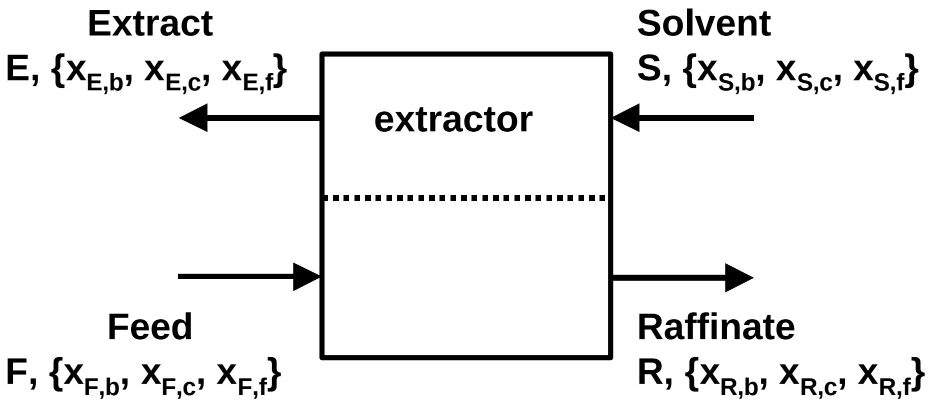
## Example Applications of systems of linear equations

Included in this hand-out are five examples of problems requiring the solution of a system of linear algebraic equations.

The examples are:

### *A. Steady state mass balances on a single-stage liquid-liquid extractor*

Consider an extractor:



This unit removes uses a recycled furfural stream as the solvent to extract benzene from a cyclohexane product stream. The data you are given is

$$\begin{array}{llll}
F = 100\ \mathrm{mol/hr} & S = 150\ \mathrm{mol/hr} & R = 95\ \mathrm{mol/hr} & E = 155\ \mathrm{mol/hr} \\
x_{F,b} = 0.1 & x_{S,b} = 0.0010 & x_{R,b} = ? & x_{E,b} = ? \\
x_{F,c} = 0.9 & x_{S,c} = 0.0001 & x_{R,c} = ? & x_{E,c} = ? \\
x_{F,f} = 0.0 & x_{S,f} = 0.9989 & x_{R,f} = ? & x_{E,f} = ?
\end{array}$$

The equilibrium constants are: $K_b = \frac{x_{E,b}}{x_{R,b}} = 20.0$ and $K_c = \frac{x_{E,c}}{x_{R,c}} = 0.05$.

You have six unknowns, the compositions of the raffinate stream and the composition of the extract stream.

(a) Write six independent equations

benzene mole balance: $0 = Fx_{F,b} + Sx_{S,b} - Rx_{R,b} - Ex_{E,b}$

cyclohexane mole balance: $0 = Fx_{F,c} + Sx_{S,c} - Rx_{R,c} - Ex_{E,c}$

furfural mole balance: $0 = Fx_{F,f} + Sx_{S,f} - Rx_{R,f} - Ex_{E,f}$ **(not used, dependent)** raffinate mole fraction constraint: $1 = x_{R,b} + x_{R,c} + x_{R,f}$

extract mole fraction constraint: $1 = x_{E,b} + x_{E,c} + x_{E,f}$

benzene equilibrium constraint: $K_b = \frac{x_{E,b}}{x_{R,b}} = 20.0$

c-hexane equilibrium constraint: $K_c = \frac{x_{E,c}}{x_{R,c}} = 0.05$

(b) Put equations in linear form

benzene mole balance: $Rx_{R,b} + Ex_{E,b} = Fx_{F,b} + Sx_{S,b}$

cyclohexane mole balance: $Rx_{R,c} + Ex_{E,c} = Fx_{F,c} + Sx_{S,c}$

furfural mole balance: $Rx_{R,f} + Ex_{E,f} = Fx_{F,f} + Sx_{S,f}$ **(not used, dependent)**

raffinate mole fraction constraint: $x_{R,b} + x_{R,c} + x_{R,f} = 1$

extract mole fraction constraint: $x_{E,b} + x_{E,c} + x_{E,f} = 1$

benzene equilibrium constraint: $x_{E,b} - x_{R,b}K_b = 0$

c-hexane equilibrium constraint: $x_{E,c} - x_{R,c}K_c = 0$

(c ) Put equations in matrix form

matrix of coefficients, A (6 x 6)

| eqn/var | $x_{R,b}$ | $x_{R,c}$ | $x_{R,f}$ | $x_{E,b}$ | $x_{E,c}$ | $x_{E,f}$ |
|---|---|---|---|---|---|---|
| 1 | R | 0 | 0 | E | 0 | 0 |
| 2 | 0 | R | 0 | 0 | E | 0 |
| 3 | 1 | 1 | 1 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | 1 | 1 | 1 |
| 5 | $-K_b$ | 0 | 0 | 1 | 0 | 0 |
| 6 | 0 | $-K_c$ | 0 | 0 | 1 | 0 |

vector of right hand sides, b (6x1)

| eqn | b |
|---|---|
| 1 | $Fx_{F,b} + Sx_{S,b}$ |
| 2 | $Fx_{F,c} + Sx_{S,c}$ |
| 3 | 1 |
| 4 | 1 |
| 5 | 0 |
| 6 | 0 |

