Exam III Solutions
Administered: Wednesday, November 6, 2024
24 points

For each problem part: 0 points if not attempted or no work shown,
1 point for partial credit, if work is shown,
2 points for correct numerical value of solution

Problem 1. (16 points)
Consider a set of three first order reactions occurring in a closed pot (a batch reactor) involving compounds, OX, MX and PX.

number	reaction	rate expression	rate constant
1	OX → MX	$r_1 = k_1 OX$	$k_1 = 7\ s^{-1}$
2	MX → PX	$r_2 = k_2 MX$	$k_2 = 9\ s^{-1}$
3	PX → OX	$r_3 = k_3 PX$	$k_3 = 5\ s^{-1}$

These equations give rise to the following steady state (at infinite time) mass balances.

compound	rate expression
OX	$0 = k_3 PX - k_1 OX$
MX	$0 = k_1 OX - k_2 MX$
PX	$0 = k_2 MX - k_3 PX$

We also recognize that the sum of the mass fractions equal unity.

$$OX + MX + PX = 1$$

Your goal is to find the steady state composition in this reactor. To do so, answer the following questions.
(a) Are these equations linear or non-linear?
(b) Since you have three unknowns, which three of the four equations should be used to solve for the composition?
(c) Construct a matrix, $\underline{\underline{A}}$, and vector, $\underline{b}$, from which the compositions, $\underline{x}$, can be obtained.
(d) Provide the determinant of the matrix.
(e) Provide the rank of the matrix, $\underline{\underline{A}}$.
(f) Provide the rank of the augmented matrix, $\underline{\underline{Ab}}$.
(g) How many solutions will $\underline{\underline{A}}\underline{x}=\underline{b}$ have?
(h) Provide a solution if it exists.

Solution:

(a) Are these equations linear or non-linear?

These equations are linear because the unknowns are only multiplied by constants and added together.

(b) Since you have three unknowns, which three of the four equations should be used to solve for the composition?

The third balance is a linear combination of the first two balances. Therefore, you need two of the mass balances and the constraint that the sum of the mass fractions is unity.

(c) Construct a matrix, $\underline{\underline{A}}$, and vector, $\underline{b}$, from which the compositions, $\underline{x}$, can be obtained.

$$\begin{bmatrix} -k_1 & 0 & k_3 \\ k_1 & -k_2 & 0 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} OX \\ MX \\ PX \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

For the remaining problems, I wrote the following script

```
clear all;
%
n = 3
A = zeros(n,n);
x = zeros(n,1);
b = zeros(n,1);
%
k1 = 7;
k2 = 9;
k3 = 5;

% one of the steady state balances is not independent
% use other three equations
%
A = [-k1 0 k3
     k1 -k2 0
      % 0 k2 -k3
    1 1 1]

b = [0; 0; 1]

detA = det(A)
rankA = rank(A)
rankAb =rank([A,b])
invA = inv(A);
x = invA*b
```

This script generated the following output.

(d) Provide the determinant of the matrix.

```
detA = 143.0000
```

(e) Provide the rank of the matrix, $\underline{\underline{A}}$.

```
rankA = 3
```

(f) Provide the rank of the augmented matrix, $\underline{\underline{Ab}}$.

```
rankAb = 3
```

(g) How many solutions will $\underline{\underline{A}}\underline{x}=\underline{b}$ have?

Because the determinant of the matrix is non-zero, there is a unique solution to $\underline{\underline{A}}\underline{x}=\underline{b}$.

(h) Provide a solution if it exists.

```
x =

    0.3147
    0.2448
    0.4406
```

Therefore the steady state solutions are

$$\begin{bmatrix} OX \\ MX \\ PX \end{bmatrix} = \begin{bmatrix} 0.3147 \\ 0.2448 \\ 0.4406 \end{bmatrix}$$

Problem 2. (8 points)
The longest relaxation time of a polymer can be measured through an auto-correlation function (acf) of the polymer end-to-end distance.

$$acf = c \cdot exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where t is time (sec), τ is relaxation time (sec) and c is a prefactor. The acf is dimensionless.

For the acf vs t data given in the file, http://utkstair.org/clausius/docs/mse301/data/xm3p02_f24.txt, perform the following tasks. In this data file, the first column is time and the second column contains the values of the acf.

(a) Identify all variables, $y = mx + b$, when equation (1) is linearized.
(b) Report the best value of τ and c.
(c) Report the standard deviations of τ and c.
(d) Report the measure of fit.

Solution

(a) Identify all variables, $y = mx + b$, when equation (1) is linearized.

$$ln(acf) = ln(c) + -\frac{t}{\tau} \tag{2}$$

$$y = ln(acf) \tag{3.y}$$

$$x = t \tag{3.x}$$

$$b = ln(c) \tag{3.b}$$

$$m = -\frac{1}{\tau} \tag{3.m}$$

(b) Report the best value of τ and c.
(c) Report the standard deviations of τ and c.
(d) Report the measure of fit.

