Problem 1.

a.

C: H: O: N=47.60%/12: 7.33%/1: (1-47.60%-7.30%-7.33%-3.00%)/16: 7.30%/14=1: 1.85: 0.55: 0.13

Therefore, the elemental composition for the ash-free biomass is $CH_{1.85}O_{0.55}N_{0.13}$.

Thus, the formula weight per C-atom is:

1*12 (g/mol) +1.85*1(g/mol)+0.55*16 (g/mol)+0.13*14(g/mol)=24.5 g/mol.

Since ethane is the sole carbon source, from the conservation of C-atom, we know

Y_{sx}=moles of biomass(x)/moles of ethane(s)

=

$$[\,22.8\frac{\text{g dry weight}}{\text{mole ethane}}]\times[(1-3\%)\frac{\text{g biomass}}{\text{g dry weight}}]\div[24.5\frac{\text{g biomass}}{\text{mol biomass}}]\times\frac{\text{1 mol ethane}}{\text{2 C - mole ethane}}$$

=0.451 (C-mole biomass/C-mol ethane)

b.

If assuming that CO_2, H_2O and $CH_aO_bN_c$ are the only metabolic products, then the overall metabolic reaction is

$$0.5\ C_2H_6+Y_{so}\ O_2+Y_{sn}\ NH_3 \rightarrow Y_{sx}\ CH_{1.85}O_{0.55}N_{0.13}+Y_{sc}CO_2+Y_{sw}\ H_2O$$

From a), we already got Y_{sx}=0.451.

Use mass balance conditions on each atom:

C: $0.5*2=Y_{sx}+Y_{sc}$

N: $Y_{sn}=Y_{sx}*0.13$

H: $0.5*6+Y_{sn}*3=Y_{sx}*1.85+Y_{sw}*2$

O: $Y_{so}*2=Y_{sx}*0.55+Y_{sc}*2+Y_{sw}$

After solving this set of linear equations, we finally get

Y_{sc}=0.549 (mol CO_2/C-mol ethane),

Y_{sn}= 0.0589 (mol NH_3/C-mol ethane),

Y_{sw}=1.17 (mol H_2O/C-mol ethane),

Y_{so}=1.26 (mol O_2/C-mol ethane)

Therefore, the full stoichiometric equation for the growth process

$$0.5\ C_2H_6+1.26\ O_2+0.0589\ NH_3 \rightarrow 0.451\ CH_{1.85}O_{0.55}N_{0.13}+0.549CO_2+1.17\ H_2O$$

The oxygen consumption is

$Y_{xo}=Y_{so}/Y_{sx}$=1.26/0.451=2.79 (mol O_2/C-mol biomass)

Then we can determine the heat evolved per kilogram dry weight from the enthalpy of combustion data:

$Q=0.5*\Delta H_{comb}(\text{ethane})+0.0589*\Delta H_{comb}(NH_3)-0.451*\Delta H_{comb}(\text{biomass})$

=-(0.5*1560 kJ/mol+0.0589*383 kJ/mol-19 (kJ/g dry weight)

$$\div[(1-3\%)\frac{\text{g biomass}}{\text{g dry weight}}]\times[24.5\frac{\text{g biomass}}{\text{C - mol biomass}}]\div\frac{1\,\text{C - mol ethane}}{0.451\,\text{C - mol biomass}}$$

=-586 kJ/c-mol ethane.

Then convert back again to per kilo dry weight

Q=

$$-586\frac{\text{kJ}}{\text{c - mol ethane}}\times[(1-3\%)\frac{\text{g biomass}}{\text{g dry weight}}]\div[24.5\frac{\text{g biomass}}{\text{C - mol biomass}}]\times\frac{1\,\text{C - mol ethane}}{0.451\,\text{C - mol biomass}}\times\frac{1000\text{g}}{1\text{kg}}$$

=-51.5 (MJ/ kg dry weight)

Problem 2.

