# Final Exam
Administered: Monday, December 10, 2018
10:15 AM – 12:15 PM
24 points

**Problem 1. (6 points)**

Diffusion in solids is often an activated process, in with the diffusivity can be approximated by an Arrhenius-type temperature dependence.

$$D = D_o \, exp\left(-\frac{E_a}{RT}\right)$$

where *D* is the diffusivity, *T* is the temperature, *R* is the gas constant (8.314 J/mol/K), $E_a$ is the activation energy and $D_o$ is the exponential prefactor.

(a) Linearize this equation so that it is linear in the unknown parameters, $E_a$ and $D_o$.
(b) Using the table of data providing *D* and *T* in the file "xm4p01_f18.txt" on the exam portion of the course website, perform a linear regression to determine the mean values of $E_a$ and $D_o$ for this data.
(c) Also report the standard deviations of $E_a$ and $D_o$.

**Solution:**

(a) Linearize this equation so that it is linear in the unknown parameters, $E_a$ and $D_o$.

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

$$D = D_o \, exp\left(-\frac{E_a}{RT}\right)$$

$$ln(D) = ln(D_o) - \frac{E_a}{RT}$$

This equation is in linear form, $y = mx + b$, where the independent variable, $x = -\frac{1}{RT}$, the dependent variable, $y = ln[D]$, the slope, $m = E_a$, and the intercept, $b = ln(kD_o)$.

(b) Using the table of data providing *D* and *T* in the file "xm4p01_f18.txt" on the exam portion of the course website, perform a linear regression to determine the mean values of $E_a$ and $D_o$ for this data.

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

I wrote the small script xm4p01_f18.m

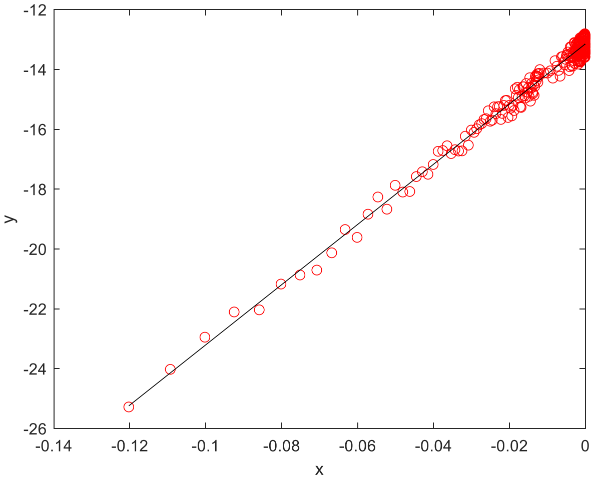
```
clear all;
format long;

M = [1      1.05057E-11
1.1   3.69164E-11
1.2   1.08156E-10
... omitted a bunch of data here ...
1800  2.58202E-06
1900  1.42443E-06];

n = max(size(M));
R = 8.314;
for i = 1:1:n
    x(i) = -1.0/(R*M(i,1));
    y(i) = log(M(i,2));
end
[b,bsd,MOF] = linreg1(x, y)
Ea_mean = b(2)
Do_mean = exp(b(1))

Ea_sd = bsd(2)
Do_sd = abs(bsd(1)/b(1))*Do_mean
```

At the command line prompt, I executed the script

```
>> xm4p01_f18
```

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

```
>> xm4p01_f18

b = 1.0e+02 *
  -0.131434625777366
   1.005956757207290

bsd =
   0.016154541590667
   0.725060410001251

MOF = 0.985763368900783

Ea_mean = 1.005956757207290e+02
Do_mean = 1.958243661081438e-06
Ea_sd = 0.725060410001251
Do_sd = 2.406864133442713e-09
```



The mean value of $E_a$ is 100.6 J/mol.
The mean value of $D_o$ is $1.96\text{x}10^{-6}$ $\text{cm}^2/\text{s}$

The code also generated a plot, shown here.

(c) Also report the standard deviations of $E_a$ and $D_o$.

Since the slope was $E_a$, the standard deviation of $E_a$ is simply the standard deviation of the slope. The standard deviation of $E_a$ is 0.73 J/mol.

For the standard deviation of *D<sub>o</sub>*, we use the relation for the propagation of error that the relative error of $D_o$ is equal to the relative error of the intercept.

$\frac{s_{Do}}{\overline{x}_{Do}} = \left|\frac{s_b}{\overline{x}_b}\right|$ so $s_{Do} = \left|\frac{s_b}{\overline{x}_b}\right| \overline{x}_{Do}$

The standard deviation of $D_o$ is 2.41x10$^{-9}$ cm$^2$/s.

