

Engine Cycle Analysis comparing Methane and Hydrogen:

Adiabatic Constant Volume Equilibrium, work done during adiabatic expansion, heat released at constant pressure

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Recommended Textbooks for further learning: Multivariable Calculus by James Stewart, Thermodynamics by Yunus Cengel and Micheal Boles, An Introduction to Combustion by Stephen Turns

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Method of lagrange multipliers: To find maximum and minimum values of $f(x,y,z)$ subject to the constraint $g(x,y,z)=k$
 (assuming that these extreme values exist and $\nabla g \neq 0$ on the surface $g(x, y, z) = k$)

(a) find all values of x, y, z ,and λ

$$\nabla f(x, y, z) = \lambda \nabla g(x, y, z)$$

and

$$g(x, y, z) = k$$

(b) Evaluate f at all the points (x,y,z) that results from step (a). The largest of these values is the maximum value of f ; the smallest is the minimum value of f .

Simple Example: This problem is asking to find the max and min values of $f(x,y)$ along the constraint $g(x,y)$

$$f(x, y) = x + y$$

$$g(x, y) = x^2 + y^2 = 1$$

$$\nabla = \begin{bmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \end{bmatrix} \quad \nabla f = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad \nabla g = \begin{bmatrix} 2x \\ 2y \end{bmatrix}$$

$$\nabla f = \lambda \nabla g \quad \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \lambda \begin{bmatrix} 2x \\ 2y \end{bmatrix} \quad x^2 + y^2 = 1$$

$$x = y = \lambda = \frac{1}{\sqrt{2}}$$

Explanation:

First off having the constraint equation $x^2 + y^2 = 1$ is simply saying, we are only looking at points on that line.

With the $\nabla f = \lambda \nabla g$ or $\begin{bmatrix} 1 \\ 1 \end{bmatrix} = \lambda \begin{bmatrix} 2x \\ 2y \end{bmatrix}$ equation we are basically saying are there x and y values where the gradients of f and g are parallel? λ would be the ratio of magnitudes and directions of the gradients.

The best way I can conceptually explain why this is where the max and mins are is that by having the gradients parallel means the point on constraint $g(x,y)$ has traveled the furthest in the direction of the x-y plane that would cause the largest increase or decrease in $f(x,y)$.

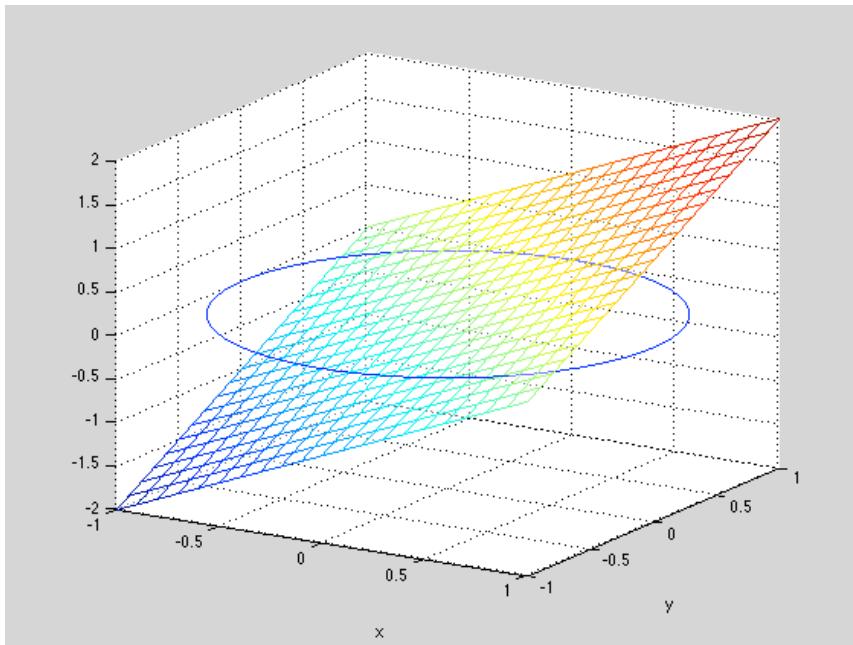
The gradient of the constraint is saying hey I've been climbing in this direction on the x-y plane in order to make that value of the constraint. And then the $f(x,y)$ gradient says I have also been climbing (or falling) in that direction, since we are climbing in the same direction I must be at my highest point on this constraint line, because the other points have not traveled in the x-y direction I am going in.