For the reaction, $2NO + O_2 \xrightarrow{k_2} 2NO_2$, it is not possible for the apparent activation energy to be negative, or equivalently, the rate constant decreases as T increases. We are asked to write down the elementary steps which include an NO_3 species as an intermediate to explain this strange behavior.

A possible mechanism:

$$NO + O_2 \xrightarrow{k_1} NO_3$$

$$NO_3 \xrightarrow{k_{-1}} NO + O_2$$

$$NO_3 + NO \xrightarrow{k_2} 2NO_2$$

So the reaction rates: $r_1=k_1[NO][O_2]$, $r_{-1}=k_{-1}[NO_3]$, $r_2=k_2[NO_3][NO]$

If using PSSH for the intermediate NO_3, we have

$$\frac{d[NO_3]}{dt} = k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO_3][NO] = 0$$

From this we can obtain $[NO_3] = \dfrac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$

Thus

$$\begin{aligned} r_{NO} &= -\frac{d[NO]}{dt} = -k_1[NO][O_2] + k_{-1}[NO_3] - k_2[NO_3][NO] \\ &= -k_1[NO][O_2] + (k_{-1} - k_2[NO])\frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]} \\ &= -\frac{2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[NO]} \end{aligned}$$

In order to have third-order reaction kinetics as the form $r_{NO} = -k_{\text{effective forward}}[NO]^2[O_2]$, we have to assume $k_{-1} \gg k_2[NO]$, so that the overall reaction rate for NO is

$$r_{NO} = -\frac{2k_1k_2[NO]^2[O_2]}{k_{-1}}$$

where $k_{\text{effective forward}} = \dfrac{2k_1k_2}{k_{-1}}$

It is therefore under the condition when $k_{-1} \sim k_2[NO]$ or $k_{-1} \ll k_2[NO]$ for r_{NO} to deviate significantly from the normal third-order expression above.

Also let's see what happens to the activation energy.

$$E_{a,\text{overall}} \propto \ln\frac{2k_1k_2}{k_{-1}} \propto E_{a1} - E_{a,-1} + E_{a2} \sim \Delta H_{1,\text{rxn}} + E_{a2}$$

If $E_{a1}+E_{a2}-E_{a,-1} \sim \Delta H_{1,\text{rxn}}+E_{a2}<0$, then we can have a negative apparent activation energy, for example, if elementary step 1 has a significantly negative $\Delta H_{1,\,rxn}$, so as long as E_{a2} is not too high the overall process will have a negative $E_{a,\,overall}$.

For the reverse reaction of the overall reaction, including the reverse reaction for the second elementary step, i.e.

$$NO + O_2 \xrightarrow{k_1} NO_3$$

$$NO_3 \xrightarrow{k_{-1}} NO + O_2$$

$$NO_3 + NO \xrightarrow{k_2} 2NO_2$$

$$2NO_2 \xrightarrow{k_{-2}} NO_3 + NO$$

and still using PSSH on the intermediate NO_3

$$\frac{d[NO_3]}{dt} = k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO_3][NO] + k_{-2}[NO_2]^2 = 0$$

we can have the intermediate concentration:

$$[NO_3] = \frac{k_1[NO][O_2] + k_{-2}[NO_2]^2}{k_{-1} + k_2[NO]}$$

Then in this case, the overall reaction rate is

$$\begin{aligned} r_{NO} &= -\frac{d[NO]}{dt} = -k_1[NO][O_2] + k_{-1}[NO_3] - k_2[NO_3][NO] + k_{-2}[NO_2]^2 \\ &= -k_1[NO][O_2] + (k_{-1} - k_2[NO])\frac{k_1[NO][O_2] + k_{-2}[NO_2]^2}{k_{-1} + k_2[NO]} + k_{-2}[NO_2]^2 \\ &= \frac{2(k_{-1}k_{-2}[NO_2]^2 - k_1k_2[NO]^2[O_2])}{k_{-1} + k_2[NO]} \end{aligned}$$

Again, if $k_2[NO] << k_{-1}$, then

$r_{NO} = 2\ k_{-2}[NO2]^2 - 2\ k_1k_2/k_{-1}\ [NO]^2[O_2]$

Notice that the second term is what we got before for the forward reaction, i.e.