(d) Compute the determinant and rank of the matrix.

detA = 3.2829e+005

rank(A) = 6

rank(A|b) = 6

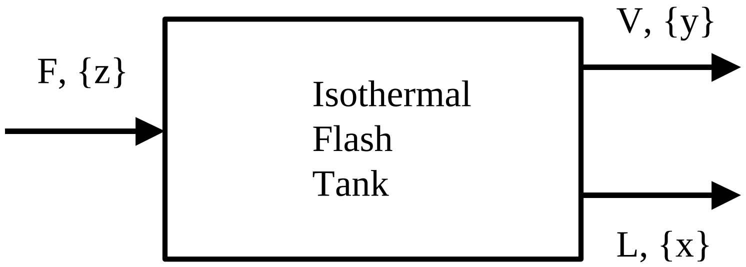
(e) Using MATLAB, solve for the steady-state values of the unknowns.

x(1) = 0.0033 = $x_{R,b}$ x(2) = 0.8448 = $x_{R,c}$ x(3) = 0.1519 = $x_{R,f}$

x(4) = 0.0651 = $x_{E,b}$ x(5) = 0.0422 = $x_{E,c}$ x(6) = 0.8927= $x_{E,f}$

### *B. Steady state mass balances on a flash tank*

Consider an isothermal flash tank:



This unit takes a pressurized liquid, three-component feed stream and exposes it to a low pressure vessel maintained under isothermal conditions. The net result is that some of the fluid is vaporized, while some fluid remains liquid. The compositions of the liquid and vapor phase are determined by the combined analysis of mass balances and Raoult's Law for vapor-liquid equilibrium.

The temperature in the flash tank is $T = 298K$ and the pressure in the tank is $P = 101kPa$.

Raoult's Law states that the product of the liquid mole fraction of component i and the vapor pressure of component i is equal to the partial pressure of component i in the vapor phase:

$$x_i P_i^{vap} = y_i P$$

Use the following data for the temperature given above

$$P_A^{vap} = 0.6bar \ @ \ T = 298K$$
$$P_B^{vap} = 1.0bar \ @ \ T = 298K$$
$$P_C^{vap} = 2.0bar \ @ \ T = 298K$$

$$\begin{array}{lll} F = 100 \text{ mol/hr} & V = 44.738 \text{mol/hr} & L = F - V \text{ mol/hr} \\ z_A = 0.4 & y_A = ? & x_A = ? \\ z_B = 0.3 & y_B = ? & x_B = ? \\ z_C = 0.3 & y_C = ? & x_C = ? \end{array}$$

Then you have six unknowns, the compositions of the liquid stream and the composition of the vapor stream.

(a) Write equations

A mole balance: $0 = Fz_A - Lx_A - Vy_A$

B mole balance: $0 = Fz_B - Lx_B - Vy_B$ **(not used, dependent)**

C mole balance: $0 = Fz_C - Lx_C - Vy_C$ **(not used, dependent)**

liquid mole fraction constraint: $1 = x_A + x_B + x_C$

vapor mole fraction constraint: $1 = y_A + y_B + y_C$

A equilibrium constraint: $x_A P_A^{vap} = y_A P$

B equilibrium constraint: $x_B P_B^{vap} = y_B P$

C equilibrium constraint: $x_C P_C^{vap} = y_C P$

(b) Put equations in linear form

A mole balance: $Lx_A + Vy_A = Fz_A$

B mole balance: $Lx_B + Vy_B = Fz_B$ **(not used, dependent)**

C mole balance: $Lx_C + Vy_C = Fz_C$ **(not used, dependent)**

liquid mole fraction constraint: $x_A + x_B + x_C = 1$

vapor mole fraction constraint: $y_A + y_B + y_C = 1$

A equilibrium constraint: $x_A P_A^{vap} - y_A P = 0$

B equilibrium constraint: $x_B P_B^{vap} - y_B P = 0$

C equilibrium constraint: $x_C P_C^{vap} - y_C P = 0$

(c ) Put equations in matrix form

matrix of coefficients, A (6 x 6)

| eqn/var | $x_A$ | $x_B$ | $x_C$ | $y_A$ | $y_B$ | $y_C$ |
|---|---|---|---|---|---|---|
| 1 | $L$ | 0 | 0 | $V$ | 0 | 0 |
| 2 | 1 | 1 | 1 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | 1 | 1 | 1 |
| 4 | $P_A^{vap}$ | 0 | 0 | $-P$ | 0 | 0 |
| 5 | 0 | $P_B^{vap}$ | 0 | 0 | $-P$ | 0 |
| 6 | 0 | 0 | $P_C^{vap}$ | 0 | 0 | $-P$ |

vector of right hand sides, b (6x1)

| eqn | b |
|---|---|
| 1 | $Fz_A$ |
| 2 | 1 |
| 3 | 1 |
| 4 | 0 |
| 5 | 0 |
| 6 | 0 |