Matlab code to plot $f(x,y)$ and constraint $g(x,y)$

```

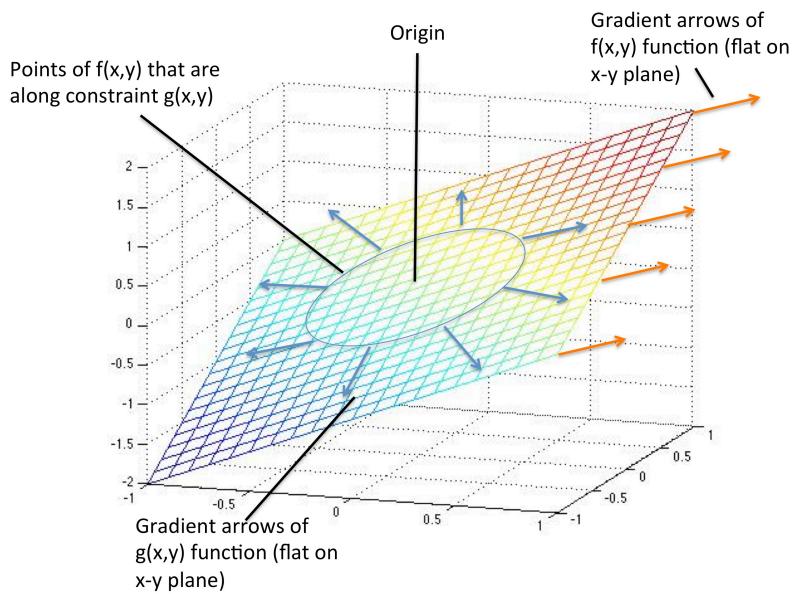
x=-1:0.1:1;
y=-1:0.1:1;
for i=1:length(x)
    for j=1:length(y)
        f(j,i)=x(i)+y(j);
    end
end
ang=0:0.01:2*pi;
gx=cos(ang);
gy=sin(ang);
mesh(x,y,f)
alpha(.4)
hold on;
plot(gx,gy)
xlabel('x')
ylabel('y')

```



Matlab code to solve system of equations using fsolve

```
function lagrange_example_fsolve
    %my guesses
    var0(1) = 1;
    var0(2) = 1;
    var0(3) = 1;
    var = fsolve(@fun,var0);
    var
    function F=fun(var)
        x = var(1);
        y = var(2);
        lam = var(3);
        F1 = 1-lam*2*x;
        F2 = 1-lam*2*y;
        F3 = x^2 + y^2 -1;
        F = [F1 ; F2 ; F3];
    end
end
```



Why minimization of Gibbs free energy at equilibrium?

Conceptually we first must ask, why is entropy maximum at equilibrium?

Generally speaking if you have all 2^*H_2 and O_2 , some will want to combine to form water, then if too much water is formed, some will want to break up into 2^*H_2 and O_2 , until an equilibrium is formed. Conceptually speaking having all $2^*\text{H}_2 + \text{O}_2$ or all $2^*\text{H}_2\text{O}$ is more order than having a mixture of the 3 species.

Entropy is a measure of disorder; each chemical species has a certain amount of entropy at a temperature and partial pressure. The 2nd law of thermodynamics says that entropy of a system will either increase or remain constant; eventually the maximum disorder is reached.

When we look for chemical equilibrium we keep temperature and total pressure constant. Since entropy is inversely related to partial pressure, as water is formed, eventually $2^*\text{H}_2 + \text{O}_2$ will have the same amount of entropy at $2^*\text{H}_2\text{O}$. This is why if starting with a hydrogen oxygen mixture it does not totally convert to water, because of the need for water to break up into hydrogen and oxygen once water reaches too high of a partial pressure.

For an adiabatic system, a chemical reaction proceeds in the direction of increasing entropy

$$dS_{sys} \geq 0$$

Combining first law of thermodynamics,

$$\delta Q - pdV = dU$$

δQ denotes the infinitesimal increment of heat supplied to the system from surroundings,
with 2nd law of thermodynamics,

$$dS \geq \frac{\delta Q}{T}$$

We get

$$dU + pdV - TdS \leq 0$$

The definition of Gibbs function and its differential form:

$$G = H - TS = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

for constant T and p

$$dG = dU + pdV - TdS$$

$$dG \leq 0$$

Therefore a chemical reaction at a specified temperature and pressure will proceed in the direction of a decreasing Gibbs function. The reaction will stop and chemical equilibrium will be established when the Gibbs function attains a minimum value.