$k_{forward}=2k_1k_2/k_{-1}$

The first term gives the effective rate constant for the reverse process:

$k_{reverse}=2k_{-2}$

Note that $k_{forward}/k_{reverse} = k_1k_2/k_{-1}k_{-2} = K_{c1}K_{c2} = K_{c,overall}$ where K_c's are equilibrium constants.

Prob. 3

a. For the reactions

$$S + E \xrightarrow{k_1} E\text{-}S$$

$$E\text{-}S \xrightarrow{k_{-1}} S + E$$

$$E\text{-}S \xrightarrow{k_2} P + E$$

We can write down

$$\frac{d[S]}{dt} = -k_1[S][E] + k_{-1}[E\text{-}S]$$
$$\frac{d[E]}{dt} = -k_1[S][E] + k_{-1}[E\text{-}S] + k_2[E\text{-}S]$$
$$\frac{d[E\text{-}S]}{dt} = k_1[S][E] - k_{-1}[E\text{-}S] - k_2[E\text{-}S]$$
$$\frac{d[P]}{dt} = k_2[E\text{-}S]$$

With law of mass action on enzyme $[E] + [E\text{-}S] = [E]_0$, $[S] + [P] + [E\text{-}S] = [S]_0$, $[P]_{(t=0)}=0$, $[S]_{(t=0)}=[S]_0$, $[E]_{(t=0)}=[E]_0$, and $k_{-1}=k_1/K_{eq,\,1}$

b.

```
function [t,conc] = odehw2_prob3(k1, k2, keq1, tmax)

param = [k1,k2,keq1];
%initial concentrations
%conc0 = ([S],[ES],[E],[P])
conc0 = [0.01,0,1e-6,0];

%use ode15s at the function derivhw2
%t is the time vector output
%conc is the 4 column matrix solution containing the concentrations of
%[S],[ES],[E],[P]
options = odeset('AbsTol', 1e-9, 'RelTol', 1e-6);
[t,conc] = ode15s(@derivhw2_prob3,[0;tmax],conc0,options,param);

%this is the function inputed into ode15s
function derivs = derivhw2_prob3(t,conc,param)

%extract constants
k1 = param(1);
k2 = param(2);
keq1 = param(3);

%This is the order of the variables in the concentration vector
```

```
%concS = [S] in M
%concES = [ES] in M
%concE = [E] in M
%concP = [P] in M

%switch from list of f's to actual names for ease of formulation of
concS = conc(1);
concES = conc(2);
concE = conc(3);
concP = conc(4);

%defining the rate equations
dconcSdt = -k1*concS*concE + (k1/keq1)*concES;
dconcEdt = -k1*concE*concS + k2*concES + (k1/keq1)*concES;
dconcESdt = k1*concE*concS - k2*concES - (k1/keq1)*concES;
dconcPdt = k2*concES;

%put derivative results back in column vector format for MATLAB
derivs = [dconcSdt; dconcESdt; dconcEdt; dconcPdt];
return;
```

c. Using this pseudo-steady approximation on intermediate species ES,

$$\frac{d[E-S]}{dt} = k_1[S][E] - k_{-1}[E-S] - k_2[E-S] = 0$$

we know

$$[E-S] = \frac{k_1[S][E]}{k_{-1} + k_2}$$

Using mass balance condition $[E] + [E-S] = [E]_0$

We know

$$[E-S] = \frac{[E]_0}{1 + \dfrac{k_{-1} + k_2}{k_1[S]}}$$

Therefore the reaction rate

$$-r_S = \frac{d[S]}{dt} = -\frac{d[P]}{dt} = -k_2[E-S] = -k_2[E]_0 \frac{[S]}{[S] + \dfrac{k_{-1} + k_2}{k_1}} = -\frac{V_{max}[S]}{[S] + K_m}$$

where $K_m=(k_{-1}+k_2)/k_1$ and $V_{max}=k_2[E]_0$.

d. In the limit $[S]>>K_m$, from

$$\frac{d[S]}{dt} = -\frac{V_{max}[S]}{[S]+K_m} \approx -V_{max}$$

In the limit $[S] << K_m$, from

$$\frac{d[S]}{dt} = -\frac{V_{max}[S]}{[S]+K_m} \approx -\frac{V_{max}[S]}{K_m}$$

e.

