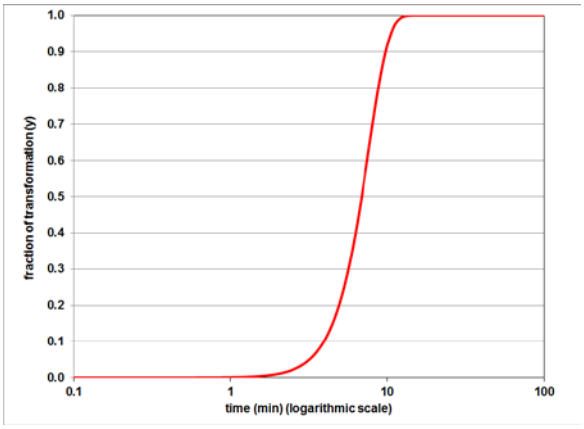
Final Exam
Administered: Friday, December 4, 2015
8:00 AM – 10:00 AM
22 points

Problem 1. (6 points)

"Most solid-state transformations do not occur instantaneously because obstacles impeded the course of the reaction and make it dependent on time." [Callister, W.D., "Materials Science and Engineering: An Introduction, Wiley & Sons, New York, Fifth Ed., p. 296]. One expression used to describe the fraction of solid that has transformed is the Avrami equation, shown in the equation and Figure below, where y is the fraction of transformation, t is time (min), k is a rate constant (min^{-1}) and n is an exponent.

$$y = 1 - \exp\left(-kt^n\right)$$



(a) Linearize this equation so that it is linear in the unknown parameters, k and n.
(b) Using the table of data providing y and t in the file "xm4p01_f15.txt" on the exam portion of the course website, perform a linear regression to determine the mean values of k and n for this data.
(c) Also report the standard deviations of k and n.

Solution:

(a) Linearize this equation so that it is linear in the unknown parameters, k and n.

Convert the data into a linear form necessary for a linear regression.

$$y = 1 - \exp\left(-kt^n\right)$$

$$1 - y = \exp\left(-kt^n\right)$$

$$\ln(1 - y) = -kt^n$$

This expression is still not linear in k and n. Rearrange and take the log again.

$$\ln\left(\frac{1}{1-y}\right) = kt^n$$

$$\ln\left[\ln\left(\frac{1}{1-y}\right)\right] = \ln(k) + n\ln(t)$$

Now this is in linear form, $z = mx + b$, where the independent variable, $x = \ln(t)$, the dependent variable, $z = \ln\left[\ln\left(\frac{1}{1-y}\right)\right]$, the slope, $m = n$, and the intercept, $b = \ln(k)$.

(b) Using the table of data providing *y* and *t* in the file "xm4p01_f15.txt" on the exam portion of the course website, perform a linear regression to determine the mean values of *k* and *n* for this data.

I used the code linreg1.m for linear regression with one independent variable.

I wrote the small script xm4p01_f15.m

```
clear all;

M = [0.10   3.03E-07
0.11  5.75E-07
0.12  7.72E-07
... bunch of data omitted in this printout ...
9.80  8.45E-01
9.90  8.66E-01
10.00 8.13E-01];

n = max(size(M));
for i = 1:1:n
    x(i) = log(M(i,1));
    y(i) = log(log(1.0/(1.0-M(i,2))));
end
[b,bsd,MOF] = linreg1(x, y)
n_mean = b(2)
k_mean = exp(b(1))

n_sd = bsd(2)
k_sd = abs(bsd(1)/b(1))*k_mean
```

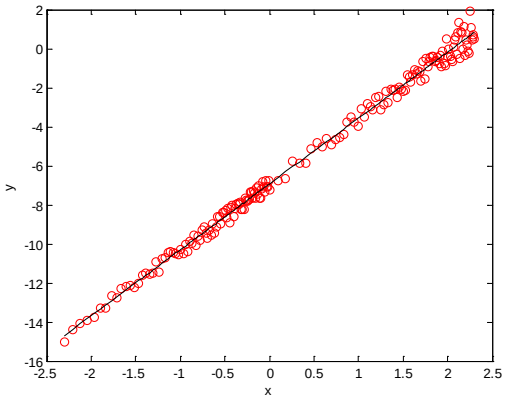
At the command line prompt, I executed the script

```
>> xm4p01_f15
```

This generated the following output for the means, standard deviations and Measure of Fit.

```
>> xm4p01_f15

b =
   -6.9298
    3.3748

bsd =
    0.0258
    0.0189
```

```
MOF =    0.9944

n_mean =    3.3748
k_mean =   9.7819e-04
n_sd =    0.0189
k_sd =   3.6439e-06
```



The mean value of *n* is 3.37.
The mean value of *k* is 9.8e-4 min^{-1}.