Derivation of Equations for chemical Equilibrium adiabatic constant volume

(constant energy): The optimization problem is minimization of Gibbs free energy, with a constraint of conserving elements. This is enough for constant temperature and pressure. After forming this set of equations using lagrange multipliers, we are going to add two more equations ($U = U_0$ and $v = v_0$) and two more unknowns (T and p) to our system. This method works because at equilibrium T and p will be constant.

$$G = \sum_i G_i = \sum_i N_i \bar{g}_i$$

Using chain rule

$$dG = \sum_i N_i d\bar{g}_i + \sum_i \bar{g}_i dN_i$$

The mole specific gibbs of a species is

$$d\bar{g}_i = -\bar{s}_i dT + \bar{v}_i dp_i$$

$$\sum_i N_i d\bar{g}_i = -\sum_i N_i \bar{s}_i dT + \sum_i N_i \bar{v}_i dp_i = -SdT + Vdp$$

$$dG = -SdT + Vdp + \sum_i \bar{g}_i dN_i$$

The optimization problem can be formulated as:

$$\text{max of } G(T, p, N_i) = \sum_i N_i \bar{g}_i (T, p_i)$$

subject to constraint

$$\sum_j \alpha_{ij} N_j = a_i^0 = \text{total \# of } i^{\text{th}} \text{ element} \quad \text{for } i = 1, 2, \dots, \# \text{ of elements}$$

Using lagrangian multipliers, the optimization problem can be transformed into the following equations

$$\nabla G(T, p, N_i) = \sum_i \lambda_i \nabla \left(\sum_j \alpha_{ij} N_j \right)$$

$$\sum_j \alpha_{ij} N_j = a_i^0$$

$$\nabla = \left[\frac{\partial}{\partial N_1}, \frac{\partial}{\partial N_2}, \dots, \frac{\partial}{\partial N_K} \right]^T$$

The equations can be further expanded for our final set of equations before adding additional variables and constraints

$$\bar{g}_j = \sum_i \lambda_i \alpha_{ij} \quad \text{for } j = 1, 2, \dots, \# \text{ of species}$$

$$\sum_j \alpha_{ij} N_j = a_i^0 \quad \text{for } i = 1, 2, \dots, \# \text{ of elements}$$

What does \bar{g}_i equal?

$$\begin{aligned} \bar{g}_i(T, p_i) &= \bar{g}_i(T, p) + R_u T \ln \left(\frac{p_i}{p} \right) = \bar{g}_i(T, p) + R_u T \ln(X_i) \\ \bar{g}_i(T, p) &= \bar{g}_i(T, p^0) + R_u T \ln \left(\frac{p}{p^0} \right) \end{aligned}$$

Now add two more equations ($U = U_0$ and $v = v_0$) and two more unknowns (T and p) to our system

$$U = U_0$$

$$U_0 = \sum_i N_i^0 \bar{u}_i(T_0)$$

$$U = \sum_i N_i \bar{u}_i(T)$$

$$v = v_0$$

$$v_0 = \frac{R_u T_0}{p_0 W_{m,0}}$$

$$v = \frac{R_u T}{p W_m}$$

$$W_{m,0} = \sum_i W_i X_{i,0} \quad X_{i,0} = \frac{N_{i,0}}{\sum_i N_{i,0}}$$

$$W_m = \sum_i W_i X_i \quad X_i = \frac{N_i}{\sum_i N_i}$$

Note about normalizing and using log/exp:

Matlab's fsolve function will try to guess negative N_i and T values, which will cause problems, therefore, if we assume that the input is log of N_i or T , then we can take $\exp()$ of that, and our values will stay positive.

Also we divide our equation $\bar{g}_j = \sum_i \lambda_i \alpha_{ij}$ by $R_u T$ to normalize it and bring its values closer to about 1, fsolve does not like huge values. That $R_u T$ gets absorbed into our λ_i values.

How to find amount of oxygen for fuel mixture?