(d) Compute the determinant and rank of the matrix. (Here is the contents of a Matlab m-file I used to do this.)

```
F = 100;
V = 44.738;
```

```
L = F - V;

zA = 0.4;
zB = 0.3;
zC = 0.3;

PvapA = 0.6;
PvapB = 1.0;
PvapC = 2.0;

P = 1.01325;

A = [L   0  0  V  0  0
   1  1  1  0  0  0
   0  0  0  1  1  1
   PvapA 0  0  -P 0  0
   0  PvapB 0  0  -P 0
   0  0  PvapC 0  0  -P]

b =[F*zA; 1; 1; 0; 0; 0]

rankA = rank(A)

detA = det(A)

x = A\b

xA = x(1);
xB = x(2);
xC = x(3);
yA = x(4);
yB = x(5);
yC = x(6);
```

The output from the code yielded:

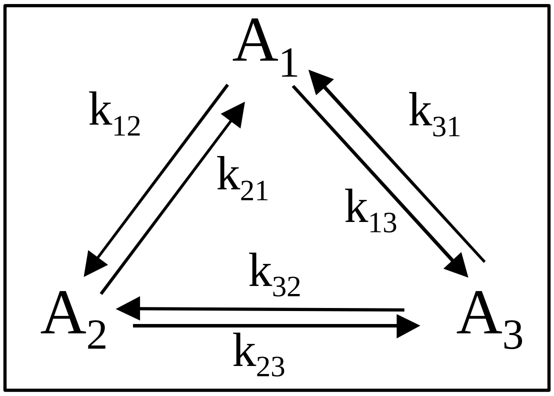
```
rankA =6
detA =-83.9346

x =    [0.4893
   0.3018
   0.2090
   0.2897
   0.2978
   0.4125]
```

$x_A$ =0.4893 $x_B$ =0.3018 $x_C$ =0.2090

$y_A$ =0.2897 $y_B$ =0.2978 $y_C$ =0.4125

### *C. Chemical Reaction Equilibria*

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.

Now suppose we want to know what the concentration is as a function of time. We can write the mass balances for each component. There are no in and out terms (the reactor is a batch reactor). There is only the accumulation term and the reaction terms. Also, assume each reaction is first order in concentration.

$$\begin{aligned}\frac{dA_1}{dt} &= -k_{12}A_1 + k_{21}A_2 - k_{13}A_1 + k_{31}A_3\\ \frac{dA_2}{dt} &= -k_{21}A_2 + k_{12}A_1 - k_{23}A_2 + k_{32}A_3\\ \frac{dA_3}{dt} &= -k_{31}A_3 + k_{13}A_1 - k_{32}A_3 + k_{23}A_2\end{aligned} \tag{28.6}$$

We can gather like terms and rearrange the right hand side:

$$\begin{aligned}\frac{dA_1}{dt} &= -(k_{12} + k_{13})A_1 + k_{21}A_2 + k_{31}A_3\\ \frac{dA_2}{dt} &= k_{12}A_1 - (k_{21} + k_{23})A_2 + k_{32}A_3\\ \frac{dA_3}{dt} &= k_{13}A_1 + k_{23}A_2 - (k_{31} + k_{32})A_3\end{aligned} \tag{28.7}$$

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

$$\frac{d\underline{A}}{dt} = \underline{\underline{X}}\,\underline{A} \tag{28.8}$$

where

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

$$\underline{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \qquad (28.9)$$

One underbar denotes a column vector; two underbars denotes a matrix. This is a system of linear differential equations. If we want the steady-state solution to the differential equations, we set the accumulation term to zero. Then we have a system of linear algebraic equations, as shown:

$$\underline{0} = \underline{\underline{X}}\underline{A} \qquad (28.10)$$

Let's solve for the steady-state concentration.

The rate constants are given as:

$$k_{12} = 0.50\,\text{sec}^{-1} \qquad k_{13} = 0.20\,\text{sec}^{-1} \qquad k_{23} = 0.30\,\text{sec}^{-1}$$
$$k_{21} = 0.25\,\text{sec}^{-1} \qquad k_{31} = 0.05\,\text{sec}^{-1} \qquad k_{32} = 0.15\,\text{sec}^{-1}$$

The determinant of $\underline{\underline{X}}$ is 0 and the rank is 2. Therefore we have an infinite number of solutions. Why?

If we look at $\underline{\underline{X}}$, we see that ROW3 = -ROW1 - ROW2. Since equation 3 is not linearly independent we can drop it. Then we have 2 equation and three unknowns. We have 2 options.