The code also generated a plot, shown here.

(c) Also report the standard deviations of *k* and *n*.

Since the slope was n, the standard deviation of n is simply the standard deviation of the slope. The standard deviation of *n* is 0.02.

For the standard deviation of *k*, we use the relation for the propagation of error that the relative error of *k* is equal to the relative error of the intercept.

$$\frac{s_k}{\bar{x}_k} = \left|\frac{s_b}{\bar{x}_b}\right| \text{ so } s_k = \left|\frac{s_b}{\bar{x}_b}\right| \bar{x}_k$$

The standard deviation of *k* is 3.6e-6 min^{-1}.

Problem 2. (4 points)

Measurements of the elastic modulus, *E*, of large-particle composites, formed by particles (*p*) distributed in a matrix (*m*) at a particle volume fraction, V_p, ($V_m = 1 - V_p$) known to fall between an upper limit, given by [Callister, W.D., "Materials Science and Engineering: An Introduction, Wiley & Sons, New York, Fifth Ed., pp. 523-524].

$$E_{upper} = E_m V_m + E_p V_p$$

and a lower limit given by

$$E_{lower} = \frac{E_m E_p}{E_m V_p + E_p V_m}.$$

Experiments are performed tungsten particles dispersed in a copper matrix and the following results are obtained. For $V_p = 0.6$, $E_{upper} = 260$ GPa and $E_{lower} = 180$ GPa. (See Figure 17.3 of Callister, p. 524.)

(a) Given this information, what numerical method can be used to determine the intrinsic elastic moduli of the matrix, E_m, and the particle, E_p.

(b) Determine E_m and E_p.

Solution:

I would use the multivariate Newton Raphson method with numerical approximations to the derivatives to solve a set of non-linear algebraic equations,

$$f_1(E_m, E_p) = E_{upper} - (E_m V_m + E_p V_p) = 0$$

$$f_2(E_m, E_p) = E_{lower} - \frac{E_m E_p}{E_m V_p + E_p V_m} = 0$$

Alternatively, since equation (1) is linear, one of the two variables could be eliminated and the single variable version of the Newton-Raphson method could be used.

$$E_p = \frac{E_{upper} - E_m V_m}{V_p}$$

$$f(E_m) = E_{lower} - \frac{E_m \dfrac{E_{upper} - E_m V_m}{V_p}}{E_m V_p + \dfrac{E_{upper} - E_m V_m}{V_p} V_m} = 0$$

(b) Determine E_m and E_p.

I wrote a little script in the file xm4p02_f15.m

```
clear all;
format long;
Eupper = 260.0;
Elower = 180.0;
Eavg = (Eupper + Elower)/2.0;
Emo = Eavg;
Epo = Eavg;
xo = [Emo,Epo]
tol = 1.0e-6;
iprint = 1;
[x,err,f] = nrndn(xo,tol,iprint)
```

I modified the input function for nrndn.m as follows

```
function f = funkeval(x)
n = max(size(x));
f = zeros(n,1);
Em = x(1);
Ep = x(2);
Vp = 0.6;
Vm = 1.0 - 0.6;
Eupper = 260.0;
Elower = 180.0;
f(1) = Eupper - (Vm*Em + Vp*Ep);
f(2) = Elower - Em*Ep/(Vm*Ep + Vp*Em);
```