Consider the conditions: $k_1=10^9$ liter/mole-s, $k_2=1\ s^{-1}$, $K_{eq,1}= 1$ liter/mole, $[E]_0=10^{-6}$ M, $[S]_0=0.01$ M.

We know that now $K_m=(k_{-1}+k_2)/k_1=k_2/k_1+1/K_{eq,1}\sim 1$ M, $[S]_0=0.01$ M,

therefore, $[S]_0<<K_m$

since [S] is decreasing monotonically, $[S]<<K_m$ is always correct.

So now we can use the result from d)

$$\frac{d[S]}{dt} = -\frac{V_{max}[S]}{K_m}$$

This gives an exponential function for [S](t)

$$[S](t) = [S](t=0)\exp(-\frac{V_{max}}{K_m}t) = [S]_0 \exp(-\frac{V_{max}}{K_m}t)$$

While for [ES],

$$[ES](t) = \frac{[E]_0}{1+\frac{k_M}{[S]}} \approx \frac{[E]_0}{k_M}[S] = \frac{[E]_0}{k_M}[S]_0 \exp(-\frac{V_{max}}{K_m}t)$$

And for [P]

$$[P](t)=[S]_0-[ES](t)-[S](t) \approx [S]_0[1-\exp(-\frac{V_{max}}{K_m}t)]$$

Use matlab to solve the following non-linear ODE IVP:

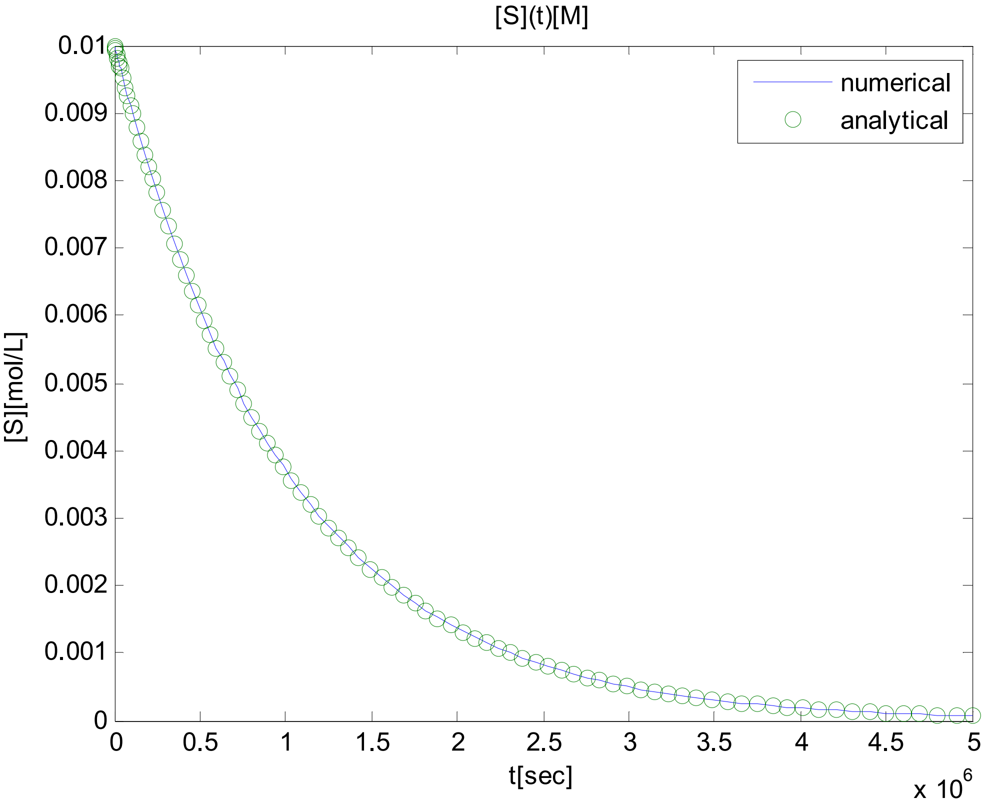
$$\frac{d[S]}{dt} = -k_1[S][E] + \frac{k_1}{K_{eq,1}}([E]_0 - [E])$$

