

Exam III Solutions
Administered: Friday, November 6, 2015
22 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. (12 points)

Consider an isothermal flow reactor with a volume, $V = 10$ liters, in which the following set of elementary reactions take place

reaction 1: $A \rightarrow B$ with rate constant $k_1 = 1 \text{ s}^{-1}$

reaction 2: $B \rightarrow C$ with rate constant $k_2 = 2 \text{ s}^{-1}$

reaction 3: $A \rightarrow C$ with rate constant $k_3 = 3 \text{ s}^{-1}$

reaction 4: $C \rightarrow D$ with rate constant $k_4 = 4 \text{ s}^{-1}$

The inlet flow rates are given by

$$F_{A,in} = F_{B,in} = 2 \frac{\text{mole}}{\ell \cdot \text{s}} \quad \text{and} \quad F_{C,in} = F_{D,in} = 0 \frac{\text{mole}}{\ell \cdot \text{s}}$$

The outlet flow rates are given by

$$F_{A,out} = \hat{F}_{out} C_A, \quad F_{B,out} = \hat{F}_{out} C_B, \quad F_{C,out} = \hat{F}_{out} C_C \quad \text{and} \quad F_{D,out} = \hat{F}_{out} C_D \frac{\text{mole}}{\ell \cdot \text{s}}$$

where $\hat{F}_{out} = 4 \text{ s}^{-1}$ and concentrations are measured in moles/liter.

The steady state mass balances are

accumulation = in – out + generation – consumption

$$0 = F_{A,in} - \hat{F}_{out} C_A - k_1 C_A - k_3 C_A$$

$$0 = F_{B,in} - \hat{F}_{out} C_B + k_1 C_A - k_2 C_B$$

$$0 = F_{C,in} - \hat{F}_{out} C_C + k_2 C_B + k_3 C_A - k_4 C_C$$

$$0 = F_{D,in} - \hat{F}_{out} C_D + k_4 C_C$$

(a) Write this set of equations in matrix notation, $\underline{\underline{A}}\underline{x} = \underline{b}$. Identify all three quantities, $\underline{\underline{A}}$, \underline{x} and \underline{b} .

(b) Calculate the determinant of $\underline{\underline{A}}$.

(c) Calculate the rank of $\underline{\underline{A}}$.

(d) Calculate the rank of $\underline{\underline{A}}|\underline{b}$

(e) How many solutions are there to this problem?

(f) Calculate the steady state concentrations of A, B, C and D in this reactor under these conditions.

Solution:

(a) Write this set of equations in matrix notation, $\underline{\underline{A}}\underline{x} = \underline{b}$. Identify all three quantities, $\underline{\underline{A}}$, \underline{x} and \underline{b} .

I rearranged the equations to put constants on the right hand side and grouped the coefficients by variable.

$$\begin{aligned}
 (\hat{F}_{out} + k_1 + k_3)C_A &= F_{A,in} \\
 -k_1C_A + (\hat{F}_{out} + k_2)C_B &= F_{B,in} \\
 -k_3C_A - k_2C_B + (\hat{F}_{out} + k_4)C_C &= F_{C,in} \\
 -k_4C_C + \hat{F}_{out}C_D &= F_{D,in}
 \end{aligned}$$

$$\underline{\underline{A}} = \begin{bmatrix} \hat{F}_{out} + k_1 + k_3 & 0 & 0 & 0 \\ -k_1 & (\hat{F}_{out} + k_2) & 0 & 0 \\ -k_3 & -k_2 & (\hat{F}_{out} + k_4) & 0 \\ 0 & 0 & -k_4 & \hat{F}_{out} \end{bmatrix}, \underline{x} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix}, \underline{b} = \begin{bmatrix} F_{A,in} \\ F_{B,in} \\ F_{C,in} \\ F_{D,in} \end{bmatrix}$$

For the remaining parts of this problem, I wrote the following Matlab script, xm3p01_2015.m

```

clear all;
k1 = 1;
k2 = 2;
k3 = 3;
k4 = 4;
FAin = 2;
FBin = 2;
FCin = 0;
FDin = 0;
Fout = 4;
A = [(Fout+k1+k3) 0 0 0
      -k1 (Fout+k2) 0 0
      -k3 -k2 (Fout+k4) 0
      0 0 -k4 Fout]
b = [FAin; FBin; FCin; FDin]
detA = det(A)
rankA = rank(A)
Ab = [A,b];
rankAb = rank(Ab)
invA = inv(A);
x = invA*b

```

To execute the script, at the Matlab command prompt, I typed

```
>> xm3p01_2015
```

which yielded the following result:

$$A = \begin{bmatrix} 8 & 0 & 0 & 0 \\ -1 & 6 & 0 & 0 \\ -3 & -2 & 8 & 0 \\ 0 & 0 & -4 & 4 \end{bmatrix}$$

$$b =$$

$$\begin{bmatrix} 2 \\ 2 \\ 0 \\ 0 \end{bmatrix}$$

$$\det A = 1536$$

$$\text{rank} A = 4$$

$$\text{rank} Ab = 4$$

$$x =$$

$$\begin{bmatrix} 0.2500 \\ 0.3750 \\ 0.1875 \\ 0.1875 \end{bmatrix}$$

(b) Calculate the determinant of $\underline{\underline{A}}$.

