# Homework Assignment Number One Solutions

For Problems 1 through 3 below, find
(a) the determinant of A
(b) the reduced row echelon form of A
(c) the reduced row echelon form of the Augmented Ab matrix.
(d) the rank of A.
(e) the rank of the augmented Ab matrix.
(f) the inverse of A if it exists
(g) a solution to $\underline{\underline{A}}\underline{x} = \underline{b}$ if it exists.

**Problem 1.**

$$\underline{\underline{A}} = \begin{bmatrix} 1 & 2 & -1 \\ 1 & 5 & 1 \\ 1 & 4 & 2 \end{bmatrix} \text{ and } \underline{b} = \begin{bmatrix} 1 \\ 2 \\ 5 \end{bmatrix}$$

**Solution:**

This problem has one unique solution.

This was my MatLab script in hw9p01.m

```
clear all;
A = [1 2 -1; 1 5 1; 1 4 2]
b = [1; 2; 5]
detA = det(A)
rrefA = rref(A)
rankA = rank(A)
Ab = [A,b]
rrefAb = rref(Ab)
rankAb = rank(Ab)
invA = inv(A)
x = invA*b
bcheck = A*x
bdiff = b - bcheck
```

This was the output:
```
>> hw9p01

A =
     1     2    -1
     1     5     1
     1     4     2

b =
     1
     2
     5

detA =     5

rrefA =
     1     0     0
     0     1     0
     0     0     1

rankA =     3
```

1

```
Ab =

     1     2    -1     1
     1     5     1     2
     1     4     2     5

rrefAb =
     1     0     0     5
     0     1     0    -1
     0     0     1     2

rankAb =     3

invA =
    1.2000   -1.6000    1.4000
   -0.2000    0.6000   -0.4000
   -0.2000   -0.4000    0.6000

x =
    5.0000
   -1.0000
    2.0000

bcheck =
    1.0000
    2.0000
    5.0000

bdiff =    1.0e-15 *
    0.8882
    0.8882
    0.8882
```

**Problem 2.**

$$\underline{\underline{A}} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 2 & 1 & -1 \\ 1 & 3 & 2 & -2 \\ 1 & 4 & 3 & -3 \end{bmatrix} \text{ and } \underline{b} = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 2 \end{bmatrix}$$

**Solution:**

This problem has an infinite number of solutions.
This was my MatLab script in hw9p02.m

```
clear all;
A = [1 1 1 1; 1 2 1 -1; 1 3 2 -2; 1 4 3 -3]
b = [1; 0; 1; 2]
detA = det(A)
rrefA = rref(A)
rankA = rank(A)
Ab = [A,b]
rrefAb = rref(Ab)
rankAb = rank(Ab)
A3 =rrefAb(1:3,1:3)
x4 = 1
b3 = rrefAb(1:3,5) - rrefAb(1:3,4)*x4
invA3 = inv(A3)
x3 = invA3*b3
x = [x3; x4]
bcheck = A*x
```

2

```
bdiff = b - bcheck
```

This was the output:
```
>> hw9p02

A =
     1     1     1     1
     1     2     1    -1
     1     3     2    -2
     1     4     3    -3

b =
     1
     0
     1
     2

detA =   3.3307e-16

rrefA =
     1     0     0     2
     0     1     0    -2
     0     0     1     1
     0     0     0     0

rankA =     3

Ab =
     1     1     1     1     1
     1     2     1    -1     0
     1     3     2    -2     1
     1     4     3    -3     2

rrefAb =
     1     0     0     2     0
     0     1     0    -2    -1
     0     0     1     1     2
     0     0     0     0     0

rankAb =     3

A3 =
     1     0     0
     0     1     0
     0     0     1

x4 =     1

b3 =
    -2
     1
     1

invA3 =
     1     0     0
     0     1     0
     0     0     1

x3 =
    -2
     1
     1

x =
    -2
     1
     1
     1

bcheck =
     1
     0
     1
     2
```

```
bdiff =
     0
     0
     0
     0
```

**Problem 3.**

$$\underline{\underline{A}} = \begin{bmatrix} 1 & 2 & -1 \\ 1 & 5 & 1 \\ 2 & 7 & 0 \end{bmatrix} \text{ and } \underline{b} = \begin{bmatrix} 1 \\ 2 \\ 5 \end{bmatrix}$$

**Solution:**

This problem has no solutions.