Option Number One:

Since, we have an infinite number of solutions, we can just make one of the variables no longer variable. Then we will have the rest of $\underline{A}$ relative to this basis. This requires us to rearrange $\underline{\underline{X}}$ since $A_3$ is no longer a variable. We come up with the new equations

$$\underline{\underline{X}}\underline{A} = \underline{b}$$

where

$$\underline{\underline{X}} = \begin{bmatrix} -(k_{12}+k_{13}) & k_{21} \\ k_{12} & -(k_{21}+k_{23}) \end{bmatrix} \quad \underline{A} = \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} \qquad \underline{b} = \begin{bmatrix} -k_{31}A_3 \\ -k_{32}A_3 \end{bmatrix}$$

One can see that we have dropped the third equation and since $A_3$ is no longer a variable, we have moved it to the right hand side of the equations. (If you don't see this, right these equations out in non-matrix form and then move $A_3$ to the right-hand-side of the equation, and then change back into matrix form. You will get this result.)

With these new definitions, we can pick a value for $A_3$, like $A_3 = 1$. Now MATLAB says det(x) =0.26 . MATLAB gives the inv(x) upon request and provides the solution

$$\underline{A} = \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} 0.25 \\ 0.5 \end{bmatrix}$$

which gives us the example solution vector:

$$\underline{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \begin{bmatrix} 0.25 \\ 0.5 \\ 1 \end{bmatrix}$$

If we want to find the molar compositions, then we will require that $\sum_{i=1}^{3} A_i = 1$ . In order to normalize our solution vector so that they sum to one, we use the standard normalization equation:

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

then we find the steady state molar compositions to be:

$$z = \begin{bmatrix} 1/7 \\ 2/7 \\ 4/7 \end{bmatrix} .$$

Option Number Two:

If we only have 2 equations for 3 unknowns, we can find another independent equation. If our unknowns are mole fractions we know they must sum to one.

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

This is our third equation. We drop equation three from the previous formulation of the problem and we have

$$\underline{\underline{X}}\,\underline{A} = \underline{b}$$

where

$$\underline{\underline{X}} = \begin{bmatrix} -(k_{12}+k_{13}) & k_{21} & k_{31} \\ k_{12} & -(k_{21}+k_{23}) & k_{32} \\ 1 & 1 & 1 \end{bmatrix} \quad \underline{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \quad \underline{b} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

This matrix has a determinant of 0.455 and rank of 3. Therefore we have a set of 3 independent equations. Solving for $\underline{A}$ yields

$$\underline{A} = \begin{bmatrix} 1/7 \\ 2/7 \\ 4/7 \end{bmatrix}$$

which is the same result we obtained doing the problem the other way.

### *D. Determination of an independent set of chemical reactions*

Problem 1.

Determine the number of independent reaction in the following set by examining the rank of the stoichiometric coefficient matrix. (In the stoichiometric coefficient, the rows represent reactions and the columns represent molecules.)

$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$
$4\ NH_3 + 3\ O_2 = 4\ N_2 + 6\ H_2O$
$2\ NO + O_2 = 2\ NO_2$
$4\ NH_3 + 6\ NO = 5\ N_2 + 6\ H_2O$
$N_2 + O_2 = 2\ NO$

$$\text{reactions}\quad \overset{\text{molecules}}{\begin{bmatrix} NH_3 & O_2 & N_2 & NO & NO_2 & H_2O \\ -4 & -5 & 0 & 4 & 0 & 6 \\ -4 & -3 & 2 & 0 & 0 & 6 \\ 0 & -1 & 0 & -2 & 2 & 0 \\ -4 & 0 & 5 & -6 & 0 & 6 \\ 0 & -1 & -1 & 2 & 0 & 0 \end{bmatrix}}$$

This is a non-square matrix, five rows, six columns. We can do the same NGE on a non-square matrix as on a square matrix to reach Upper triangular form

STEP ONE. (zero the first column below row 1)
ROW2 = ROW2 - ROW1
ROW4 = ROW4 - ROW1

$$\text{reactions}\quad \overset{\text{molecules}}{\begin{bmatrix} NH_3 & O_2 & N_2 & NO & NO_2 & H_2O \\ -4 & -5 & 0 & 4 & 0 & 6 \\ 0 & 2 & 2 & -4 & 0 & 0 \\ 0 & -1 & 0 & -2 & 2 & 0 \\ 0 & 5 & 5 & -10 & 0 & 0 \\ 0 & -1 & -1 & 2 & 0 & 0 \end{bmatrix}}$$

STEP TWO. (zero the second column below row 2)
ROW3 = ROW3 + ½*ROW2
ROW4 = ROW4 - 5/2*ROW2
ROW5 = ROW5 - ½*ROW2

$$\text{reactions}\quad \overset{\text{molecules}}{\begin{bmatrix} NH_3 & O_2 & N_2 & NO & NO_2 & H_2O \\ -4 & -5 & 0 & 4 & 0 & 6 \\ 0 & 2 & 2 & -4 & 0 & 0 \\ 0 & 0 & 1 & -4 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}}$$

There are only three independent chemical reactions. This kind of analysis is important when you are doing an process analysis on a reactive system. You need to have only independent reactions incorporated in your material and energy balances.