I executed the script and received the following output:

```
>> xm4p02_f15

xo =   220   220

iter =    1, err =  4.15e+11 f =  4.00e+01
 iter =    2, err =  4.14e+11 f =  6.90e+11
 iter =    3, err =  4.67e+08 f =  3.75e+08
 iter =    4, err =  1.52e+04 f =  2.76e+04
 iter =    5, err =  4.53e+02 f =  5.83e+02
 iter =    6, err =  9.70e+01 f =  8.16e+01
 iter =    7, err =  1.43e+01 f =  9.16e+00
 iter =    8, err =  4.14e-01 f =  2.51e-01
 iter =    9, err =  3.61e-04 f =  2.18e-04
 iter =   10, err =  2.74e-10 f =  1.66e-10

x =   1.0e+02 *
   4.577638883463117   1.281574077691255
```

```
err =     2.738129993897519e-10
f =     1.656811805361797e-10
```

Based on this information, the intrinsic elastic modulus of the matrix (copper), E_m, is 458 GPa and the intrinsic elastic modulus of the particle (tungsten), E_p, is 128 GPa.

Problem 3. (4 points)

It has been observed that the relative weight gain, *W*, as a function of time, *t*, due to formation of oxides on metals follows the following functional form [Callister, W.D., "Materials Science and Engineering: An Introduction, Wiley & Sons, New York, Fifth Ed., p. 593]

$$W(t) = K_1 \ln\left(K_2 t + K_3\right)$$

where three empirically determined constants appear and time is measure in days. This expression arises from a weight gain rate equation of the form

$$\frac{dW(t)}{dt} = \frac{K_1 K_2}{K_2 t + K_3}$$

For a surface with a composition gradient, the constants become dependent on the local composition and are therefore functions of time. We propose a form

$$K_1(t) = c_1 \exp\left(-\frac{(t - t_{\max})^2}{s_1}\right).$$

such that the weight gain is now given by

$$W(t) = \int_{t=0}^{t} \frac{K_1(t) K_2}{K_2 t + K_3} dt$$

(a) What method could be used to evaluate the weight gain as a function of time?
(b) Determine the weight gain of such a model at t = 14 days with the following parameters: $c_1 = 0.2$, $s_1 = 3$, $t_{\max} = 4$, $K_2 = 5$, and $K_3 = 6$.

Solution:

(a) What method could be used to evaluate the weight gain as a function of time?

A method for numerical integration, such as the Simpson's second order method, should be used.

(b) Determine the weight gain of such a model at t = 14 days with the following parameters: $c_1 = 0.2$, $s_1 = 3$, $t_{\max} = 4$, $K_2 = 5$, and $K_3 = 6$.

I wrote a little script in the file xm4p03_f15.m, which contained the following text

```
clear all;
format long;
a = 0;
b = 14;
nintervals = 10;
```

```
integral_10 = simpson2(a,b,nintervals);
nintervals = 100;
integral_100 = simpson2(a,b,nintervals);
nintervals = 1000;
integral_1000 = simpson2(a,b,nintervals);
```

I altered the input file for the simpson2.m code as follows

```
function f = funkeval(t)
c1 = 0.2;
s1 = 3;
tmax = 4;
K2 = 5;
K3 = 6;
K1 = c1*exp(-(t-tmax)^2/s1);
f = K1*K2/(K2*t+K3);
```

At the command line prompt, I executed the code and received the following output

```
>> xm4p03_f15

Using the Simpsons Second Order method
to integrate from 0.000000 to 14.000000 with 10 nintervals,
the integral is 1.265478e-01

Using the Simpsons Second Order method
to integrate from 0.000000 to 14.000000 with 100 nintervals,
the integral is 1.258627e-01

Using the Simpsons Second Order method
to integrate from 0.000000 to 14.000000 with 1000 nintervals,
the integral is 1.258627e-01
```

Therefore the relative weight gain after 14 days is 12.58%. We know this is a converged number since the integrals with 100 and 1000 intervals gave the same result.

Alternate Solution to Problem 3:

The problem can also be solved as an ODE, using, for example, the Runge-Kutta method.

$$\frac{dW(t)}{dt} = \frac{K_1 K_2}{K_2 t + K_3}$$

subject to the initial condition that the object is initially unoxidized, $W(t=0) = 0$.

I wrote a little script in xm04p03_f15.m

```
clear all;
close all;

n=1000;
xo = 0;
yo = 0;
xf = 14.0;

[x,y]=rk41(n,xo,xf,yo);

ans = y(n+1)
```

I typed the ODE into the input routine for rk1.m

```
function dydx = funkeval(x,y);
c1 = 0.2;
s1 = 3.0;
tmax = 4.0;
K2 = 5.0;
K3 = 6.0;
t = x;
K1 = c1*exp(-((t-tmax)^2)/s1);
dydx = K1*K2/(K2*t+K3);
```

At the command line prompt, I ran the script and received the following output

```
>> xm4p03_f15

ans =    0.1259
```

This is the same result from the numerical integration approach.