This was my MatLab script in hw9p03.m

```
clear all;
A = [1 2 -1; 1 5 1; 2 7 0]
b = [1; 2; 5]
detA = det(A)
rrefA = rref(A)
rankA = rank(A)
Ab = [A,b]
rrefAb = rref(Ab)
rankAb = rank(Ab)
```

This was the output:
```
>> hw9p03

A =
     1      2     -1
     1      5      1
     2      7      0

b =
     1
     2
     5

detA =     0

rrefA =
    1.0000          0   -2.3333
         0    1.0000    0.6667
         0         0         0

rankA =     2

Ab =
     1      2     -1      1
     1      5      1      2
     2      7      0      5

rrefAb =
    1.0000          0   -2.3333          0
         0    1.0000    0.6667          0
         0         0         0    1.0000

rankAb =     3
```
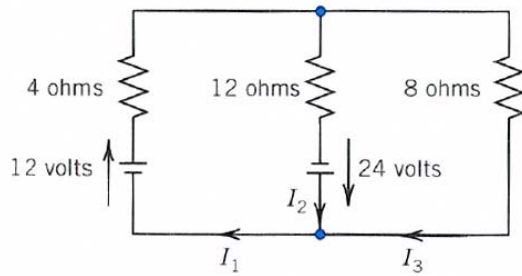
Problem 4. (Kreyszig, 8<sup>th</sup> Edition, page 330, Problem Set 6.3, Problem 18)



Using Kirchoff's Current & Voltage laws, determine the three unknown currents.
(http://en.wikipedia.org/wiki/Kirchhoff's_circuit_laws)

**Solution:**
Given the electrical circuit, we write Kirchoff's current law for the top node:

$$i_1 - i_2 - i_3 = 0$$

and we write Kirchoff's current law for the bottom node:

$$-i_1 + i_2 + i_3 = 0$$

By inspection, these 2 applications of Kirchoff's current law are linearly dependent. We can only use one of them. We can also write Kirchoff's voltage law for the left loop (going clockwise):

$$R_1 i_1 + R_2 i_2 = E_1 + E_2$$

and we can also write Kirchoff's voltage law for the right loop (going clockwise):

$$-R_2 i_2 + R_3 i_3 = -E_2$$

where $R_1 = 4, R_2 = 12, R_3 = 8, E_1 = 12, E_2 = 24$

The three independent equations can be written in matrix form as:

$$\begin{bmatrix} -1 & 1 & 1 \\ R_1 & R_2 & 0 \\ 0 & -R_2 & R_3 \end{bmatrix} \begin{bmatrix} i_1 \\ i_2 \\ i_3 \end{bmatrix} = \begin{bmatrix} 0 \\ E_1 + E_2 \\ -E_2 \end{bmatrix}$$

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If we plug in our numerical values, we find the rank of the matrix to be 3 and the determinant to be -176 so all of our equations are linearly independent and we can solve. First we obtain the inverse.

$$
\left[\begin{array}{ccc|ccc}
-1 & 1 & 1 & 1 & 0 & 0 \\
R_1 & R_2 & 0 & 0 & 1 & 0 \\
0 & -R_2 & R_3 & 0 & 0 & 1
\end{array}\right]
$$

Zero off-diagonal elements of column one. $(\text{Row2} = \text{Row2} + R_1 * \text{Row1})$

$$
\left[\begin{array}{ccc|ccc}
-1 & 1 & 1 & 1 & 0 & 0 \\
0 & R_2+R_1 & R_1 & R_1 & 1 & 0 \\
0 & -R_2 & R_3 & 0 & 0 & 1
\end{array}\right]
$$

Make the diagonal element of row one unity. $(\text{Row1} = -\text{Row1})$

$$
\left[\begin{array}{ccc|ccc}
1 & -1 & -1 & -1 & 0 & 0 \\
0 & R_2+R_1 & R_1 & R_1 & 1 & 0 \\
0 & -R_2 & R_3 & 0 & 0 & 1
\end{array}\right]
$$

Make the diagonal element of row two unity. $\left(\text{Row2} = \dfrac{1}{R_2+R_1}\text{Row2}\right)$

$$
\left[\begin{array}{ccc|ccc}
1 & -1 & -1 & -1 & 0 & 0 \\
0 & 1 & \dfrac{R_1}{R_2+R_1} & \dfrac{-1}{R_2+R_1} & \dfrac{1}{R_2+R_1} & 0 \\
0 & -R_2 & R_3 & 0 & 0 & 1
\end{array}\right]
$$