The stoichiometric coefficient matrix tells the engineer, given a set of reactions, how many of those reactions are (linearly) independent. It will not give the engineer a complete set of reactions, unless (1) the number of reactions in the set is greater than or equal to the total number of independent reactions and (2) all components in the system appear in at least one reaction.

Problem 2.
Determine the number of independent reactions by using the atomic matrix. (The atomic matrix has atoms on the rows and molecules along the columns

$$\text{atoms}\quad \begin{array}{c} \\ N \\ O \\ H \end{array} \overset{\text{molecules}}{\begin{bmatrix} N_2 & O_2 & NH_3 & NO & NO_2 & H_2O \\ 2 & 0 & 1 & 1 & 1 & 0 \\ 0 & 2 & 0 & 1 & 2 & 1 \\ 0 & 0 & 3 & 0 & 0 & 2 \end{bmatrix}}$$

This matrix is already in upper triangular form. The rank of the matrix is three.

In reactive process analysis, the total number of independent reactions is equal to the number of components less the rank of atom matrix. Since we have six components and a rank of three, we have three independent reactions. The atomic matrix tells the engineer how many independent reactions there can be. This is different in several ways from the stoichiometric matrix above.

From atomic matrix,

# of independent reactions = # of chemical species - rank of atomic matrix

If you want to find a set of three reactions that are complete and independent, then you must postulate three reactions, and use the stoichiometric matrix technique, outlined above, to verify that they are independent. The reactions you postulate must contain all of the chemical species.

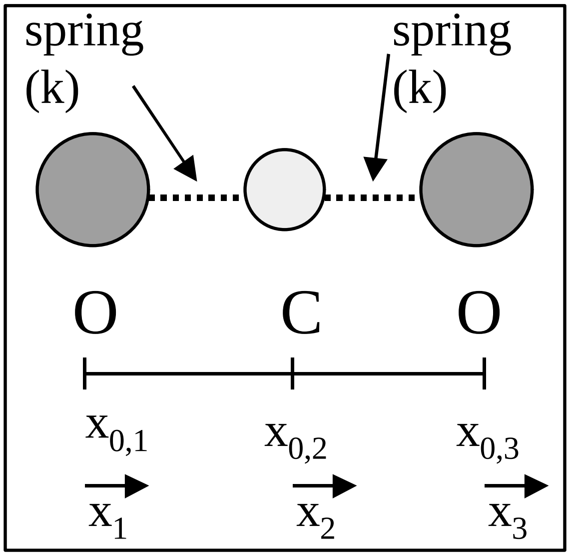
Here is an example set of reactions:

$N_2 + O_2 = 2\ NO$
$2\ NO + O_2 = 2\ NO_2$
$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$

These are guaranteed to be linearly independent since each reaction contains a unique species. Reaction 1 is the only reaction to contain $N_2$. Reaction 2 is the only reaction to contain $NO_2$. Reaction 3 is the only reaction to contain $NH_3$.

### *E. Normal Mode Analysis of the Vibrational Spectrum of a Molecule*

Consider that we want to investigate the vibrational properties of carbon dioxide, $CO_2$. Our model of the molecule looks like this:



We model the interaction between molecules as Hookian springs. For a Hookian spring, the potential energy, $U$, is

$$U = \frac{k}{2}(x - x_0)^2 \tag{28.1}$$

and the force, $F$, is

$$F = -k(x - x_0) \tag{28.2}$$

where $k$ is the spring constant (units of kg/s$^2$), $x_0$ is the equilibrium displacement, and $x$ is the actual displacement.

We can write Newton's equations of motion for the three molecules:

$$\begin{aligned} m_O a_1 &= F_1 = k(x_2 - x_1) \\ m_C a_2 &= F_2 = -k(x_2 - x_1) + k(x_3 - x_2) \\ m_O a_3 &= F_3 = -k(x_3 - x_2) \end{aligned} \tag{28.3}$$

Knowing that the acceleration is the second derivative of the position, we can rewrite the above equations in matrix form as (first divide both side of all of the equations by the masses)

$$\frac{d^2 \underline{x}}{dt^2} = \underline{\underline{A}}\,\underline{x} \tag{28.4}$$

where

$$\underline{\underline{A}} = \begin{bmatrix} -k/m_O & k/m_O & 0 \\ k/m_C & -2k/m_C & k/m_C \\ 0 & k/m_O & -k/m_O \end{bmatrix} \tag{28.5}$$

$$\underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}$$

Solving this system of second order linear differential equations yields the integrated equations of motion for carbon dioxide. However, even without solving this system, because the system is linear, there are special techniques we can use to tell us a lot about the system's behavior.