Problem 4. (8 points)

Consider the dimerization reaction:

$$2A \rightarrow B$$

The reaction rate is given by

$$rate = C_A^2 k_o e^{-\frac{E_a}{RT}} \qquad [\text{moles/m}^3\text{/sec}]$$

where

concentration of A: C_A [moles/m^3]
prefactor: k_o [m^3/(moles·sec)]
activation energy for reaction: E_a [Joules/mole]
constant: $R = 8.314$ [Joules/mole/K]
temperature: T [K]

If this reaction were to take place in a continuous stirred tank reactor, the mole balances on A and B would have the form

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

$$V\frac{dC_A}{dt} = C_{A,in}F - C_A F - 2rate \qquad (1)$$

$$V\frac{dC_B}{dt} = C_{B,in}F - C_B F + rate \qquad (2)$$

Equations (1) and (2) represent a set of two non-linear coupled ordinary differential equations.

Assume the following parameter values:

inlet concentration of A: $C_{A,in} = 2{,}000$ [moles/m^3]
inlet concentration of B: $C_{B,in} = 0$ [moles/m^3]
prefactor: $k_o = 0.90$ [m^3/(moles·sec)]
activation energy for reaction: $E_a = 56{,}000$ [Joules/mole]
temperature: $T = 500$ [K]
reactor volume: $V = 1$ [m^3]
flowrate: $F = 0.01$ [m^3/sec]

Also, assume that reactor initially has no A or B in it, so that the initial conditions are given by

initial concentration of A: $C_A(t=0) = 0$ [moles/m^3]
initial concentration of B: $C_B(t=0) = 0$ [moles/m^3]

Numerically solve the ordinary differential equations.
(a) Sketch the plot of the concentrations for A and B as a function of time.
(a) Report the steady state concentration of A and B.
(c) From this calculation, how do you know that the function is at steady state?
(d) From this calculation, verify that you have used a sufficiently fine temporal resolution.

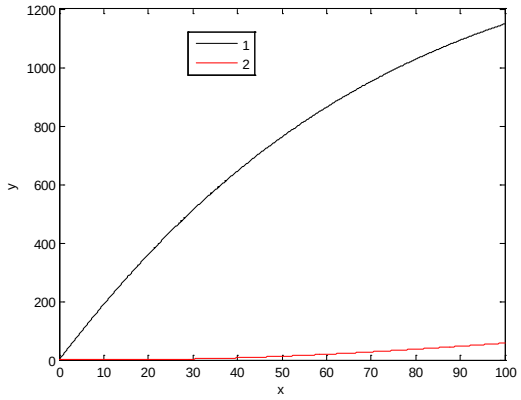
Solution:

Use the routine rk4n.m. Change the input file to look like:

```
function dydx = funkeval(x,y);
CA = y(1);
CB = y(2);
CAin = 2000.0; % mol/m^3
CBin = 0.0; % mol/m^3
R = 8.314; % J/mol/K
T = 500.0; % K
Ea = 56000.0; % J/mol
ko = 0.90; % m^3/mol/sec
V = 1; % m^3
F = 0.01; % m^3/sec
rate = CA*CA*ko*exp(-Ea/(R*T));
dCAdt = 1/V*(CAin*F – CA*F -2*rate);
dCBdt = 1/V*(CBin*F – CB*F + rate);
dydx(1) = dCAdt;
dydx(2) = dCBdt;
```

We don't know how long to run this. We choose to solve from $x_0 = 0$ to $x_f = 100$ initially. We first use n = 1000 steps. We create a little script, xm4p04_f15.m,

```
clear all;
format long

n = 1000;
xo = 0;
xf = 100;
yo = [0,0];
[x,y]=rk4n(n,xo,xf,yo);
y_n1000_t100 = y(n+1,1)
```