Zero off-diagonal elements of column two. $(\text{Row1} = \text{Row1} + \text{Row2})$ $(\text{Row3} = \text{Row3} + R_2\text{Row2})$

$$
\left[\begin{array}{ccc|ccc}
1 & 0 & -1+\dfrac{R_1}{R_2+R_1} & -1+\dfrac{R_1}{R_2+R_1} & \dfrac{1}{R_2+R_1} & 0 \\
0 & 1 & \dfrac{R_1}{R_2+R_1} & \dfrac{R_1}{R_2+R_1} & \dfrac{1}{R_2+R_1} & 0 \\
0 & 0 & R_3+\dfrac{R_2R_1}{R_2+R_1} & \dfrac{R_2R_1}{R_2+R_1} & \dfrac{R_2}{R_2+R_1} & 1
\end{array}\right]
$$

Make the diagonal element of row three unity. $\left(\text{Row3} = \dfrac{1}{R_3 + \dfrac{R_2 R_1}{R_2 + R_1}}\,\text{Row3}\right)$

$$\begin{bmatrix} 1 & 0 & -1+\dfrac{R_1}{R_2+R_1} & -1+\dfrac{R_1}{R_2+R_1} & \dfrac{1}{R_2+R_1} & 0 \\[4mm] 0 & 1 & \dfrac{R_1}{R_2+R_1} & \dfrac{R_1}{R_2+R_1} & \dfrac{1}{R_2+R_1} & 0 \\[4mm] 0 & 0 & 1 & \dfrac{\dfrac{R_2 R_1}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \dfrac{\dfrac{R_2}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \dfrac{1}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} \end{bmatrix}$$

Zero off-diagonal elements of column three. $\left(\text{Row1} = \text{Row1} + \left(1 - \dfrac{R_1}{R_2+R_1}\right)\text{Row3}\right)$ and

$\left(\text{Row2} = \text{Row2} + -\dfrac{R_1}{R_2+R_1}\,\text{Row3}\right)$

So that the left hand side of the above matrix becomes the identity matrix and the right hand side becomes the inverse, namely:

$$\begin{bmatrix} -1+\dfrac{R_1}{R_2+R_1}+\left(1-\dfrac{R_1}{R_2+R_1}\right)\dfrac{\dfrac{R_2 R_1}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \dfrac{1}{R_2+R_1}+\left(1-\dfrac{R_1}{R_2+R_1}\right)\dfrac{\dfrac{R_2}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \left(1-\dfrac{R_1}{R_2+R_1}\right)\dfrac{1}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} \\[8mm] \dfrac{R_1}{R_2+R_1}-\left(\dfrac{R_1}{R_2+R_1}\right)\dfrac{\dfrac{R_2 R_1}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \dfrac{1}{R_2+R_1}-\left(\dfrac{R_1}{R_2+R_1}\right)\dfrac{\dfrac{R_2}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & -\left(\dfrac{R_1}{R_2+R_1}\right)\dfrac{1}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} \\[8mm] \dfrac{\dfrac{R_2 R_1}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \dfrac{\dfrac{R_2}{R_2+R_1}}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} & \dfrac{1}{R_3+\dfrac{R_2 R_1}{R_2+R_1}} \end{bmatrix}$$

We can simplify this matrix to obtain:

$$\underline{\underline{A}}^{-1} = \begin{bmatrix} \dfrac{-R_2R_3}{\sum RR} & \dfrac{\sum RR + R_2R_2}{(R_1 + R_2)\sum RR} & \dfrac{R_2}{\sum RR} \\[2ex] \dfrac{R_1R_3}{\sum RR} & \dfrac{R_3}{\sum RR} & \dfrac{-R_1}{\sum RR} \\[2ex] \dfrac{R_1R_2}{\sum RR} & \dfrac{R_2}{\sum RR} & \dfrac{R_2 + R_1}{\sum RR} \end{bmatrix}$$

where $\sum RR = R_1R_2 + R_1R_3 + R_2R_3$

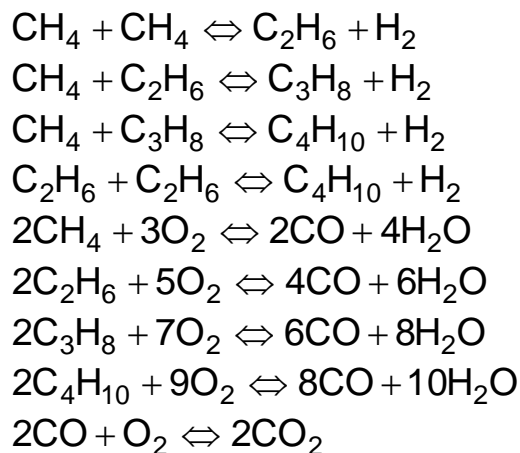Numerical substitution into this matrix will show that the inverse satisfies the equation:

$$\underline{\underline{A}}^{-1}\underline{\underline{A}} = \underline{\underline{I}}$$

