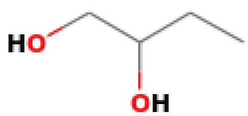
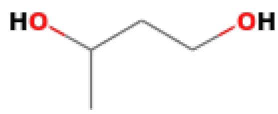
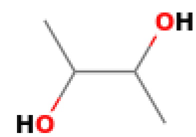
Exam III Solutions
Administered: Monday, November 14, 2022
24 points

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. (14 points)
Consider a mixture of four butanediol ($C_4O_2H_{10}$) isomers shown below.

			
1,2-Butanediol	1,3-Butanediol	1,4-Butanediol	2,3-Butanediol

Equilibrium coefficients, which relate mole fractions of components to one another, are given below:

$$K_{1,3-1,2}^{eq} = x_{1,3}/x_{1,2} = 0.665$$

$$K_{1,4-1,3}^{eq} = x_{1,4}/x_{1,3} = 0.740$$

$$K_{2,3-1,4}^{eq} = x_{2,3}/x_{1,4} = 0.542$$

The sum of the mole fractions is unity.

$$x_{1,2} + x_{1,3} + x_{1,4} + x_{2,3} = 1$$

(a) Is this system of algebraic equations linear or nonlinear? (2 pts)
(b) If linear, rearrange the problem as $\underline{A}\underline{x} = \underline{b}$ and identify $\underline{A}, \underline{x}$ *and* $\underline{b}$.
If nonlinear, rearrange the problem as $\underline{J}\underline{\delta x} = -\underline{R}$ and identify $\underline{J}, \underline{\delta x}$ *and* $\underline{R}$. (6 pts)
(c) Determine the composition of this mixture. (6 pts)

Solution:

(a) Is this system of algebraic equations linear or nonlinear? (2 pts)

This set of equations can be expressed as a system of linear algebraic equations,

$$\begin{gathered} x_{1,2}K_{1,3-1,2}^{eq} - x_{1,3} = 0 \\ x_{1,3}K_{1,4-1,3}^{eq} - x_{1,4} = 0 \\ x_{1,4}K_{2,3-1,4}^{eq} - x_{2,3} = 0 \\ x_{1,2} + x_{1,3} + x_{1,4} + x_{2,3} = 1 \end{gathered}$$

(b) If linear, rearrange the problem as $\underline{A}\underline{x} = \underline{b}$ and identify $\underline{A}, \underline{x}$ *and* $\underline{b}$.
If nonlinear, rearrange the problem as $\underline{J}\underline{\delta x} = -\underline{R}$ and identify $\underline{J}, \underline{\delta x}$ *and* $\underline{R}$. (6 pts)

This set of linear algebraic equations can be written in matrix form as

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

where $\underline{A} = \begin{bmatrix} K^{eq}_{1,3-1,2} & -1 & 0 & 0 \\ 0 & K^{eq}_{1,4-1,3} & -1 & 0 \\ 0 & 0 & K^{eq}_{2,3-1,4} & -1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$, $\underline{b} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$ and $\underline{x} = \begin{bmatrix} x_{1,2} \\ x_{1,3} \\ x_{1,4} \\ x_{2,3} \end{bmatrix}$.

(c) Determine the composition of this mixture. (6 pts)

To solve this problem, I wrote the following Matlab script, `xm03p01_f22.m`.

```
clear all;
format long;
Keq_13_12 = 0.665;
Keq_14_13 = 0.740;
Keq_23_14 = 0.542;
%
A = [Keq_13_12 -1.0 0.0 0.0
    0.0 Keq_14_13 -1.0 0.0
    0.0 0.0  Keq_23_14 -1.0
    1.0 1.0 1.0 1.0];
b = [0; 0; 0; 1];
detA = det(A)
invA = inv(A)
x = invA*b
```

At the command line prompt, I executed the script with the command

```
>> xm03p01_f22
```

which generated the following output

```
A =
   0.665000000000000  -1.000000000000000                   0                   0
                   0   0.740000000000000  -1.000000000000000                   0
                   0                   0   0.542000000000000  -1.000000000000000
   1.000000000000000   1.000000000000000   1.000000000000000   1.000000000000000

detA =   2.423818200000000

x =
   0.412572197040191
   0.274360511031727
   0.203026778163478
   0.110040513764605
```

Therefore the composition of the mixture is given by

$$\underline{x} = \begin{bmatrix} x_{1,2} \\ x_{1,3} \\ x_{1,4} \\ x_{2,3} \end{bmatrix} = \begin{bmatrix} 0.413 \\ 0.274 \\ 0.203 \\ 0.110 \end{bmatrix}$$