The determinant of $\underline{\underline{A}}$ is 1536.

(c) Calculate the rank of $\underline{\underline{A}}$.

Because the determinant of $\underline{\underline{A}}$ is non-zero, you know that the rank of $\underline{\underline{A}}$ must be full, $n=4$. The Matlab calculation confirms this.

(d) Calculate the rank of $\underline{\underline{A}}|b$

Because the rank of $\underline{\underline{A}}$ is 4, you know that the rank of $\underline{\underline{A}}|b$ must also be 4. The Matlab calculation confirms this.

(e) How many solutions are there to this problem?

Because the determinant of $\underline{\underline{A}}$ is non-zero, there is a one solution.

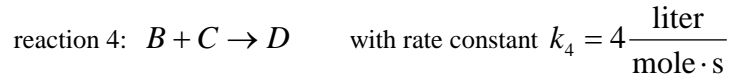
(f) Calculate the steady state concentrations of A, B, C and D in this reactor under these conditions.

We solved for the steady state concentrations in the x vector.

$$\underline{x} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} = \begin{bmatrix} 0.25 \\ 0.375 \\ 0.1875 \\ 0.1875 \end{bmatrix} \text{ mole/liter}$$

Problem 2. (10 points)

If we rework problem 1 with the single change that we replace reaction 4 with



Then the steady state mass balances become

accumulation = in – out + generation -consumption

$$0 = F_{A,in} - \hat{F}_{out} C_A - k_1 C_A - k_3 C_A$$

$$0 = F_{B,in} - \hat{F}_{out} C_B + k_1 C_A - k_2 C_B - k_4 C_C C_B$$

$$0 = F_{C,in} - \hat{F}_{out} C_C + k_2 C_B + k_3 C_A - k_4 C_C C_B$$

$$0 = F_{D,in} - \hat{F}_{out} C_D + k_4 C_C C_B$$

- (a) Is this system of equation linear or nonlinear?
- (b) What numerical technique is appropriate for solving this problem?
- (c) Solve for the steady state concentrations. (6 points)

Solution:

(a) Is this system of equation linear or nonlinear?

This system of equations is nonlinear because of the $k_4 C_C C_B$ term in the third and fourth equation.

(b) What numerical technique is appropriate for solving this problem?

An appropriate technique for solving a system of nonlinear algebraic equations is the multivariate Newton-Raphson method with numerical approximations to the derivatives.

(c) Solve for the steady state concentrations. (6 points)

For this problem, I wrote the following Matlab script, xm3p02_2015_input.m. The initial guess comes from the solution of the linear version in problem 1.

```
clear all;
x0 = [0.2500
      0.3750
      0.1875
      0.1875];
tol = 1.0e-6;
iprint = 1;
[x,err,f] = nrndn(x0,tol,iprint)
```

In the input subroutine for nrndn.m, I put the following code

```
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
%
CA = x(1);
CB = x(2);
CC = x(3);
CD = x(4);
k1 = 1;
k2 = 2;
k3 = 3;
k4 = 4;
FAin = 2;
FBin = 2;
FCin = 0;
FDin = 0;
Fout = 4;
f(1) = FAin - (Fout+k1+k3)*CA;
f(2) = FBin + k1*CA - (Fout+k2)*CB -k4*CC*CB;
f(3) = FCin + k3*CA + k2*CB - Fout*CC - k4*CC*CB;
f(4) = FDin + k4*CC*CB - Fout*CD;
```

To execute the script, at the Matlab command prompt, I typed

```
>> xm3po2_f15_input
```

which yielded the following result:

```
iter = 1, err = 6.84e-02 f = 3.60e-01
iter = 2, err = 2.34e-03 f = 1.44e-02
iter = 3, err = 3.39e-06 f = 2.09e-05
iter = 4, err = 7.09e-12 f = 4.38e-11
```

```
x =
  0.2500
  0.3190
  0.2631
  0.0839
```

```
err = 7.0937e-12
```

```
f = 4.3828e-11
```

The error indicates that the value converged. So the steady state concentrations are

$$\underline{x} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} = \begin{bmatrix} 0.25 \\ 0.3190 \\ 0.2631 \\ 0.0839 \end{bmatrix} \text{ mole/liter}$$