The solution is then:

$$\underline{i} = \underline{\underline{A}}^{-1}\underline{b} = \begin{bmatrix} \dfrac{-R_2R_3}{\sum RR} & \dfrac{\sum RR + R_2R_2}{(R_1 + R_2)\sum RR} & \dfrac{R_2}{\sum RR} \\[2ex] \dfrac{R_1R_3}{\sum RR} & \dfrac{R_3}{\sum RR} & \dfrac{-R_1}{\sum RR} \\[2ex] \dfrac{R_1R_2}{\sum RR} & \dfrac{R_2}{\sum RR} & \dfrac{R_2 + R_1}{\sum RR} \end{bmatrix} \begin{bmatrix} 0 \\ E_1 + E_2 \\ -E_2 \end{bmatrix} = \frac{1}{11}\begin{bmatrix} 27 \\ 24 \\ 3 \end{bmatrix} = \begin{bmatrix} 2.4545 \\ 2.1818 \\ 0.2727 \end{bmatrix}$$

**Problem 5.**
Given the set of chemical reactions:

$$CH_4 + CH_4 \Leftrightarrow C_2H_6 + H_2$$
$$CH_4 + C_2H_6 \Leftrightarrow C_3H_8 + H_2$$
$$CH_4 + C_3H_8 \Leftrightarrow C_4H_{10} + H_2$$
$$C_2H_6 + C_2H_6 \Leftrightarrow C_4H_{10} + H_2$$
$$2CH_4 + 3O_2 \Leftrightarrow 2CO + 4H_2O$$
$$2C_2H_6 + 5O_2 \Leftrightarrow 4CO + 6H_2O$$
$$2C_3H_8 + 7O_2 \Leftrightarrow 6CO + 8H_2O$$
$$2C_4H_{10} + 9O_2 \Leftrightarrow 8CO + 10H_2O$$
$$2CO + O_2 \Leftrightarrow 2CO_2$$

(a) Write out the stoichiometric coefficient matrix.
(b) Determine the number of independent reactions using the stoichiometric coefficient matrix.
(c) Write a complete set of independent reactions.
(d) Write out the atomic matrix.
(e) Determine the number of independent reactions using the atomic matrix

**Solution:**
       (a) Write out the stoichiometric coefficient matrix

There are nine reactions and nine molecules involved.

| rxn | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $H_2$ | CO | $O_2$ | $H_2O$ | $CO_2$ |
|-----|------|-------|-------|--------|-----|----|-----|------|------|
| 1 | -2 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| 2 | -1 | -1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 |
| 3 | -1 | 0 | -1 | 1 | 1 | 0 | 0 | 0 | 0 |
| 4 | 0 | -2 | 0 | 1 | 1 | 0 | 0 | 0 | 0 |
| 5 | -2 | 0 | 0 | 0 | 0 | 2 | -3 | 4 | 0 |
| 6 | 0 | -2 | 0 | 0 | 0 | 4 | -5 | 6 | 0 |
| 7 | 0 | 0 | -2 | 0 | 0 | 6 | -7 | 8 | 0 |
| 8 | 0 | 0 | 0 | -2 | 0 | 8 | -9 | 10 | 0 |
| 9 | 0 | 0 | 0 | 0 | 0 | -2 | -1 | 0 | 2 |

(b)  Determine the number of independent reactions using the stoichiometric coefficient matrix
Find the rank of the matrix of the stoichiometric matrix.

```
A=[-2   1    0    0    1    0    0    0    0
   -1  -1    1    0    1    0    0    0    0
   -1   0   -1    1    1    0    0    0    0
    0  -2    0    1    1    0    0    0    0
   -2   0    0    0    0    2   -3    4    0
    0  -2    0    0    0    4   -5    6    0
    0   0   -2    0    0    6   -7    8    0
    0   0    0   -2    0    8   -9   10    0
    0   0    0    0    0   -2   -1    0    2]
```