Find stoichiometric ratios for CH4



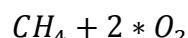
balance C: 1=A

balance H: 4=2*B

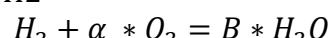
balance O: 2*\alpha=2*A+B

$$\alpha = A + \frac{B}{2} = 1 + 1 = 2$$

Therefore stoichiometric is



Find stoichiometric ratios for H2

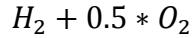


balance H: 2=2*B

balance O: 2*\alpha=B

$$\alpha = \frac{B}{2} = \frac{1}{2}$$

Therefore stoichiometric is



Derivation of equations for adiabatic expansion/decompression step as equilibrium pressure, p_1 , goes back to initial pressure, p_0 : (assume no change in chemical concentrations)

$$du = -pdv = dw \quad dh = du + pdv + vdp \quad dh = vdp$$

time: from 0 to 1 seconds

$$p(t) = p_1 - (p_1 - p_0) * t$$

$$\frac{dp}{dt} = p_0 - p_1$$

$$\frac{dh}{dt} = c_{p_m} \frac{dT}{dt} = v \frac{dp}{dt} \quad c_{p_m} = \frac{(\sum X_k \bar{c}_{p,k})}{W_m} \quad W_m = \sum_i W_i X_i$$

$$v = \frac{R_u T}{p W_m}$$

note: work done is the change in energy before and after expansion step

Explanation about how change in enthalpy of products at post-expansion temperature, T_2 , and T_0 is heat released:

Heat released at constant pressure is not the change in energy of products at post-expansion temperature, T_2 , and T_0 because when the gas shrinks as it is cooled work is done on the product gases.

$$du = -pdv - q_{out}$$

$$dh = du + pdv \quad (\text{constant pressure})$$

$$dh = -q_{out} \quad (\text{heat out is decrease in enthalpy})$$

Engine Cycle:

Background: After presenting my software at a maker faire, I was approached to analyze an engine cycle to calculate work output and heat released, and to compare hydrogen and methane fuels.

This simplified cycle is sufficient to analyze client's engine design:

(1) Chemical equilibrium at constant volume adiabatic, energy is conserved.

Input: initial pressure (p_0), initial temperature (T_0), initial mole fraction (X_0)

Output: pressure (p_1), temperature (T_1), mole fraction (X_1)

(2) Adiabatic expansion/decompression as pressure, p_1 , goes back to initial

pressure, p_0 , T_1 decreases to T_2 . Work done is change in energy, specific volume from ideal gas law.

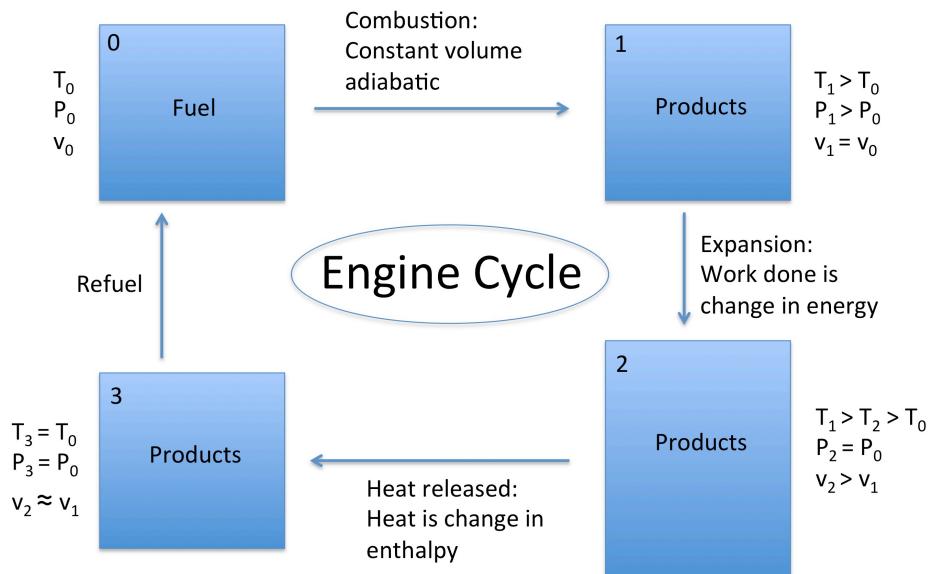
Input: pressure (p_1), temperature (T_1), mole fraction (X_1)

Output: expansion temperature (T_2), work, initial (v_1) and expansion specific volume (v_2) are calculated

(3) Heat released at constant pressure as T_2 goes to T_0

Input: expansion temperature (T_2), initial temperature (T_0), mole fraction (X_1)

Output: heat released



Parameters to be analyzed:

Initial temperature will always be 300K, fuel and oxygen at stoichiometric with no nitrogen.