**Problem 2. (6 points)**

Consider the following steady-state mass and energy balance for a non-isothermal continuous stirred tank reactor with an irreversible first order reaction:

$$0 = F_{in}C_{A,in} - F_{out}C_A - C_A V k_o e^{-\frac{E_a}{RT}}$$
$$0 = \Delta H_r C_A k_o e^{-\frac{E_a}{RT}} - \dot{Q}$$

where $F_{in} = F_{out} = 10.0\ l/s$ , $C_{A,in} = 1.0\ mol/l$, $V = 100.0\ l$ , $k_o = 1.0 \cdot 10^{-1}$ 1/s, $E_a =$ 10.0 kJ/mol, $\Delta\dot{H}_r = 50.0\ kJ/mol$ ,$\dot{Q} = 0.2\ kJ/l/s$ and $R = 0.008314\ kJ/mol/K$.

(a) Is this system of equations linear or nonlinear?
(b) What is the appropriate technique to solve this system of equations?
(c) Determine the steady values of the outlet concentration of A, $C_A$, and the temperature, *T*.

**Solution:**

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

This system of equations is non-linear in the unknowns, $C_A$ and *T*.

(b) What is the appropriate technique to solve this system of equations?

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

$$f_1(C_A, T) = F_{in}C_{A,in} - F_{out}C_A - C_A V k_o e^{-\frac{E_a}{RT}} = 0$$

$$f_2(C_A, T) = \Delta H_r C_A k_o e^{-\frac{E_a}{RT}} - \dot{Q} = 0$$

(c) Determine the steady values of the outlet concentration of A, $C_A$, and the temperature, *T*.

I wrote a little script in the file xm4p02_f18.m

```
clear all;
CA = 0.5;
T = 500.0
x0 = [CA,T];
tol = 1.0e-6;
iprint = 1;
[x,err,f] = nrndn(x0,tol,iprint)
```

I modified the input function for nrndn.m as follows

```
function f = funkeval(x)
n = max(size(x));
f = zeros(n,1);
%
Ca = x(1);
T = x(2);
%
Fin = 10.0; % l/s
Fout = 10.0; % l/s
Cain = 1.0; % mol/l
V = 100.0; % l
ko = 1.0e-1; % 1/s
Ea = 10.0; % kJ/mol
Qdot = 0.2; % kJ/l/s
R = 0.008314; % kJ/mol/K
dHr = 50.0; % kJ/mol
rate = ko*exp(-Ea/(R*T));
%
f(1) = Fin*Cain - Fout*Ca - Ca*V*rate;
f(2) = dHr*Ca*rate - Qdot;
```

I executed the script and received the following output:

```
>> xm4p02_f18

 iter =     1, err =  1.52e+02 f =  3.22e+00
 iter =     2, err =  8.73e+01 f =  2.04e-01
 iter =     3, err =  2.06e+01 f =  8.39e-02
 iter =     4, err =  8.05e-01 f =  3.03e-03
 iter =     5, err =  1.42e-03 f =  5.33e-06
 iter =     6, err =  4.43e-09 f =  1.66e-11

x = 1.0e+02 *
   0.009600000000000   3.784676214146318

err = 4.427839677216035e-09
f = 1.662775493878008e-11
```

Based on this information, the steady state concentration of A is 0.96 mol/l and the final temperature is 378.5 K.

**Correction:**
In the exam as given, there was a typographical error in the second equation, in which the sign of the heat removal term, $\dot{Q}$, was positive instead of negative.

$$f_2(C_A,T) = \Delta H_r C_A k_o e^{-\frac{E_a}{RT}} + \dot{Q} = 0$$

In this case, there are no real roots to this system of equations.

**Problem 3. (8 points)**

Consider the following transient mass and energy balance for a non-isothermal continuous stirred tank reactor with an irreversible first order reaction:

$$V\frac{dC_A}{dt} = F_{in}C_{A,in} - F_{out}C_A - C_A V k_o e^{-\frac{E_a}{RT}}$$
$$C_p\frac{dT}{dt} = \Delta H_r C_A k_o e^{-\frac{E_a}{RT}} - \dot{Q}$$

where all the variables are the same as they were in problem 2 and the heat capcity per unit volume, $C_p = \ 2.3\ kJ/l/K$.

(a) Is this system of ordinary differential equations linear or nonlinear?
(b) What is the appropriate technique to solve this system of equations?
(c) Solve the transient behavior of the concentration of A, $C_A$, and the temperature, $T$, up to 1000 seconds, if the initial concentration of the reactor is $C_{A,o} = C_{A,in}$ and the initial temperature is $T_o = 400.0\ K$. Sketch a plot of the concentration and temperature.
(d) Report values of the concentration of A, $C_A$, and the temperature, $T$ at 1000 seconds.