rank(A) = 6
The number of independent reactions is equal to the rank of the stoichiometric matrix = 6.
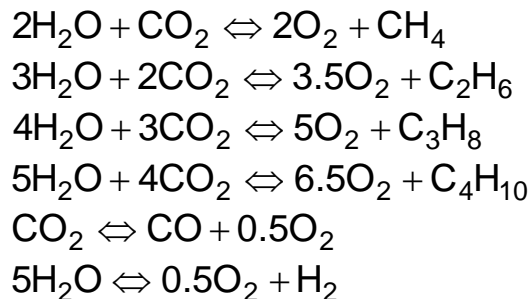
(c)  Write a complete set of independent reactions
Put the matrix in (upper triangular form, or using MATLAB, put the matrix in "reduced row echelon form").
rref(A)  =

```
 1.0000      0       0       0       0       0   2.0000      -2.0000  -1.0000
      0  1.0000      0       0       0       0   3.5000      -3.0000  -2.0000
      0       0  1.0000      0       0       0   5.0000      -4.0000  -3.0000
      0       0       0  1.0000      0       0   6.5000      -5.0000  -4.0000
      0       0       0       0  1.0000      0   0.5000      -1.0000       0
      0       0       0       0       0  1.0000  0.5000           0  -1.0000
      0       0       0       0       0       0       0            0       0
      0       0       0       0       0       0       0            0       0
      0       0       0       0       0       0       0            0       0
```

So, a set of independent equations is:

$$2H_2O + CO_2 \Leftrightarrow 2O_2 + CH_4$$
$$3H_2O + 2CO_2 \Leftrightarrow 3.5O_2 + C_2H_6$$
$$4H_2O + 3CO_2 \Leftrightarrow 5O_2 + C_3H_8$$
$$5H_2O + 4CO_2 \Leftrightarrow 6.5O_2 + C_4H_{10}$$
$$CO_2 \Leftrightarrow CO + 0.5O_2$$
$$5H_2O \Leftrightarrow 0.5O_2 + H_2$$

(d)  Write out the atomic matrix

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| atom | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $H_2$ | CO | $O_2$ | $H_2O$ | $CO_2$ |
|------|--------|----------|----------|-------------|-------|-----|-------|--------|--------|
| C    | 1      | 2        | 3        | 4           | 0     | 1   | 0     | 0      | 1      |
| H    | 4      | 6        | 8        | 10          | 2     | 0   | 0     | 2      | 0      |
| O    | 0      | 0        | 0        | 0           | 0     | 1   | 2     | 1      | 2      |

(e) Determine the number of independent reactions using the atomic matrix

Row2 = 4*Row1 - Row2

| atom | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $H_2$ | CO | $O_2$ | $H_2O$ | $CO_2$ |
|------|--------|----------|----------|-------------|-------|-----|-------|--------|--------|
| C    | 1      | 2        | 3        | 4           | 0     | 1   | 0     | 0      | 1      |
| H    | 0      | 2        | 4        | 6           | -2    | 4   | 0     | -2     | 4      |
| O    | 0      | 0        | 0        | 0           | 0     | 1   | 2     | 1      | 2      |

This matrix is in upper triangular form. The rank is 3.
The number of independent reactions = number of components - rank of atomic matrix.
The number of independent reactions = 9 - 3 = 6

## Problem 6.
Find the eigenvalues and eigenvectors that describe the vibrational motion of acetylene, HCCH. Assume that the molecule is one-dimensional. Solve either symbolically in terms of $m_H$, $m_c$, $k_{HC}$ and $k_{CC}$, or assign numbers to these four variables and solve numerically. Explain the significance of the eigenvalues and eigenvectors.

**Solution:**

Following the procedure used in class for carbon dioxide, we write Newton's equations in matrix form as:

$$
\begin{bmatrix}
-\dfrac{k_{HC}}{m_H} & \dfrac{k_{HC}}{m_H} & 0 & 0 \\
\dfrac{k_{HC}}{m_C} & -\dfrac{k_{HC}+k_{CC}}{m_C} & \dfrac{k_{CC}}{m_C} & 0 \\
0 & \dfrac{k_{CC}}{m_C} & -\dfrac{k_{HC}+k_{CC}}{m_C} & \dfrac{k_{HC}}{m_C} \\
0 & 0 & \dfrac{k_{HC}}{m_H} & -\dfrac{k_{HC}}{m_H}
\end{bmatrix}
\begin{bmatrix}
x_{H1} \\ x_{C1} \\ x_{C2} \\ x_{H2}
\end{bmatrix}
= \underline{\ddot{x}}
$$

The determinant of this matrix is 0 and the rank is 3 so one of the eigenvalues is zero. (Just as in the carbon dioxide case).

