Exam III Solutions
Administered: Monday, November 2, 2020
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 $k_1 = 2$ s^{-1}
reaction 2: $B \rightarrow C$ with rate constant $k_2 = 5$ s^{-1}
reaction 3: $A \rightarrow D$ with rate constant $k_3 = 3$ s^{-1}
reaction 4: $C \rightarrow D$ with rate constant $k_4 = 1$ s^{-1}

The inlet flow rates are given by

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

The outlet flow rates are given by

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

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

The steady state mass balances are

accumulation = in – out + generation -consumption

$$0 = F_{A,in} - \hat{F}_{out}C_A - k_1C_A - k_3C_A$$
$$0 = F_{B,in} - \hat{F}_{out}C_B + k_1C_A - k_2C_B$$
$$0 = F_{C,in} - \hat{F}_{out}C_C + k_2C_B - k_4C_C$$
$$0 = F_{D,in} - \hat{F}_{out}C_D + k_3C_A + k_4C_C$$

(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.

$$\left(\hat{F}_{out} + k_1 + k_3\right)C_A = F_{A,in}$$
$$-k_1C_A + \left(\hat{F}_{out} + k_2\right)C_B = F_{B,in}$$

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

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

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

```
clear all;
k1 = 2;
k2 = 5;
k3 = 3;
k4 = 1;
FAin = 2;
FBin = 2;
FCin = 0;
FDin = 0;
Fout = 4;
A = [(Fout+k1+k3) 0          0          0
    -k1           (Fout+k2)  0          0
      0          -k2        (Fout+k4)  0
     -k3              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_2020
```

which yielded the following result:

```
A =
     9     0     0     0
    -2     9     0     0
     0    -5     5     0
    -3     0    -1     4

b =
     2
     2
     0
     0

detA =  1620

rankA =   4
```

```
rankAb = 4

invA =
    0.1111         0         0         0
    0.0247    0.1111         0         0
    0.0247    0.1111    0.2000         0
    0.0895    0.0278    0.0500    0.2500

x =
    0.2222
    0.2716
    0.2716
    0.2346
```

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

The determinant of $\underline{A}$ is 1620.

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

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

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

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

Because the determinant of $\underline{A}$ 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.

$$\underline{x} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} = \begin{bmatrix} 0.2222 \\ 0.2716 \\ 0.2716 \\ 0.2346 \end{bmatrix} \text{mole/liter}$$

Problem 2. (10 points)

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

reaction 4: $B + C \rightarrow D$ with rate constant $k_4 = 4\,\frac{\text{liter}}{\text{mole}\cdot s}$

Then the steady state mass balances become

accumulation = in – out + generation -consumption

$$0 = F_{A,in} - \hat{F}_{out}C_A - k_1 C_A - k_3 C_A$$
$$0 = F_{B,in} - \hat{F}_{out}C_B + k_1 C_A - k_2 C_B - k_4 C_C C_B$$
$$0 = F_{C,in} - \hat{F}_{out}C_C + k_2 C_B - k_4 C_C C_B$$
$$0 = F_{D,in} - \hat{F}_{out}C_D + k_3 C_A + k_4 C_C C_B$$

(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_2020.m. The initial guess comes from the solution of the linear version in problem 1.

```
clear all;
x0 =    [0.2222
    0.2716
    0.2716
    0.2346];
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 = 2;
k2 = 5;
k3 = 3;
k4 = 1;
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  + k2*CB - Fout*CC - k4*CC*CB;
f(4) = FDin + k3*CA + k4*CC*CB - Fout*CD;
```

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

```
>> xm3p02_f20
```

which yielded the following result:

```
 iter =    1, err =  3.03e-02 f =  1.45e-01
 iter =    2, err =  6.85e-05 f =  2.84e-04
 iter =    3, err =  7.51e-10 f =  3.11e-09

x =
    0.2222
    0.2626
    0.3080
    0.1869

err =   7.5125e-10

f =   3.1098e-09
```

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

$$\underline{x} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} = \begin{bmatrix} 0.2222 \\ 0.2626 \\ 0.3080 \\ 0.1869 \end{bmatrix} \text{ mole/liter}$$