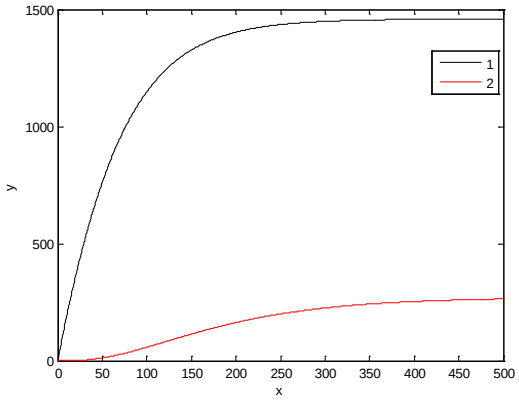
At the command prompt, we type and receive the following output:

```
>> xm4p04_f15

y_n1000_t100 =     1.148938691858799e+03
```

The code executes without any warning messages. The plot is shown above. Clearly, the slope is not zero at t = 100. We need to solve the ODE for a longer time.

We next choose to solve from $x_0 = 0$ to $x_f = 500$. We first use n = 1000 steps. We change one number in our script,

```
clear all;
format long

n = 1000;
xo = 0;
xf = 500;
yo = [0,0];
[x,y]=rk4n(n,xo,xf,yo);
y_n1000_t500 = y(n+1,1)
```



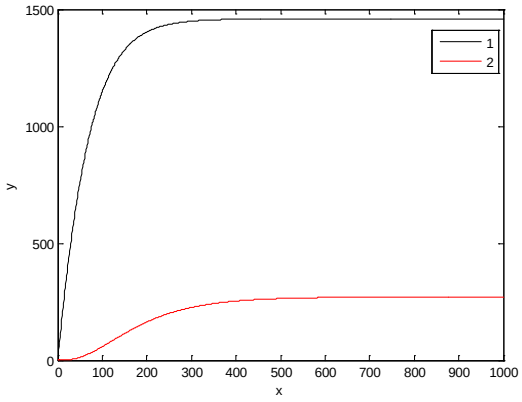
At the command prompt, we type and receive the following output:

```
>> xm4p04_f15

y_n1000_t500 =      1.458911283067430e+03
```

The code executes without any warning messages. The plot is shown above. The slope is close to zero at t = 500. However, the value of the concentration of A is very different from t=100 and t=500. We should solve the ODE for a longer time.

We next choose to solve from $x_0 = 0$ to $x_f = 1000$. We first use n = 1000 steps. We change one number in our script,

```
clear all;
format long

n = 1000;
xo = 0;
xf = 1000;
yo = [0,0];
[x,y]=rk4n(n,xo,xf,yo);
y_n1000_t1000 = y(n+1,1)
```



At the command prompt, we type and receive the following output:

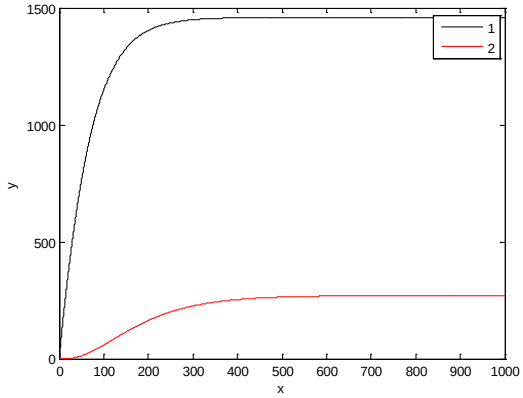
```
>> xm4p04_f15

y_n1000_t1000 =      1.459218193716320e+03
```

The code executes without any warning messages. The plot is shown above. The slope is close to zero at t = 1000. The value of the concentration of A is the same to three digits at t=500 and t=1000. We have solved the ODE for a sufficiently long time.

Finally, we want to make sure that we have used a sufficiently fine resolution in time. We rerun the script with n = 10000 intervals.

We change one number in our script,

```
clear all;
format long

n = 10000;
xo = 0;
xf = 1000;
yo = [0,0];
[x,y]=rk4n(n,xo,xf,yo);
y_n10000_t1000 = y(n+1,1)
```



At the command prompt, we type and receive the following output:

```
>> xm4p04_f15

y_n10000_t1000 =      1.459218193716320e+03
```

This number is the same as what was obtained for n=1000 intervals, therefore we have a reliable solution.

The concentration of A at steady state is about 1460 mol/m^3.