The characteristic equation of the matrix is:

$$\lambda \left[ \begin{array}{l} \lambda^3 + 2\left( \dfrac{k_{HC}+k_{CC}}{m_C} + \dfrac{k_{HC}}{m_H} \right)\lambda^2 + \left( \dfrac{2k_{HC}k_{CC}}{m_C}\left( \dfrac{2}{m_H}+\dfrac{1}{m_C} \right) + \dfrac{k_{HC}{}^2}{m_C}\left( \dfrac{1}{m_H}+\dfrac{1}{m_C} \right)^2 \right)\lambda \\[12pt] + \dfrac{2k_{HC}{}^2 k_{CC}}{m_H m_C}\left( \dfrac{1}{m_H}+\dfrac{1}{m_C} \right) \end{array} \right] = 0$$

The roots of this fourth order polynomial are the eigenvalues. The eigenvalues are

$$\lambda_1 = 0$$
$$\lambda_2 = -\frac{k_{HC}(m_H + m_C)}{m_H m_C}$$
$$\lambda_3 = \frac{-k_{HC}m_H - 2k_{CC}m_H - k_{HC}m_C + K}{2m_H m_C}$$
$$\lambda_4 = \frac{-k_{HC}m_H - 2k_{CC}m_H - k_{HC}m_C - K}{2m_H m_C}$$

where

$$K = \sqrt{k_{HC}{}^2 m_H{}^2 + 4k_{HC}k_{CC}m_H{}^2 + 2k_{HC}{}^2 m_H m_C + 4k_{CC}{}^2 m_H{}^2 - 4k_{HC}k_{CC}m_H m_C + k_{HC}{}^2 m_C{}^2}$$

These roots can be obtained by grievously laborious hand manipulations or by entering the matrix in a symbolic manipulator software, like Maple, and typing eigenvals(a).

The eigenvectors are as follows:

$$\underline{w}_1 = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \qquad \underline{w}_2 = \begin{bmatrix} 1 \\ -\dfrac{m_H}{m_C} \\ -\dfrac{m_H}{m_C} \\ 1 \end{bmatrix} \qquad \underline{w}_3 = \begin{bmatrix} -1 \\ -b_+ \\ b_+ \\ 1 \end{bmatrix} \qquad \underline{w}_4 = \begin{bmatrix} -1 \\ -b_- \\ b_- \\ 1 \end{bmatrix}$$
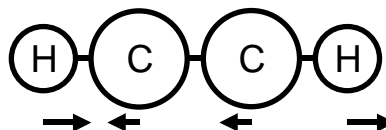
where

$$b_+ = \frac{-k_{HC}m_H - 2k_{CC}m_H - k_{HC}m_C + K}{2k_{HC}m_C} + 1 = \frac{m_H \lambda_3}{k_{HC}} + 1$$
$$b_- = \frac{-k_{HC}m_H - 2k_{CC}m_H - k_{HC}m_C - K}{2k_{HC}m_C} + 1 = \frac{m_H \lambda_4}{k_{HC}} + 1$$
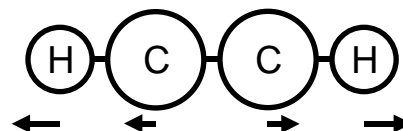
Pictorially we see that eigenvalue one corresponds to a uniform translation:
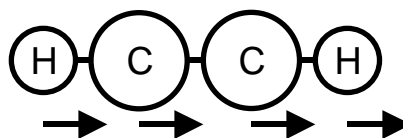
Eigenvalue two corresponds to the vibration (no change in center of mass, compress one C-H bonds and extend one C-H bond, no change to C-C bond):



Eigenvalue three corresponds to the vibration (no change in center of mass, extend C-H bonds and extend C-C bond):
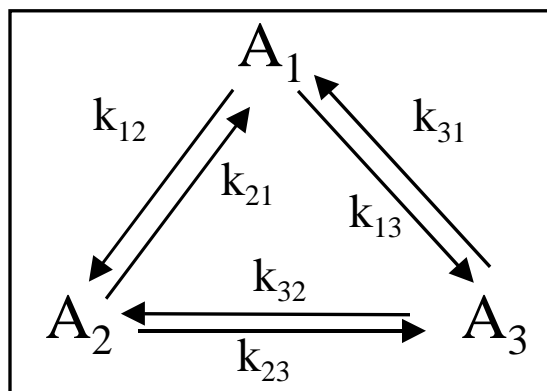