Let us determine the eigenvalues and the eigenvectors of the matrix $\underline{\underline{A}}$.

First we have:

$$\underline{\underline{A}} - \lambda \underline{\underline{I}} = \begin{bmatrix} -k/m_O - \lambda & k/m_O & 0 \\ k/m_C & -2k/m_C - \lambda & k/m_C \\ 0 & k/m_O & -k/m_O - \lambda \end{bmatrix} \tag{28.6.5}$$

The characteristic equation is given by (using equation 28.19)

$$\begin{aligned} \det\left(\underline{\underline{A}} - \lambda \underline{\underline{I}}\right) &= \left(-k/m_O - \lambda\right)\left(-2k/m_C - \lambda\right)\left(-k/m_O - \lambda\right) \\ &\quad - k/m_O \, k/m_C \left(-k/m_O - \lambda\right) - k/m_O \, k/m_C \left(-k/m_O - \lambda\right) = 0 \end{aligned} \tag{28.6.6}$$

Solving this for $\lambda$, we have

$$\begin{aligned} \det\left(\underline{\underline{A}} - \lambda \underline{\underline{I}}\right) &= \left(-k/m_O - \lambda\right)\left(-2k/m_C - \lambda\right)\left(-k/m_O - \lambda\right) \\ &\quad + 2k^3/m_O{}^2 m_C + 2k^2/m_O m_C \, \lambda = 0 \end{aligned} \tag{28.6.7}$$

$$\det\left(\underline{\underline{A}} - \lambda \underline{\underline{I}}\right) = -\lambda\left(\lambda^2 + \left(2k/m_O + 2k/m_C\right)\lambda + \left(k^2/m_O{}^2 + 2k^2/m_O m_C\right)\right) = 0 \tag{28.6.8}$$

$$\det\left(\underline{\underline{A}} - \lambda \underline{\underline{I}}\right) = -\lambda\left(\lambda + \frac{k}{m_O}\right)\left(\lambda + \frac{k}{m_O}\left(1 + 2\frac{m_O}{m_C}\right)\right) = 0 \tag{28.6.9}$$

So the roots to the characteristic equation are

$$\lambda_1 = 0 \qquad \lambda_2 = -\frac{k}{m_O} \qquad \lambda_3 = -\frac{k}{m_O}\left(1 + 2\frac{m_O}{m_C}\right) \tag{28.6.10}$$

The eigenvectors for each of these eigenvalues are given by

$$\left(\underline{\underline{A}}_3 - \lambda_m \underline{\underline{I}}_3\right)\underline{w}_m = \underline{0} \tag{28.6.4}$$

$$\left(\underline{\underline{A}} - \lambda_1 \underline{\underline{I}}\right)\underline{w}_m = \begin{bmatrix} -{}^{k}\!/_{m_O} & {}^{k}\!/_{m_O} & 0 \\ {}^{k}\!/_{m_C} & -{}^{2k}\!/_{m_C} & {}^{k}\!/_{m_C} \\ 0 & {}^{k}\!/_{m_O} & -{}^{k}\!/_{m_O} \end{bmatrix}\underline{w}_m = \underline{0} \tag{28.6.11}$$

since the determinant of $\underline{\underline{A}}$ is zero, we cannot use the inverse to calculate the solution, but we can still use NGE if we augment the matrix by the solution vector. Since the equations are not linearly independent, we can remove $w_{3,1}$ as a variable and set it equal to one. Then our system becomes:

$$\begin{bmatrix} -{}^{k}\!/_{m_O} & {}^{k}\!/_{m_O} \\ {}^{k}\!/_{m_C} & -{}^{2k}\!/_{m_C} \end{bmatrix}\begin{bmatrix} w_{1,1} \\ w_{2,1} \end{bmatrix} = \begin{bmatrix} 0 \\ -{}^{k}\!/_{m_C} \end{bmatrix} \tag{28.6.12}$$

With this new matrix, we can calculate the determinant

$$\det(\underline{\underline{A}}_2) = \frac{k^2}{m_O m_C} \neq 0$$

so it has an inverse which is

$$\underline{\underline{A}}_2^{-1} = \frac{1}{\dfrac{k^2}{m_O m_C}}\begin{bmatrix} -{}^{2k}\!/_{m_C} & -{}^{k}\!/_{m_O} \\ -{}^{k}\!/_{m_C} & -{}^{k}\!/_{m_O} \end{bmatrix} = \begin{bmatrix} -{}^{2m_O}\!/_{k} & -{}^{m_C}\!/_{k} \\ -{}^{m_O}\!/_{k} & -{}^{m_C}\!/_{k} \end{bmatrix}$$

So that the solution to equation (28.6.12) is

$$\begin{bmatrix} w_{1,1} \\ w_{2,1} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

and the eigenvector that corresponds to $\lambda_1 = 0$ is

$$\underline{w}_1 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \qquad (28.6.15)$$

