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:

$1*12 \text{ (g/mol)} +1.85*1\text{ (g/mol)} +0.55*16\text{ (g/mol)} +0.13*14\text{ (g/mol)} = 24.5 \text{ g/mol}$.

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

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

$$= \frac{[22.8 \text{ g dry weight/mole ethane}] \times [(1 - 3\%)] \text{ g biomass/g dry weight} + [24.5 \text{ g biomass/mol biomass}] \times \frac{1 \text{ mol ethane}}{2 \text{ C - mole ethane}}}{0.451 \text{ (C-mole biomass/C-mol ethane)}}$$

$=0.451 \text{ (C-mole biomass/C-mol ethane)}$

b. If assuming that CO$_2$, H$_2$O, and CH$_3$ON are the only metabolic products, then the overall metabolic reaction is

$$0.5 \text{ C}_2\text{H}_6 + Y_{so} \text{ O}_2 + Y_{sn} \text{ NH}_3 \rightarrow Y_{sx} \text{ CH}_{1.85}\text{O}_{0.55}\text{N}_{0.13} + Y_{sc} \text{CO}_2 + Y_{sw} \text{H}_2\text{O}$$

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:

$Y_{sc}=0.549 \text{ (mol CO}_2/\text{C-mol ethane)}$, $Y_{sn}=0.0589 \text{ (mol NH}_3/\text{C-mol ethane)}$, $Y_{sw}=1.17 \text{ (mol H}_2\text{O/C-mol ethane)}$, $Y_{so}=1.26 \text{ (mol O}_2/\text{C-mol ethane)}$

Therefore, the full stoichiometric equation for the growth process

$$0.5 \text{ C}_2\text{H}_6 + 1.26 \text{ O}_2 + 0.0589 \text{ NH}_3 \rightarrow 0.451 \text{ CH}_{1.85}\text{O}_{0.55}\text{N}_{0.13} + 0.549\text{CO}_2 + 1.17 \text{H}_2\text{O}$$

The oxygen consumption is

$Y_{xo}=Y_{so}/Y_{sx}=1.26/0.451=2.79 \text{ (mol O}_2/\text{C-mol biomass)}$

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

$Q=0.5*\Delta H_{\text{comb}}(\text{ethane})+0.0589*\Delta H_{\text{comb}}(\text{NH}_3)-0.451*\Delta H_{\text{comb}}(\text{biomass})$

$=-(0.5*1560 \text{kJ/mol}+0.0589*383 \text{kJ/mol-19 (kJ/g dry weight)}}$
\[ \hat{\frac{1}{[(1 - 3\%) \frac{g \text{ biomass}}{g \text{ dry weight}}] \times [24.5 \frac{g \text{ biomass}}{C \cdot \text{ mol biomass}}] \div 1 \frac{C \cdot \text{ mol ethane}}{0.451 C \cdot \text{ mol biomass}}} = -586 \text{ kJ/c-mol ethane.} \]

Then convert back again to per kilo dry weight

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

\[ = -51.5 \text{ (MJ/ kg dry weight)} \]
Problem 2.

For the reaction, \(2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2\), 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 \(\text{NO}_3\) species as an intermediate to explain this strange behavior.

A possible mechanism:

\[
\begin{align*}
\text{NO} + \text{O}_2 & \rightarrow k_1 \rightarrow \text{NO}_3 \\
\text{NO}_3 & \rightarrow k_1 \rightarrow \text{NO} + \text{O}_2 \\
\text{NO}_3 + \text{NO} & \rightarrow k_2 \rightarrow 2\text{NO}_2
\end{align*}
\]

So the reaction rates: 
\(r_1 = k_1[\text{NO}][\text{O}_2]\), \(r_{-1} = k_{-1}[\text{NO}_3]\), \(r_2 = k_2[\text{NO}_3][\text{NO}]\)

If using PSSH for the intermediate \(\text{NO}_3\), we have

\[
\frac{d[\text{NO}_3]}{dt} = k_1[\text{NO}][\text{O}_2] - k_{-1}[\text{NO}_3] - k_2[\text{NO}_3][\text{NO}] = 0
\]

From this we can obtain

\[
[\text{NO}_3] = \frac{k_1[\text{NO}][\text{O}_2]}{k_{-1} + k_2[\text{NO}]}
\]

Thus

\[
r_{\text{NO}} = -\frac{d[\text{NO}]}{dt} = -k_1[\text{NO}][\text{O}_2] + k_{-1}[\text{NO}_3] - k_2[\text{NO}_3][\text{NO}]
\]

\[
= -k_1[\text{NO}][\text{O}_2] + (k_{-1} - k_2[\text{NO}]) \frac{k_1[\text{NO}][\text{O}_2]}{k_{-1} + k_2[\text{NO}]}
\]

\[
= -\frac{2k_1k_2[\text{NO}]^2[\text{O}_2]}{k_{-1} + k_2[\text{NO}]}
\]