Eigenvalue four corresponds to the vibration (no change in center of mass, extend C-H bonds and compress C-C bond):
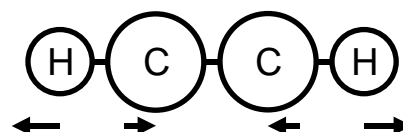


**Problem 7.**
Consider that you have a three-component reactive mixture, all undergoing reversible reactions, as pictured below:



In this picture, the A's are concentrations of the three species and the k's are rate constants. An example of this system is the kinetic equilibrium between para-, meta-, and ortho-xylene.

(a) Find the eigenvalues and eigenvectors for the following rate constants in a batch reactor.
```
k12 = 0.50;
k21 = 0.25;
k13 = 0.20;
k31 = 0.05;
k23 = 0.30;
k32 = 0.15;
```

(b) Give a physical interpretation of these eigenvalues and eigenvectors.


**Solution:**
(a) Find the eigenvalues and eigenvectors for the following rate constants in a batch reactor.

From class we know that the steady state molar balances are written as:

$$\frac{dA_1}{dt} = -(k_{12} + k_{13})A_1 + k_{21}A_2 + k_{31}A_3$$

$$\frac{dA_2}{dt} = k_{12}A_1 - (k_{21} + k_{23})A_2 + k_{32}A_3$$

$$\frac{dA_3}{dt} = k_{13}A_1 + k_{23}A_2 - (k_{31} + k_{32})A_3$$

and we change this system of equations into matrix & vector form:

$$\frac{d\underline{A}}{dt} = \underline{\underline{X}}\,\underline{A}$$

where

$$\underline{\underline{X}} = \begin{bmatrix} -(k_{12} + k_{13}) & k_{21} & k_{31} \\ k_{12} & -(k_{21} + k_{23}) & k_{32} \\ k_{13} & k_{23} & -(k_{31} + k_{32}) \end{bmatrix}$$

$$\underline{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}$$

In MATLAB:

```
» A=[-(k12+k13) k21 k31
```

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```
k12 -(k21+k23) k32
k13 k23 -(k31+k32)]