Create a table for initial pressure 1 atm, methane and hydrogen

-max temperature

-max pressure

-initial specific volume

-expansion specific volume

-work

-heat release

Vary initial pressure from 0.3 to 10 atm, and plot the following

-max temperature

-max pressure

-expansion ratio (expansion specific volume divided by initial)

-change in initial and expansion specific volumes

-work

-heat release

Results:

Initial temperature: 300K

Initial pressure: 1 atm

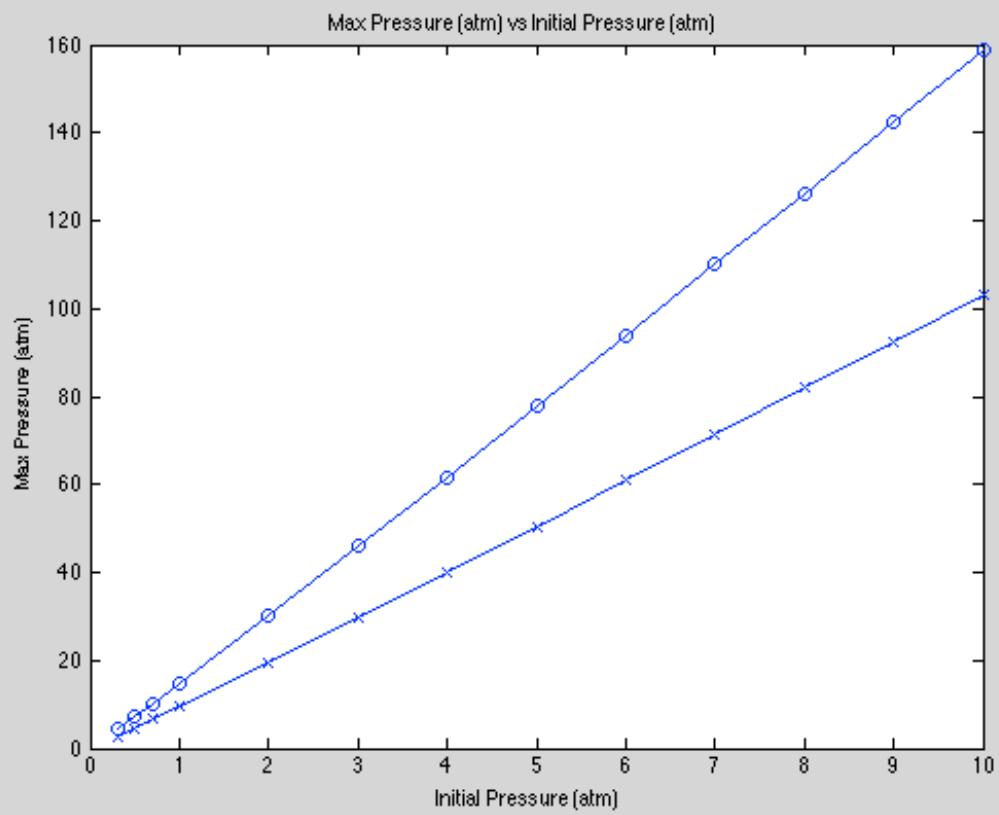
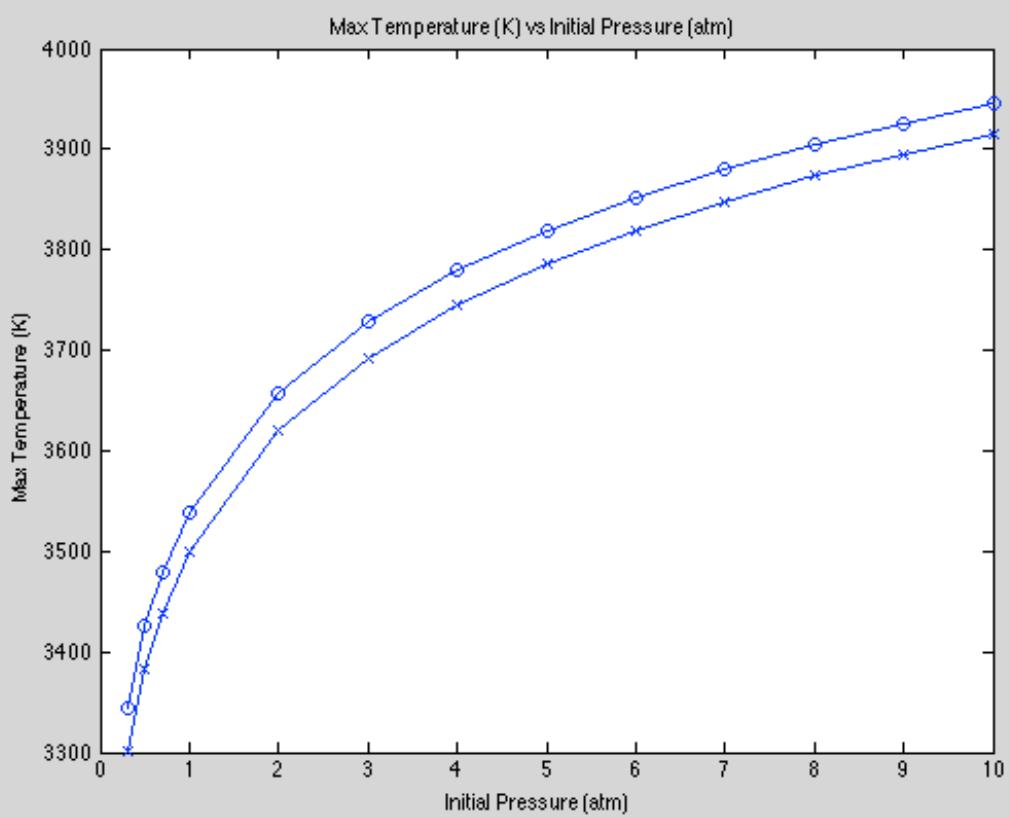
Fuel	$\text{CH}_4 + 2*\text{O}_2$	$2*\text{H}_2+\text{O}_2$
Max temperature (K)	3.5392e+03	3.4987e+03
Max pressure (atm)	1.4751e+01	9.5490e+00
Initial specific volume (cm ³ /gram)	9.2269e+02	2.0497e+03
Expansion specific volume (cm ³ /gram)	8.3230e+03	1.2933e+04
Work (Joule / gram)	2.4045e+03	2.9997e+03
Heat release (Joule / gram)	3.3463e+03	5.1649e+03