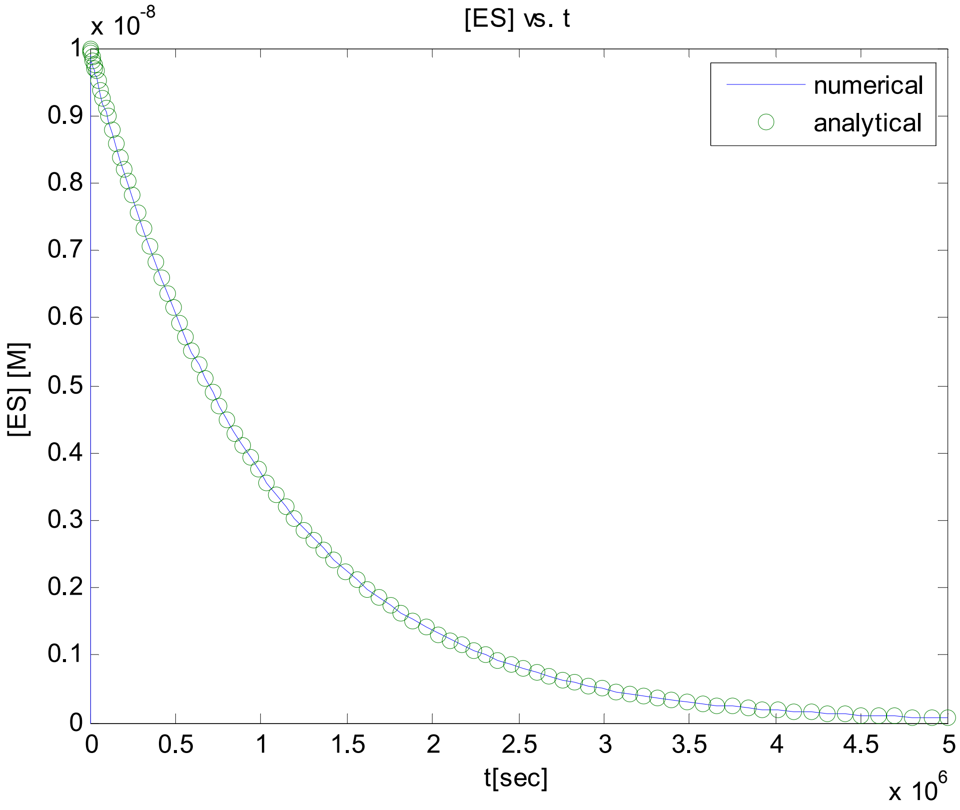
$$\frac{d[E]}{dt} = -k_1[S][E] + (\frac{k_1}{K_{eq,1}} + k_2)([E]_0 - [E])$$

$$r = \frac{d[P]}{dt} = k_2[E-S] = k_2([E]_0 - [E])$$

with the initial conditions $[S]_{t=0}=[S]_0=0.01$M, $k_1=10^9$ liter/mole-s, $k_2=1\ s^{-1}$, $K_{eq,1}= 1$ liter/mole, and $[E]_0=10^{-6}$ M. From d[ES]/dt=0, we can determine the time to reach pseudo steady state is approximately 7×10^{-9} sec, which is really really short. For this specific condition, pseudo steady state works very well. This may also be seen from a direct comparison of the analytical/full numerical solutions [ES](t) plots on a short time scale. [E-S] should rapidly rise from zero to the

PSSA value (on the order of 10^{-8} seconds). The only observable difference between the numerical and analytical solutions is this initial jump in [E-S] on the short time scale.