To find the second eigenvector, the eigenvector that corresponds to $\lambda_2 = -\frac{k}{m_O}$

$$\underline{\underline{A}} - \lambda_2 \underline{\underline{I}} = \begin{bmatrix} -\frac{k}{m_O} - -\frac{k}{m_O} & \frac{k}{m_O} & 0 \\ \frac{k}{m_C} & -\frac{2k}{m_C} - -\frac{k}{m_O} & \frac{k}{m_C} \\ 0 & \frac{k}{m_O} & -\frac{k}{m_O} - -\frac{k}{m_O} \end{bmatrix}$$

$$\underline{\underline{A}} - \lambda_2 \underline{\underline{I}} = \begin{bmatrix} 0 & \frac{k}{m_O} & 0 \\ \frac{k}{m_C} & -\frac{2k}{m_C} + \frac{k}{m_O} & \frac{k}{m_C} \\ 0 & \frac{k}{m_O} & 0 \end{bmatrix}$$

$$\det(\underline{\underline{A}} - \lambda_2 \underline{\underline{I}}) = 0$$

As before, we remove the third equation and the third variable from the equation:

$$\begin{bmatrix} 0 & \frac{k}{m_O} \\ \frac{k}{m_C} & -\frac{2k}{m_C} + \frac{k}{m_O} \end{bmatrix} \begin{bmatrix} w_{1,2} \\ w_{2,2} \end{bmatrix} = \begin{bmatrix} 0 \\ -\frac{k}{m_C} \end{bmatrix} \qquad (28.6.16)$$

With this new matrix, we can calculate the determinant

$$\det(\underline{\underline{A}}_2) = -\frac{k^2}{m_O m_C} \neq 0$$

so it has an inverse which is

$$\underline{\underline{A}}_2^{-1} = \frac{1}{-\frac{k^2}{m_O m_C}} \begin{bmatrix} -\frac{2k}{m_C} + \frac{k}{m_O} & -\frac{k}{m_O} \\ -\frac{k}{m_C} & 0 \end{bmatrix} = \begin{bmatrix} \frac{2m_O}{k} - \frac{m_C}{k} & \frac{m_C}{k} \\ \frac{m_O}{k} & 0 \end{bmatrix}$$

So that the solution to equation (28.6.16) is

$$\begin{bmatrix} w_{1,2} \\ w_{2,2} \end{bmatrix} = \begin{bmatrix} -1 \\ 0 \end{bmatrix}$$

and the eigenvector that corresponds to $\lambda_2 = -{}^{k}\!/_{m_O}$ is

$$\underline{w}_2 = \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \tag{28.6.17}$$

To find the third eigenvector, the eigenvector that corresponds to $\lambda_3 = -\frac{k}{m_O}\left(1 + 2\frac{m_O}{m_C}\right)$

$$\underline{\underline{A}} - \lambda_3 \underline{\underline{I}} = \begin{bmatrix} {}^{2k}\!/_{m_C} & {}^{k}\!/_{m_O} & 0 \\ {}^{k}\!/_{m_C} & {}^{k}\!/_{m_O} & {}^{k}\!/_{m_C} \\ 0 & {}^{k}\!/_{m_O} & {}^{2k}\!/_{m_C} \end{bmatrix}$$

$$\det(\underline{\underline{A}} - \lambda_3 \underline{\underline{I}}) = 0$$

As before, we remove the third equation and the third variable from the equation:

$$\begin{bmatrix} {}^{2k}\!/_{m_C} & {}^{k}\!/_{m_O} \\ {}^{k}\!/_{m_C} & {}^{k}\!/_{m_O} \end{bmatrix} \begin{bmatrix} w_{1,3} \\ w_{2,3} \end{bmatrix} = \begin{bmatrix} 0 \\ -{}^{k}\!/_{m_C} \end{bmatrix} \tag{28.6.18}$$

With this new matrix, we can calculate the determinant

$$\det(\underline{\underline{A}}_2) = \frac{k^2}{m_O m_C} \neq 0$$

so it has an inverse which is

$$\underline{\underline{A}}_2^{-1} = \frac{1}{\frac{k^2}{m_O m_C}} \begin{bmatrix} {}^{k}\!/_{m_O} & -{}^{k}\!/_{m_O} \\ -{}^{k}\!/_{m_C} & {}^{2k}\!/_{m_C} \end{bmatrix} = \begin{bmatrix} {}^{m_C}\!/_{k} & -{}^{m_C}\!/_{k} \\ -{}^{m_O}\!/_{k} & {}^{2m_O}\!/_{k} \end{bmatrix}$$

So that the solution to equation (28.6.16) is

$$\begin{bmatrix} w_{1,3} \\ w_{2,3} \end{bmatrix} = \begin{bmatrix} 1 \\ -\dfrac{2m_O}{m_C} \end{bmatrix}$$

and the eigenvector that corresponds to $\lambda_3 = -\frac{k}{m_O}\left(1 + 2\frac{m_O}{m_C}\right)$ is

$$\underline{w}_3 = \begin{bmatrix} 1 \\ -\dfrac{2m_O}{m_C} \\ 1 \end{bmatrix} \qquad (28.6.19)$$

So we have the three eigenvalues and the three eigenvectors. So what? What good do they do us?