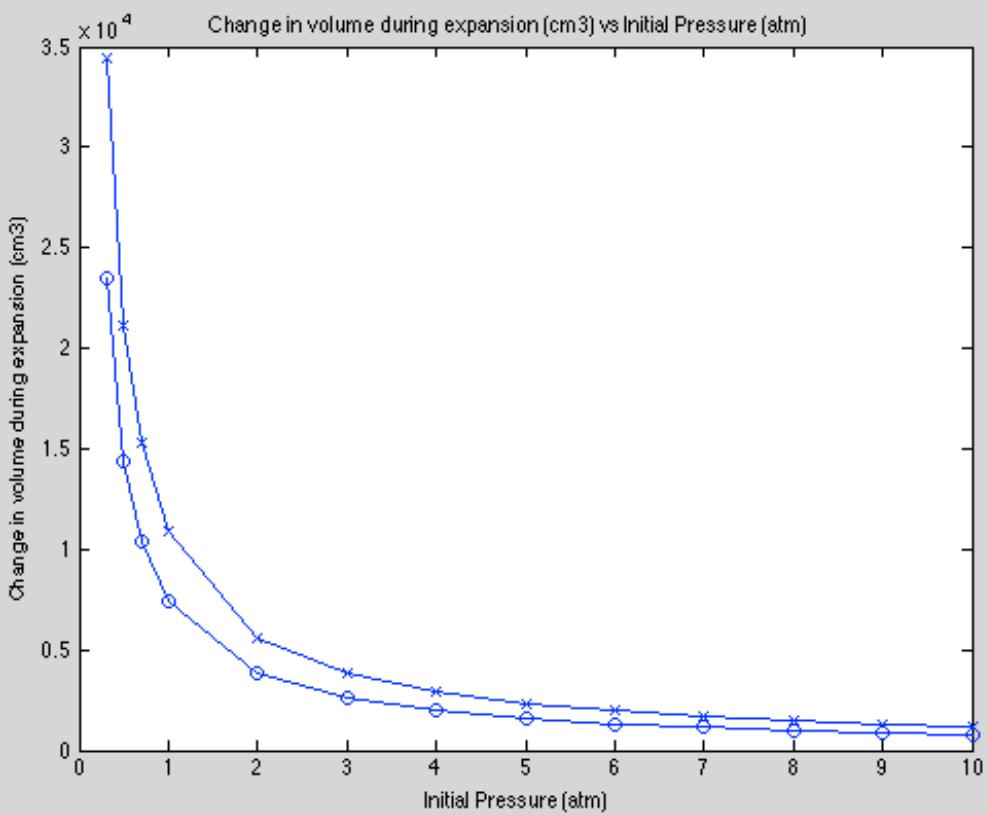
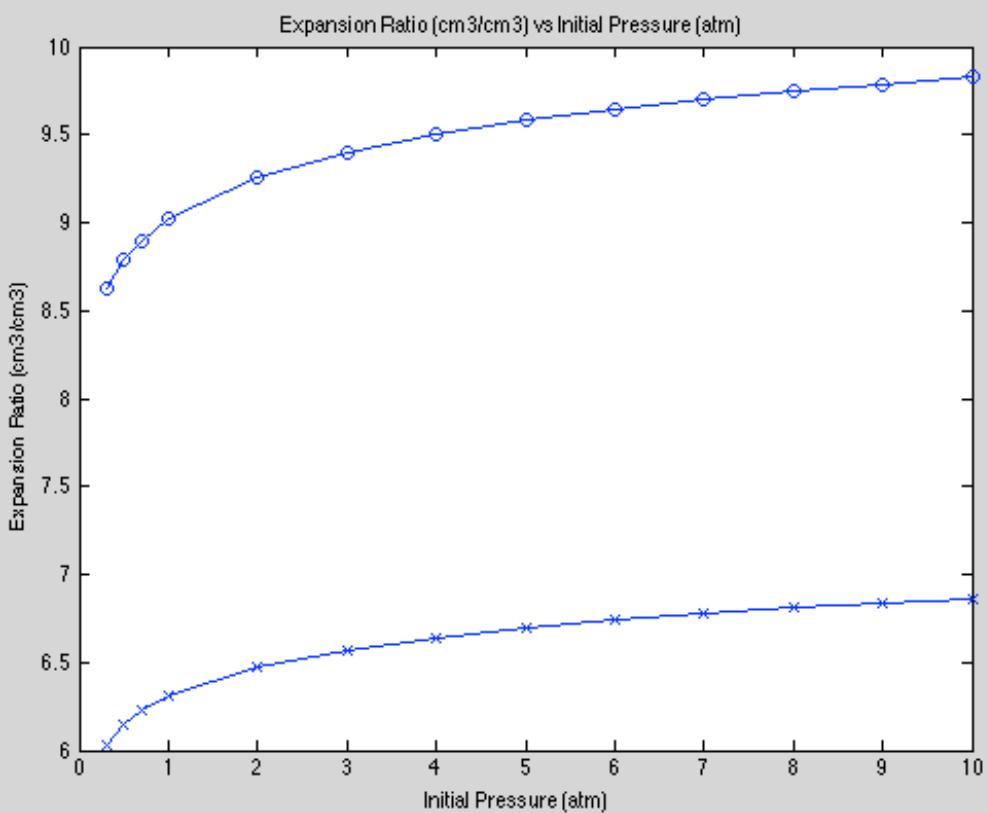
(note: 3.5392e+03 = 3.5392*10³)