**Solution:**

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

This system of equations is non-linear in the unknowns, $C_A$ and $T$.

(b) What is the appropriate technique to solve this system of equations?

I would use the classical fourth order Runge-Kutta method to solve this system of two first order ordinary differential equations.

(c) Solve the transient behavior of the concentration of A, $C_A$, and the temperature, $T$, up to 1000 seconds, if the initial concentration of the reactor is $C_{A,o} = C_{A,in}$ and the initial temperature is $T_o = 400.0\ K$. Sketch a plot of the concentration and temperature.
(d) Report values of the concentration of A, $C_A$, and the temperature, $T$ at 1000 seconds.

I wrote a little script in the file xm4p03_f18.m

```
clear all;
format long

n = 1000;
xo = 0;
xf = 1.0e+3;
Cao = 1.0; % mol/l
T = 400.0; % K
yo = [Cao, T];
```

```
[x,y]=rk4n(n,xo,xf,yo);
Ca_f = y(n+1,1)
T_f = y(n+1,2)
```

I modified the input function for rk4n.m as follows

```
function dydx = funkeval(x,y);
Ca = y(1);
T = y(2);
%
Fin = 10.0; % l/s
Fout = 10.0; % l/s
Cain = 1.0; % mol/l
V = 100.0; % l
ko = 1.0e-1; % 1/s
Ea = 10.0; % kJ/mol
Qdot = 0.2; % kJ/l/s
R = 0.008314; % kJ/mol/K
dHr = 50.0; % kJ/mol
rate = ko*exp(-Ea/(R*T));
Cp = 2.30; % kJ/mol/K
%
dCadt = 1/V*(Fin*Cain - Fout*Ca - Ca*V*rate);
dTdt = 1/Cp*(dHr*Ca*rate - Qdot);
dydx(1) = dCadt;
dydx(2) = dTdt;
```

I executed the script and received the following output:

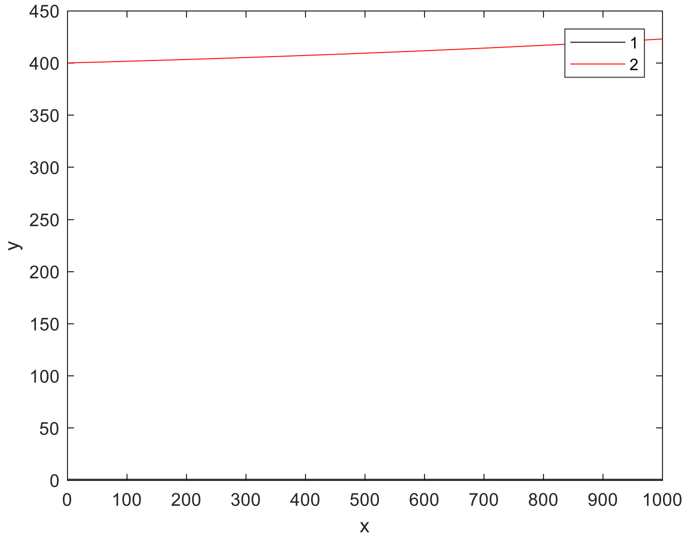
```
>> xm4p03_f18

Ca_f = 0.945075647006488
T_f = 4.230343591271803e+02
```

Based on this information, the steady state concentration of A is 0.945 mol/l and the final temperature is 423.0 K.

If I repeat the calculation with n = 10,000 time steps, I get the following result, which is the same to our desired tolerance.

```
Ca_f = 0.945075647006525
T_f = 4.230343591272344e+02
```

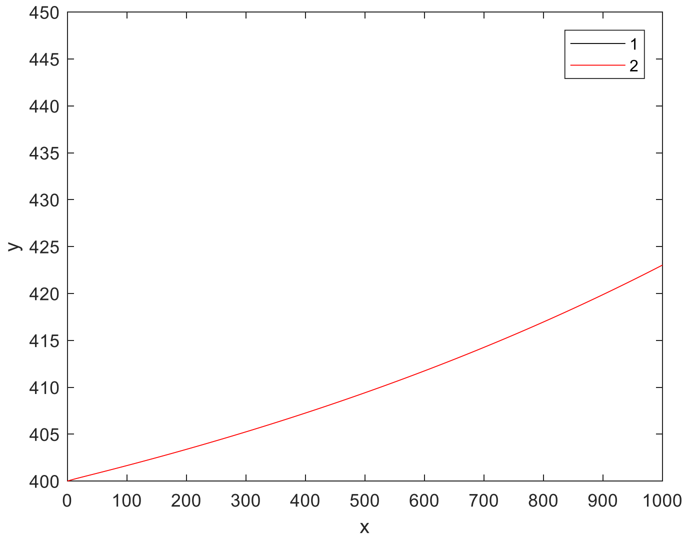
The plot of the transient behavior looks like this:



If we zoom in on the temperature, using the following commands

```
>> figure(1)
>> axis([0 1000 400 450])
```

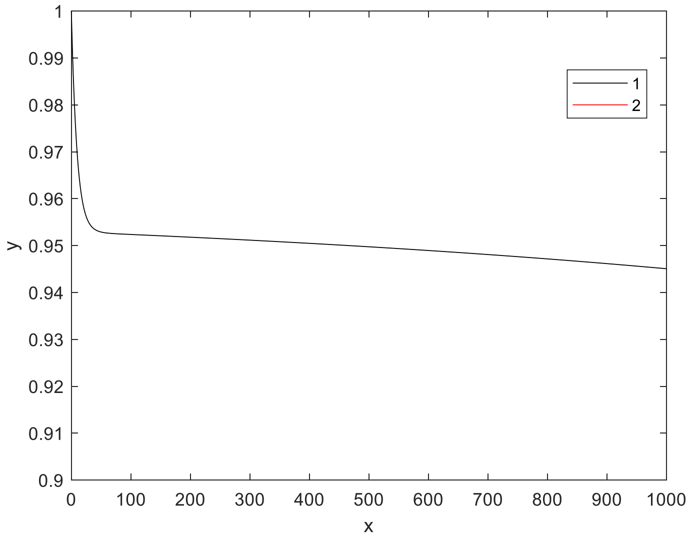
we observe a steady rise in the temperature.



If we zoom in on the concentration, using the following commands

```
>> figure(1)
>> axis([0 1000 0.9 1])
```

we observe a sudden drop in the concentration of A, followed by a slower decrease.



**Correction:**

In the exam as given, there was a typographical error in the second equation, in which the sign of the heat removal term, $\dot{Q}$, was positive instead of negative.

$$C_p \frac{dT}{dt} = \Delta H_r C_A k_o e^{-\frac{E_a}{RT}} + \dot{Q}$$

In this case, the values of the concentration and temperature at 1000 seconds are

```
Ca_f = 0.853462547803239
T_f = 6.860909864244846e+02
```

Based on this information, the steady state concentration of A is 0.853 mol/l and the final temperature is 686.0 K.

**Problem 4. (4  points)**

The gamma function is defined as

$$\Gamma(\alpha) = \int_0^\infty x^{\alpha-1} e^{-x} dx \quad \text{for } \alpha > 0$$

(a) Evaluate the gamma function for $\alpha = 6$ using the intrinsic gamma function in Matlab, `gamma`. You likely will need to use the `format long` statement in MatLab to get enough digits to display.

(b) How many intervals so you need in the second-order Simpson's method to obtain this result to four significant digits? What did you use as your upper limit of integration?

**Solution:**

(a) Evaluate the gamma function for $\alpha = 6$ using the intrinsic gamma function.

```
>> format long
>> y = gamma(6)
y =   120
```

(b) How many intervals so you need in the second-order Simpson's method to obtain this result to four significant digits? What did you use as your upper limit of integration?

I used the simpson2.m code and changed the integrand function to

```
function f = funkeval(x)
alpha = 6;
f = x^(alpha-1)*exp(-x);
```

From the command line prompt.

```
>> integral = simpson2(0,10,10000);
Using the Simpsons Second Order method
to integrate from 0.000000 to 10.000000 with 10000 nintervals,
integral = 1.119496844545163e+02
```

So using 10 as the upper limit & 10,000 intervals gives about 1 good significant digit.

```
>> integral = simpson2(0,100,1000)
Using the Simpsons Second Order method
to integrate from 0.000000 to 100.000000 with 1000 nintervals,
integral = 1.199999999999999e+02
```

So using 100 as the upper limit & 10,000 intervals gives about 15 good significant digits.

```
>> integral = simpson2(0,100,1000)
Using the Simpsons Second Order method
to integrate from 0.000000 to 100.000000 with 1000 nintervals,
integral = 1.200000000776258e+02
```

So using 100 as the upper limit & 1,000 intervals gives about 10 good significant digits.

```
>> integral = simpson2(0,100,100)
Using the Simpsons Second Order method
to integrate from 0.000000 to 100.000000 with 100 nintervals,
integral =     1.199808127755745e+02
```

So using 100 as the upper limit & 100 intervals gives about 4 good significant digits.