In order to have third-order reaction kinetics as the form \(r_{\text{NO}} = -k_{\text{effective forward}}[\text{NO}]^2[\text{O}_2]\), we have to assume \(k_{-1} >> k_2[\text{NO}]\), so that the overall reaction rate for \(\text{NO}\) is

\[
r_{\text{NO}} = -\frac{2k_1k_2[\text{NO}]^2[\text{O}_2]}{k_{-1}}
\]

where \(k_{\text{effective forward}} = \frac{2k_1k_2}{k_{-1}}\)

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

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

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

If \(E_{\text{a1}} + E_{\text{a2}} - E_{\text{a, -1}} - \Delta H_{1, \text{rxn}} + E_{\text{a2}} < 0\), 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.

$$ NO + O_2 \xrightleftharpoons{\text{k}_1} NO_3 $$
$$ NO_3 \xrightarrow{\text{k}_3} NO + O_2 $$
$$ NO_3 + NO \xrightleftharpoons{\text{k}_2} 2NO_2 $$
$$ 2NO_2 \xrightarrow{\text{k}_2} NO_3 + NO $$

and still using PSSH on the intermediate NO$_3$

$$ \frac{d[NO_3]}{dt} = k_{\text{f}}[NO][O_2] - k_{\text{i}}[NO_3] - k_{2}[NO_3][NO] + k_{2}[NO_2]^2 = 0 $$

we can have the intermediate concentration:

$$ [NO_3] = \frac{k_{\text{f}}[NO][O_2] + k_{2}[NO_2]^2}{k_{\text{i}} + k_{2}[NO]} $$

Then in this case, the overall reaction rate is

$$ r_{NO} = -\frac{d[NO]}{dt} = -k_{\text{i}}[NO][O_2] + k_{\text{i}}[NO_3] - k_{2}[NO_3][NO] + k_{2}[NO_2]^2 $$

$$ = -k_{\text{i}}[NO][O_2] + (k_{\text{i}} - k_{2}[NO]) \frac{k_{\text{f}}[NO][O_2] + k_{2}[NO_2]^2}{k_{\text{i}} + k_{2}[NO]} + k_{2}[NO_2]^2 $$

$$ = \frac{2(k_{\text{i}}k_{2}[NO_2]^2 - k_{\text{i}}k_{2}[NO]^2[O_2])}{k_{\text{i}} + k_{2}[NO]} $$

Again, if $k_{2}[NO] << k_{\text{i}}$, then

$$ r_{NO} = 2 k_{2}[NO_2]^2 - 2 k_{\text{i}}k_{2}[NO]^2[O_2] $$

Notice that the second term is what we got before for the forward reaction, i.e. $k_{\text{f}} = 2k_{\text{i}}k_{2}/k_{\text{i}}$

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

$$ k_{\text{reverse}} = 2k_{2} $$

Note that $k_{\text{f}}/k_{\text{reverse}} = k_{\text{i}}k_{2}/k_{\text{i}}k_{2} = K_{c1}K_{c2} = K_{c,overall}$ where $K_{c}$'s are equilibrium constants.
Prob. 3

a. For the reactions

\[ S + E \xrightarrow{k_1} E \cdot S \]

\[ E \cdot S \xrightarrow{k_{-1}} S + E \]

\[ E \cdot S \xrightarrow{k_1} P + E \]

We can write down

\[ \frac{d[S]}{dt} = -k_1[S][E] + k_{-1}[E \cdot S] \]

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

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

\[ \frac{d[P]}{dt} = k_2[E \cdot S] \]

With law of mass action on enzyme \([E] + [E \cdot S] = [E]_0\), \([S] + [P] + [E \cdot S] = [S]_0\), \([P](t=0) = 0\),

\([S](t=0) = [S]_0\), \([E](t=0) = [E]_0\), and \(k_{-1} = k_1/K_{eq,1}\)

b. function \([t,conc] = odehw2_prob3(k1, k2, keq1, tmax)\)

\[
\begin{align*}
\text{param} &= [k1,k2,keq1]; \\
\text{%initial concentrations} \\
\text{conc0} &= ([S],[ES],[E],[P]) \\
\text{conc0} &= [0.01,0,1e-6,0]; \\
\end{align*}
\]

%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
\[ [E-S] = \frac{[E]_0}{1 + \frac{k_1 + k_2}{k_1[S]}} \]

Therefore the reaction rate
\[ -r_s = \frac{d[S]}{dt} = -\frac{d[P]}{dt} = -k_2[E-S] = -k_2[E]_0 \frac{[S]}{[S] + \frac{k_1 + k_2}{k_1}} = -\frac{V_{max}[S]}{[S] + K_m} \]

where \( K_m = \frac{(k_1 + k_2)}{k_1} \) 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 \(K_m = \frac{(k_1+k_2)/k_1 = k_2/k_1 + 1/K_{eq,1} = 1}\) 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 \([S](t)\)

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

While for \([ES]\),

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

And for \([P]\)

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

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

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

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

with the initial conditions \([S]_0 = 0.01\) 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 \(7 \times 10^9\) 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.