so that you could perform least squares linear regression on it to determine the reaction rate constant, k_o and the activation energy, E_a, from data which gives Clearly identify all four variables in this equation, $y = b_o + b_1 x$. Clearly identify how to obtain k_o and E_a from the fit constants.

(b) Download the data file, xm03file.zip from the Homeworks section of the course website. This file has been zipped with WinZip. You must unzip the file using the WinZip utility, available on the computers in Dougherty 314. Once the file has been unzipped, you can read the data as an Excel spreadsheet, which gives concentration as a function of time and temperature. From this data, calculate

(a) k_o and E_a

(b) the standard deviations of k_o and E_a

(c) the measure of fit of the model. Clearly indicate all answers. Do not simply provide an ambiguous program output.

Solution:

```
» regress(1,1,80,1,'file.x3p3s99.dat')
COMPLETED A LINEAR REGRESSION ON THE DATA IN file.x3p3s99.dat
THE NUMBER OF PARAMETERS IS    2
The zeroth order parameter was used.
THE NUMBER OF DATA POINTS IS   80
PARAMETER    VALUE     STANDARD DEVIATION
    1   1.4057494e+001  1.2257327e+000
    2   3.5765021e+004  2.9793620e+003
  MOF =  6.4881022e-001
  F =  1.4410214e+002
  degrees of freedom =  7.8000000e+001
```

$$k_o = \exp(b_o) = \exp(14.057494) = 1.27 \cdot 10^6$$

$$E_a = b_1 = 35765.021$$

$$\sigma_{k_o} = \sigma_{\exp(b_o)} \approx \exp(\sigma_{b_o}) = 3.41$$

$$\sigma_{E_a} = \sigma_{b_1} = 2979.362$$

Measure of Fit = MOF = 0.64881022