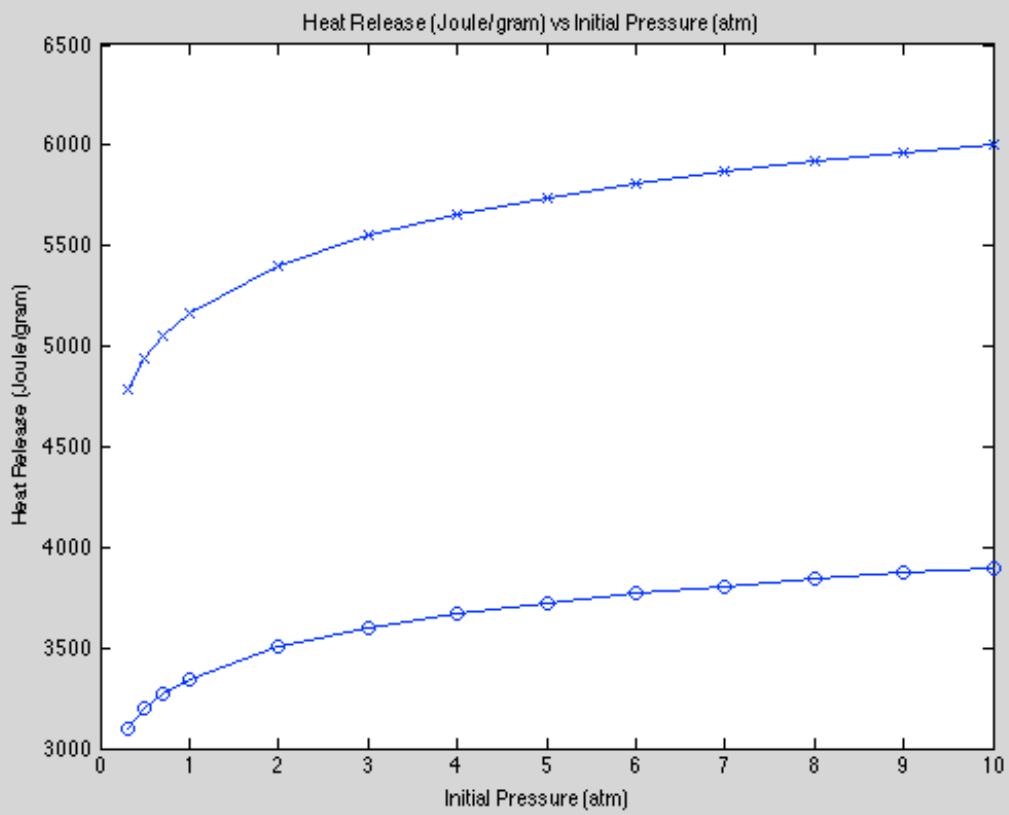
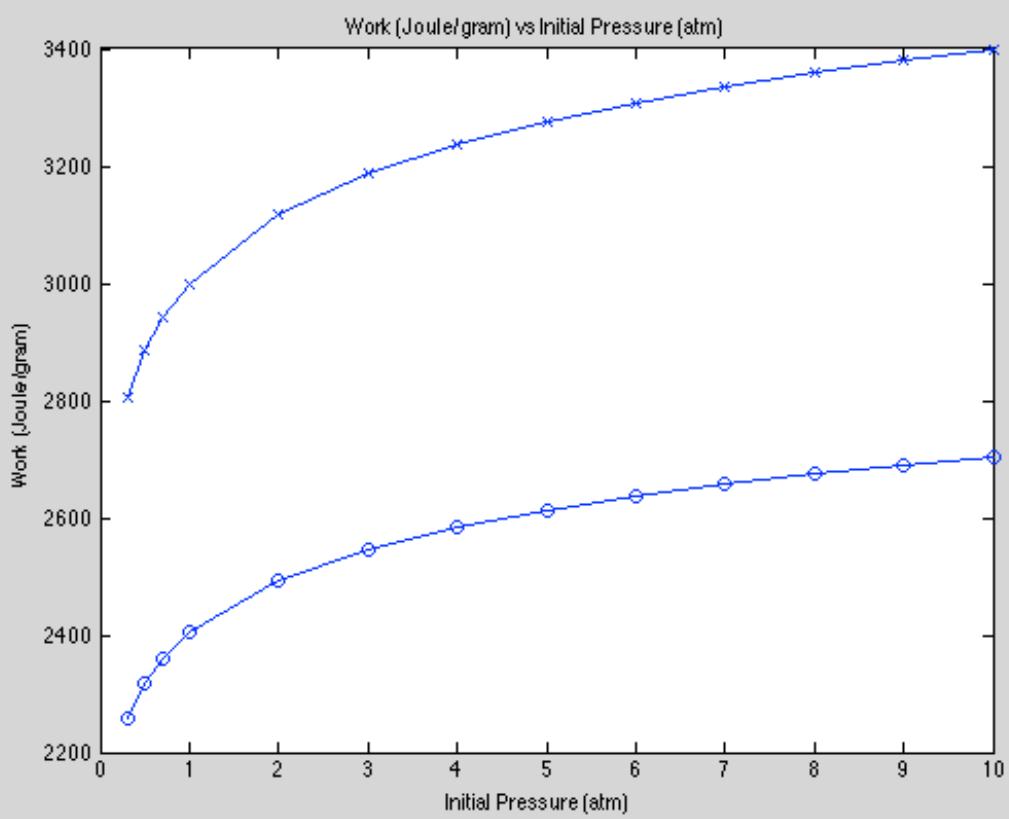
Initial temperature: 300K

Initial pressure: 0.3 to 10 atm

Key: Methane ($\text{CH}_4 + 2*\text{O}_2$) = "o" Hydrogen ($2*\text{H}_2+\text{O}_2$) = "x"







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