I wrote the following script, xm3p02_f24.m, in Matlab.

```
clear all;
format long;

M = [0      3.074847359
0.1   3.219787756
0.2   2.716009217
... [data removed for brevity] ...
```

```
44.8  0.138737897
44.9  0.141829362
45    0.150988732];

n = max(size(M));
for i = 1:1:n
    x(i) = M(i,1);
    y(i) = log(M(i,2));
end
[b,bsd,MOF] = linreg1(x, y)

slope=b(2);
intercept = b(1);
slope_sd = bsd(2);
intercept_sd = bsd(1);

tau = -1/slope
c = exp(intercept)
tau_sd = abs(slope_sd/slope*tau)
c_sd = abs(intercept_sd/intercept*c)


%
% plot model (optional)
%
yhat = zeros(n,1);
for i = 1:1:n
    yhat(i) = c*exp(-M(i,1)/tau);
end
figure(2)
plot(M(:,1),M(:,2),'ro');
hold on;
plot(M(:,1),yhat(:),'k-');
xlabel('time');
ylabel('auto correlation function');
legend('data','model');
```

At the command line prompt, I executed the script.

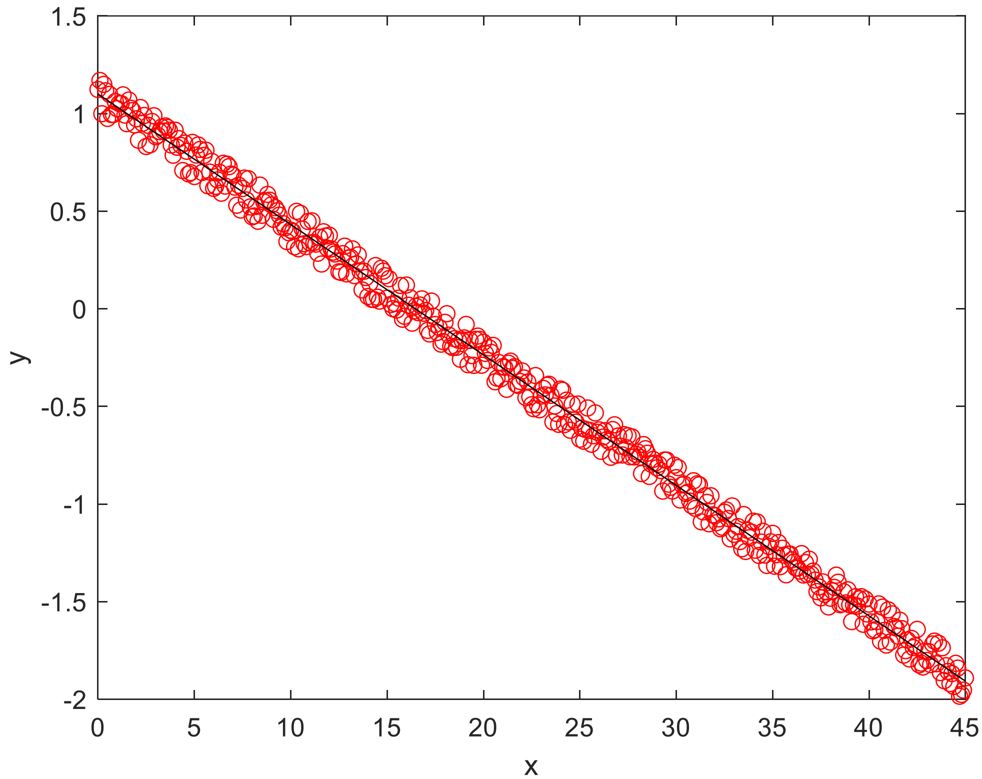
```
>> xm3p02_f24
```

This generated the following output.

```
b =
   1.100091368246491
  -0.066822731060208

bsd =
   0.005620307983136
   0.000216205674216

MOF =   0.995321619818850

tau =  14.964967521291408
c =   3.004440521868214
```

```
tau_sd =    0.048419315421945
c_sd =    0.015349525991490
```

and the plot:



Thus

(b) Report the best value of τ and c.

Based on the slope, m, and intercept, b,

$$c = exp(b) \tag{4.b}$$

$$\tau = -\frac{1}{m} \tag{4.m}$$

The mean value of these two parameters are

$\tau = 15.0$ s $\qquad c = 3.00$

(c) Report the standard deviations of τ and c.

Using rules for propagation of uncertainty,

$$\frac{\sigma_c}{c} = \left|\frac{\sigma_b}{b}\right| \tag{5.b}$$

$$\frac{\sigma_\tau}{\tau} = \left|\frac{\sigma_m}{m}\right| \tag{5.m}$$

The standard deviations of these two parameters are

$\sigma_c = 0.015 \qquad \sigma_\tau = 0.048$ s

(d) Report the measure of fit.

MOF = 0.995

Although this is not required in the exam, we also provide a comparison of the data and model for the physical variables.