A =
   -0.7000     0.2500     0.0500
    0.5000    -0.5500     0.1500
    0.2000     0.3000    -0.2000

»   [w,lam]=eig(A)
w =
   -0.6337     0.3309     0.2182
    0.7628     0.4810     0.4364
   -0.1291    -0.8119     0.8729
lam =
   -0.9908          0          0
         0    -0.4592          0
         0          0     0.0000
```

(b)  Give a physical interpretation of these eigenvalues and eigenvectors.
(c)  Find the steady-state composition.

The eigenvector corresponding to the zero eigenvalue is the infinite time (equilibrium) concentrations.  If the variables are mole fractions then the must sum to unity, and we can normalize the corresponding eigenvector from

$$\underline{w}_3 = \begin{bmatrix} 0.2182 \\ 0.4364 \\ 0.8729 \end{bmatrix} \text{ to } \underline{w}_3 = \frac{1}{7}\begin{bmatrix} 1 \\ 2 \\ 4 \end{bmatrix}$$

To get an idea of the physical meaning of the other two eigenvectors, consider that, when the variables are mole fractions, they sum to unity.  Thus at all times, the following statements are true:

$$0 \le A_i \le 1 \text{ for i} = 1 \text{ to } 3$$

$$\sum_{i=1}^{3} A_i = 1$$

These two equations form a plane in the positive quadrant of the x,y,z coordinate system.  The solution vector $\underline{A}$ lies on this plane at all times.  A vector normal to this plane is

$$\underline{n} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

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Note that

$$\underline{n} \cdot \underline{w}_1 = 0$$
$$\underline{n} \cdot \underline{w}_2 = 0$$

Thus the first two eigenvectors lie in the plane defined by $\sum_{i=1}^{3} A_i = 1$.

If we picture just the $\sum_{i=1}^{3} A_i = 1$ plane we see that, starting from any initial condition (set of mole fractions), we will reach the same equilibrium. The path that we take through time and concentration space is called the "reaction path". The first two eigenvectors represent the only straightline reaction paths. (In the figure, they are dotted). The third eigenvector is, as stated above, the steady state solution. Any other, set of initial conditions, will give a curved reaction path.

An additional feature of the eigenvectors is that a reaction path will never cross an eigenvector. We see how the eigenvectors divide the plane into 2 sections. A reaction path that starts in the top section will reach the equilibrium from the top section. Likewise, a reaction path that starts in the bottom section will reach the equilibrium from the bottom section.
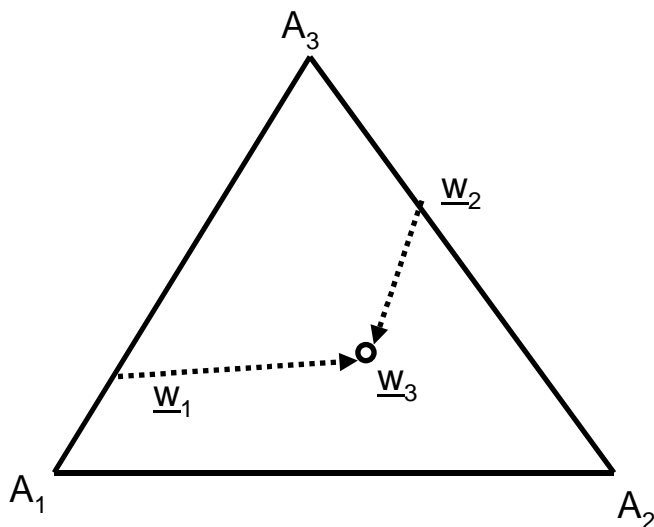


(I learned this physical explanation from Dr. Balakataia of the University of Houston, when he was on sabbatical at the University of Minnesota (1992-1993) and was teaching advanced mathematics for chemical engineers.)

(d) Find the steady-state composition.

The steady state composition is given by

$$\frac{d\underline{A}}{dt} = \underline{\underline{X}}\underline{A} = \underline{0}$$

We can solve this system of linear algebraic equations for $\underline{A}$ and find that the steady state solution is given by the third eigenvector:

$$\underline{w}_3 = \frac{1}{7}\begin{bmatrix} 1 \\ 2 \\ 4 \end{bmatrix}$$

(d)    Additionally, allow for flow into and out of the reactor, making it a CSTR.  Assume constant volume in the tank.  Derive the model, (write the mass balances).  Find the steady-state composition.

```
F1_in = 0.1;
F2_in = 0.0;
F3_in = 0.05;
```

$$\frac{dA_1}{dt} = -(k_{12} + k_{13})A_1 + k_{21}A_2 + k_{31}A_3 + F_{1,in} - F_{out}A_1$$

$$\frac{dA_2}{dt} = k_{12}A_1 - (k_{21} + k_{23})A_2 + k_{32}A_3 + F_{2,in} - F_{out}A_2$$

$$\frac{dA_3}{dt} = k_{13}A_1 + k_{23}A_2 - (k_{31} + k_{32})A_3 + F_{3,in} - F_{out}A_3$$

where
$$F_{out} = F_{1,in} + F_{2,in} + F_{3,in}$$

$$\underline{\underline{X}} = \begin{bmatrix} -(k_{12} + k_{13} - F_{out}) & k_{21} & k_{31} \\ k_{12} & -(k_{21} + k_{23} - F_{out}) & k_{32} \\ k_{13} & k_{23} & -(k_{31} + k_{32} - F_{out}) \end{bmatrix}$$

$$\underline{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \qquad \underline{b} = \begin{bmatrix} F_{1,in} \\ F_{2,in} \\ F_{3,in} \end{bmatrix}$$

so that

$$\frac{d\underline{A}}{dt} = \underline{\underline{X}}\underline{A} + \underline{b}$$

and, at steady state

$$\frac{dA}{dt} = \underline{\underline{X}}\,\underline{A} + \underline{b} = \underline{0} \ \text{ or } \ \underline{\underline{X}}\,\underline{A} = -\underline{b}$$

We then solve for $\underline{A}$ and find that the steady state solution is given by:
IN MATLAB
» fout=f1in+f2in+f3in

fout =    0.1500

» A=[-(k12+k13+fout) k21 k31
k12 -(k21+k23+fout) k32
k13 k23 -(k31+k32+fout)]
A =
  -0.8500   0.2500   0.0500
   0.5000  -0.7000   0.1500
   0.2000   0.3000  -0.3500

» rank(A)
ans = 3

» b =- [f1in;f2in;f3in]
b =
  -0.1000
       0
  -0.0500

» x = inv(A)*b

x =
   0.2266
   0.2698
   0.5036

This is the new steady state solution of the open system.