Exam III Solutions
Administered: Friday, November 8, 2018
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, if work is shown

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	$r_1 = k_1 OX$	$k_1 = 3\ s^{-1}$
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, $\underline{A}$, 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 = 3;
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 = 87.0000
```

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

```
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 =

    0.5172
    0.1724
    0.3103
```

Therefore the steady state solutions are

$$\begin{bmatrix} OX \\ MX \\ PX \end{bmatrix} = \begin{bmatrix} 0.5172 \\ 0.1724 \\ 0.3103 \end{bmatrix}$$

Problem 2. (8 points)
Consider a set of three reactions occurring in a closed pot (a batch reactor) involving compounds, OX, MX and PX.

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

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

compound	rate expression
OX	$0 = 3k_3 PX - 2k_1 OX^2 - k_2 OX \cdot MX$
MX	$0 = k_1 OX^2 - k_2 OX \cdot MX$
PX	$0 = k_2 OX \cdot MX - k_3 PX$

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) What solution technique should use you to solve this problem?
(d) Provide a solution.

Solution:

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

These three mass balances are nonlinear because they contain terms in which the unknown variables are multiplied together and/or squared.

(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. (EQN1 = -2*EQN2 -3*EQN3)
Therefore, you need two of the mass balances and the constraint that the sum of the mass fractions is unity.

(c) What solution technique should use you to solve this problem?

I would use multivariate Newton Raphson with Numerical Approximations to the derivatives to solve this system of nonlinear algebraic equations.

(d) Provide a solution.

I modified the input file for nrndn.m as follows

```
function f = funkeval(x)
%
% these two lines force a column vector of length n
%
n = max(size(x));
f = zeros(n,1);
%
% enter the functions here
%
OX = x(1);
MX = x(2);
PX = x(3);
%
k1 = 3;
k2 = 9;
k3 = 5;
%
rate1 = k1*OX*OX;
rate2 = k2*OX*MX;
rate3 = k3*PX;
%
f(1) = 3.0*rate3 - 2.0*rate1 - rate2;
f(2) = rate1 - rate2;
f(3) = OX + MX +  PX - 1.0;
```

The script to execute the code was as follows.

```
clear all;
format long;
OX = 0.5172;
MX = 0.1724;
PX = 0.3103;
x0 =    [OX; MX; PX];
tol = 1.0e-6;
iprint = 1;
[x,err,f] = nrndn(x0,tol,iprint)
```

This code produced the following output.

```
>> xm3p02_f19
iter =    1, err =  7.52e-02 f =  1.30e+00
 iter =    2, err =  1.69e-03 f =  3.06e-02
 iter =    3, err =  8.58e-07 f =  1.55e-05

x =
   0.592189968528657
   0.197396656176219
   0.210413375295124

err = 8.580668507425378e-07

f = 1.547817864644976e-05
```

Therefore the steady state solutions are

$$\begin{bmatrix} OX \\ MX \\ PX \end{bmatrix} = \begin{bmatrix} 0.5922 \\ 0.1974 \\ 0.2104 \end{bmatrix}$$