For a vibrating molecule, the square root of the absolute value of the eigenvalues from doing an eigenanalysis of Newton's equations of motion, as we have done, are the normal frequencies. You see that the units of the eigenvalues are 1/sec$^2$, so the square root has units of frequency (or inverse time).

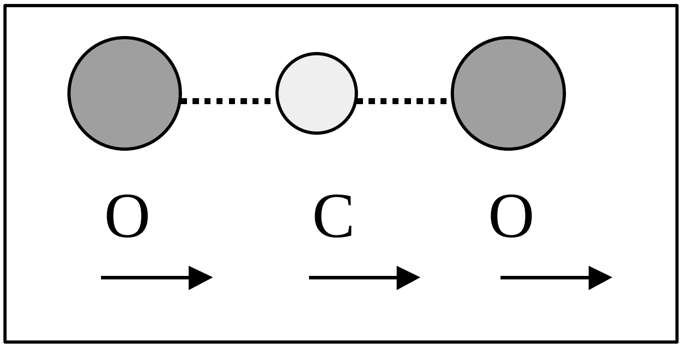
For carbon dioxide, the three normal frequencies are:

$$\underline{\omega} = \begin{bmatrix} 0 \\ \sqrt{\dfrac{k}{m_O}} \\ \sqrt{\dfrac{k}{m_O}\left(1 + \dfrac{2m_O}{m_C}\right)} \end{bmatrix}$$

The frequency of zero is no frequency at all. It is not a vibrational mode. In fact, it is a translation of the molecule. We can see this by examining the eigenvectors. The eigenvector that corresponds to $\lambda_1 = 0$ or $\omega_1 = \sqrt{|\lambda_1|} = 0$ is

$$\underline{w}_1 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \qquad (28.6.15)$$

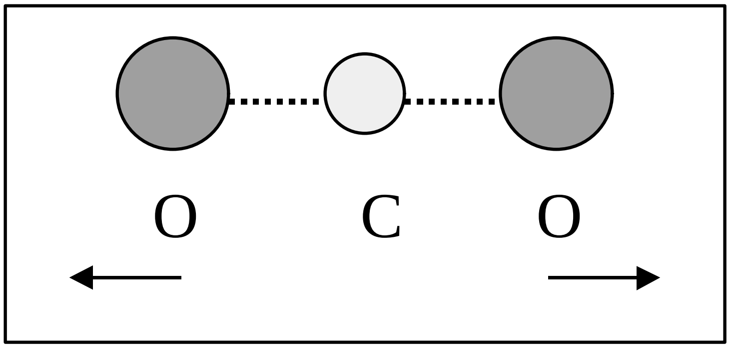
This is a description of the normal vibration associated with eigenfrequency of zero. It says that all atoms move the same amount in the x-direction.



The eigenvector that corresponds to $\lambda_2 = -{}^{k}\!/_{m_O}$ or $\omega_2 = \sqrt{|\lambda_2|} = \sqrt{\frac{k}{m_O}}$ is

$$\underline{w}_2 = \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \tag{28.6.17}$$

This eigenvector describes a vibration where both the oxygen move away from the C equally and the carbon does not move.

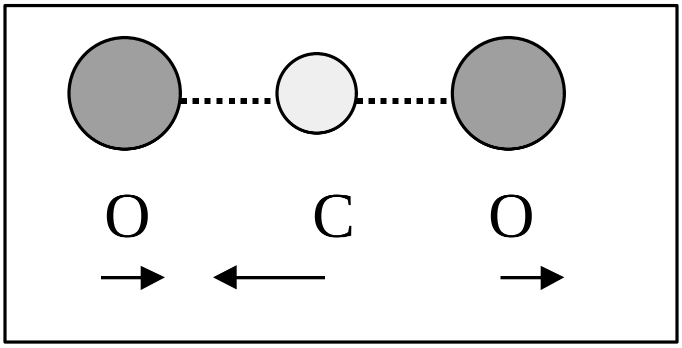


The eigenvector that corresponds to $\lambda_3 = -\frac{k}{m_O}\left(1 + 2\frac{m_O}{m_C}\right)$ or

$\omega_3 = \sqrt{|\lambda_3|} = \sqrt{\frac{k}{m_O}\left(1 + 2\frac{m_O}{m_C}\right)}$ is

$$\underline{w}_3 = \begin{bmatrix} 1 \\ -\frac{2m_O}{m_C} \\ 1 \end{bmatrix} \tag{28.6.19}$$

This eigenvector describes a vibration where both the oxygen move to the right and the carbon move more to the left, in such a way that there is no center of mass motion.



The normal modes of motion provide a complete, independent set of vibrations from which any other vibration is a linear combination.