Problem 2. (10 points)
For the system described in problem 1, the equilibrium coefficients were evaluated at 300 K, using the relation

$$K^{eq}_{1,3-1,2} = exp\left(-\frac{\Delta G_{1,3-1,2}}{RT}\right) \text{ where } \Delta G_{1,3-1,2} = 1.018\ kJ/mol$$

$$K^{eq}_{1,4-1,3} = exp\left(-\frac{\Delta G_{1,4-1,3}}{RT}\right) \text{ where } \Delta G_{1,4-1,3} = 0.750\ kJ/mol$$

$$K^{eq}_{2,3-1,4} = exp\left(-\frac{\Delta G_{2,3-1,4}}{RT}\right) \text{ where } \Delta G_{2,3-1,4} = 1.526\ kJ/mol$$

In Problem 2, you don't know the temperature but you do measure $x_{1,2} = 0.375$.

(a) Is this system of algebraic equations linear or nonlinear? (2 pts)
(b) Determine the temperature and the composition of the other three isomers. (8 pts)

Solution:

(a) Is this system of algebraic equations linear or nonlinear? (2 pts)

This is a set of non-linear algebraic equations, which can be written as follows.

$$x_{1,2}exp\left(-\frac{\Delta G_{1,3-1,2}}{RT}\right) - x_{1,3} = 0$$
$$x_{1,3}xp\left(-\frac{\Delta G_{1,4-1,3}}{RT}\right) - x_{1,4} = 0$$
$$x_{1,4}exp\left(-\frac{\Delta G_{2,3-1,4}}{RT}\right) - x_{2,3} = 0$$
$$x_{1,2} + x_{1,3} + x_{1,4} + x_{2,3} - 1 = 0$$

I will solve this using the Newton Raphson Method with Numerical Approximations to the Derivatives, as implemented in the code `nrndn.m`.

This code requires that I input my system of nonlinear algebraic equations in the function, `funkeval.m`.

```
function f = funkeval(x)
%  these two lines force a column vector of length n
n = max(size(x));
f = zeros(n,1);
%  enter the constants
dG_13_12 = 1.018; % kJ/mol
dG_14_13 = 0.750; % kJ/mol
dG_23_14 = 1.526; % kJ/mol
R = 0.008314; % kJ/mol/K
x12 = 0.375;
% identify variables
T = x(1); % K
x13 = x(2);
x14 = x(3);
```

```
x23 = x(4);
% compute equilibrium coefficients
 Keq_13_12 = exp(-dG_13_12/(R*T));
 Keq_14_13 = exp(-dG_14_13/(R*T));
 Keq_23_14 = exp(-dG_23_14/(R*T));
% write equations
f(1) = x12*Keq_13_12 - x13;
f(2) = x13*Keq_14_13 - x14;
f(3) = x14*Keq_23_14 - x23;
f(4) = x12 + x13 + x14 + x23 - 1.0;
```

The Newton Raphson method requires an initial guess. I will use the solution from problem 1 as my initial guess. I want the tolerance to be 1.0^{-6}. I set the print flag to 1. At the command line prompt, I executed the following commands:

```
clear all;
x0 = [300.0 0.274 0.203 0.110];
tol = 1.0e-6;
iprint = 1;
[x,err,f] = nrndn(x0,tol,iprint)
```

This command provided the following output.

```
 iter =    1, err =  3.60e+01 f =  2.27e-02
 iter =    2, err =  7.56e+00 f =  2.42e-03
 iter =    3, err =  2.70e-01 f =  8.25e-05
 iter =    4, err =  3.17e-04 f =  9.60e-08
 iter =    5, err =  4.35e-10 f =  1.32e-13

x =   1.0e+02 *
   3.875977611354368   0.002734232681341   0.002166496620035
0.001349270698624

err =     4.346386408959950e-10

f =     1.317278047012018e-13
```

Because the error is less than the specified tolerance, the Newton Raphson method has converged. Therefore the temperature is 387.6 K and the composition of the mixture is given by

$$\underline{x} = \begin{bmatrix} x_{1,2} \\ x_{1,3} \\ x_{1,4} \\ x_{2,3} \end{bmatrix} = \begin{bmatrix} 0.375 \\ 0.273 \\ 0.217 \\ 0.135 \end{bmatrix}$$

This solution is not especially sensitive to the initial guess. All of the following initial guesses converged to this solution.

```
x0 = [300.0 0.274 0.203 0.110];
x0 = [300.0 1.0/3.0 1.0/3.0 1.0/3.0];
x0 = [400.0 0.274 0.203 0.110];
x0 = [400.0 1.0/3.0 1.0/3.0 1.0/3.0];
```