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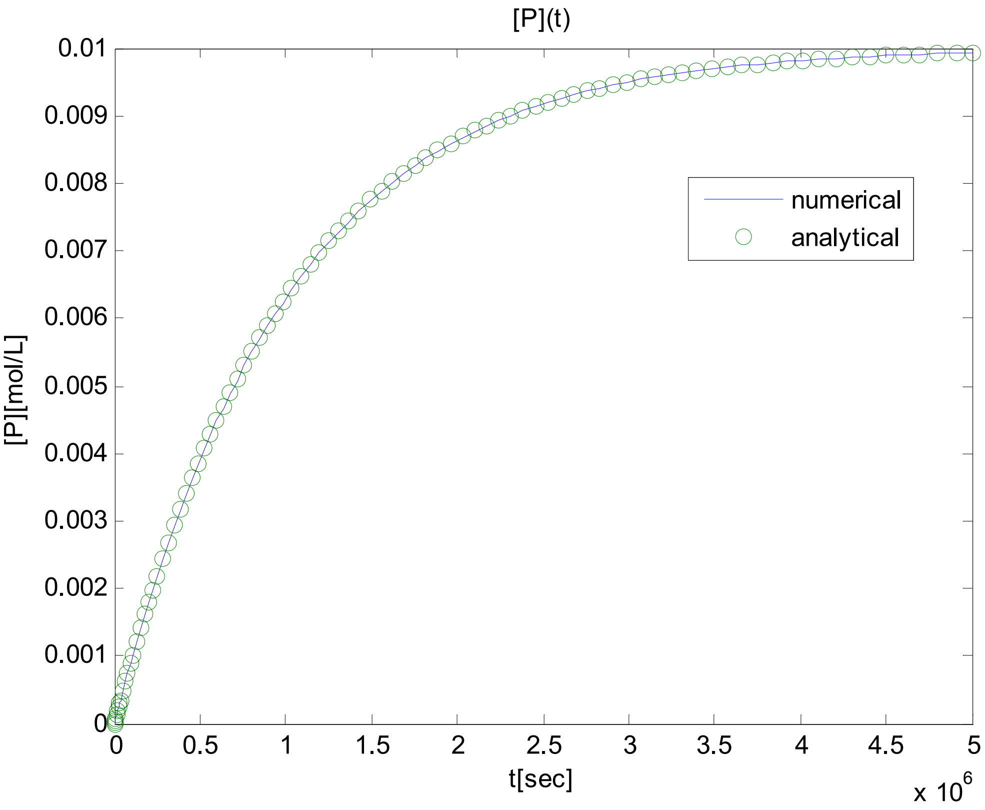
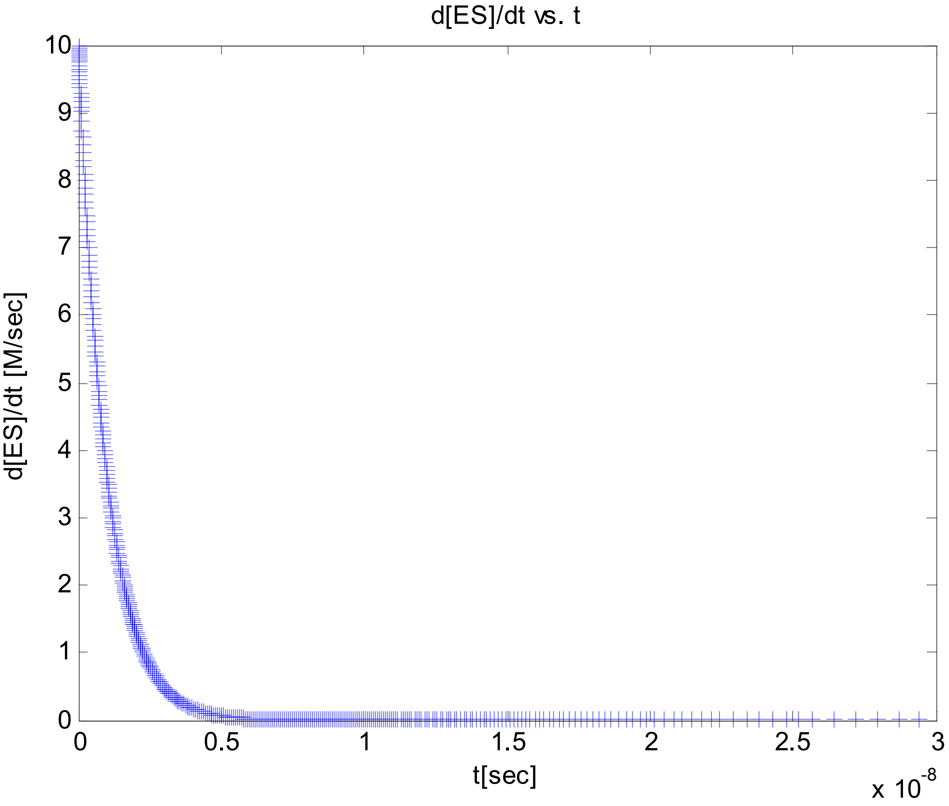
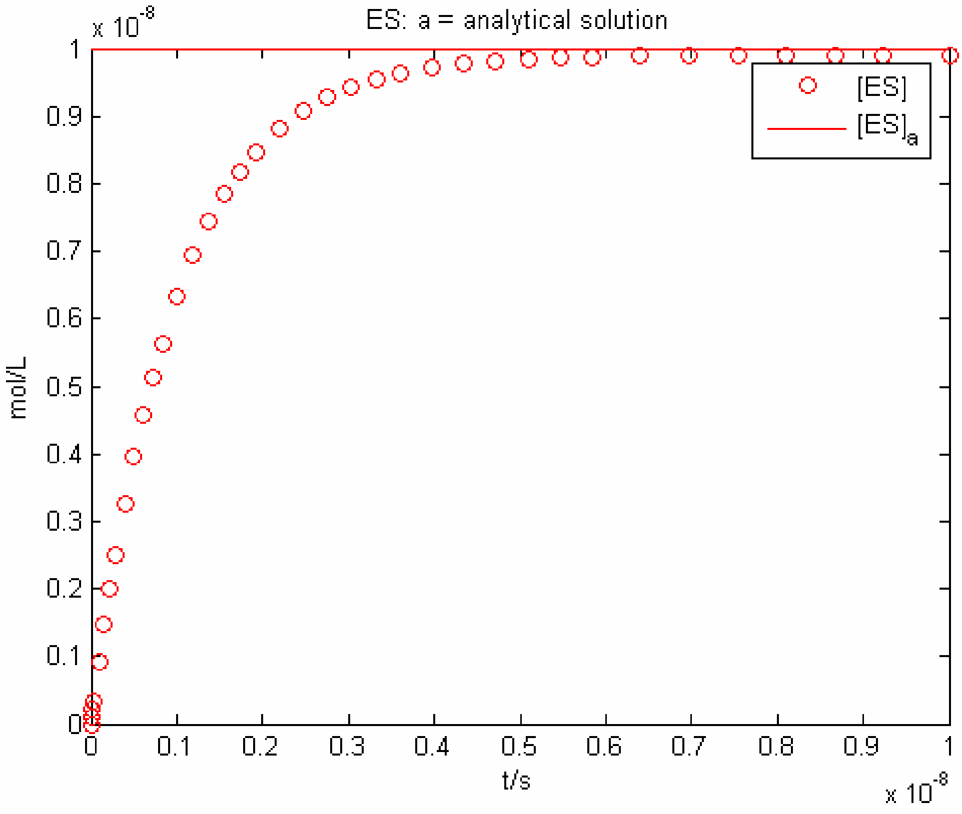

[P](t)
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
[P][mol/L]
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
t[sec]
x 10^6
numerical
analytical


d[ES]/dt vs. t
10
9
8
7
6
5
4
3
2
1
0
d[ES]/dt [M/sec]
0
0.5
1
1.5
2
2.5
3
t[sec]
x 10^-8



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