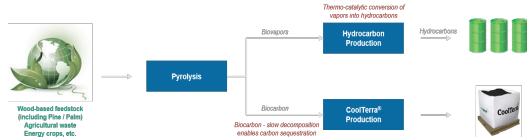


ChE-304 Problem Set 1

Week 1

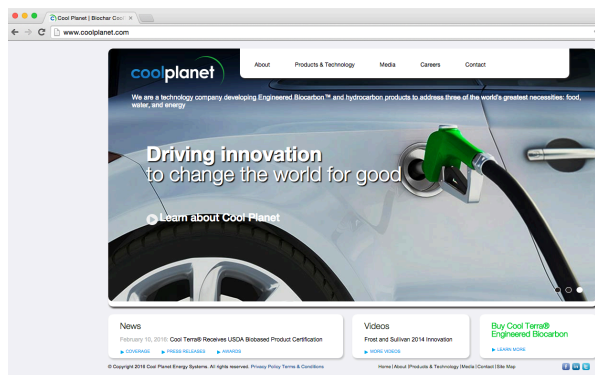
Problem 1

Every few months a new “miracle technology” appears.



Serious company: investments from BP, Google Ventures, Conoco Phillips...

Claims to produce hydrocarbons and biocarbon.

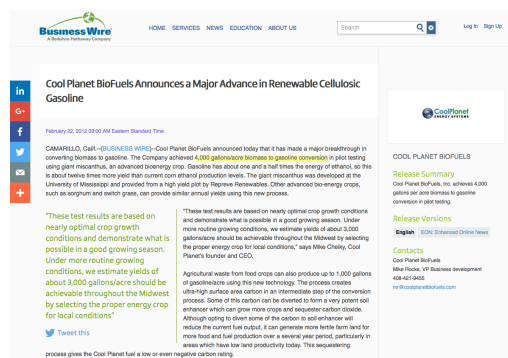


Impressive number: **3000-4000 gallons/acre gasoline**

Should you invest?

This was a real question that William Banholzer got when he was CEO of Dow Chemical.

Hint: Let's use the first law to calculate the absolute minimum amount of biomass that would require and see if it is a realistic amount to expect from one acre...



Solution:

1st Law:

$$\Delta U = Q + W \quad (\Delta E_p \text{ and } \Delta E_k \approx 0)$$

Since $P = P_{\text{atm}}$ (cst), let's use ΔH :

$$\Delta U + W_{PV} = \Delta U + P\Delta V = \Delta H = Q + W_{sh} = 0$$

$$\rightarrow \Delta H_{\text{Biomass}} = \Delta H_{\text{Gasoline}}$$

We can use HHV (reference state = fully oxidized products):

$$\Delta H_{\text{Biomass,HHV}} = \Delta H_{\text{Gasoline,HHV}}$$

$$\text{HHV}_{\text{biomass}} = 18 \text{ MJ/kg}$$

$\text{HHV}_{\text{gasoline}} = 47 \text{ MJ/kg}$

4000 gallons gas per acre $\approx 11'070 \text{ kg/acre}$

with HHVs:

biomass needed $> 11'070 \text{ kg} \times \frac{47 \text{ MJ/kg}}{18 \text{ MJ/kg}} = 28'900 \text{ kg}$

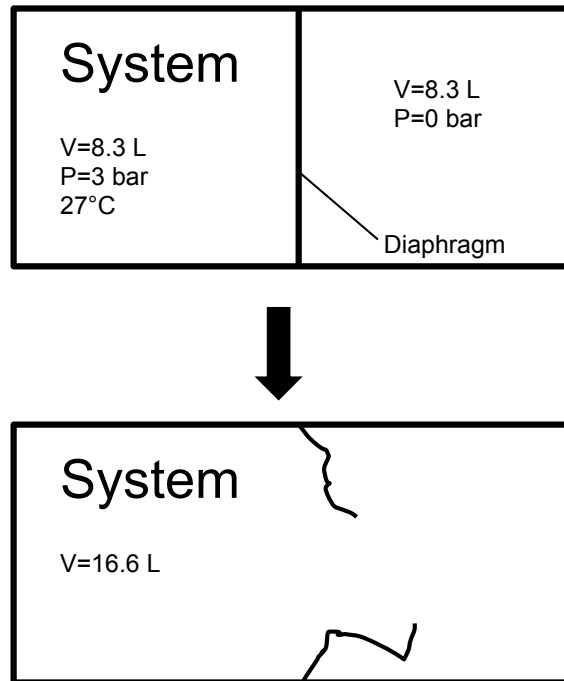
Is this realistic? This is easy to google...

No! 8-15 to/acre typical (records are around 25 to/acre)

Problem 2

Assume we have a perfectly isolated system with 1 mole of an ideal gas at a pressure $P = 3$ bar in a 16.6 L chamber that is isolated by a diaphragm from another 16.6 L chamber that has been evacuated. What is the change in entropy?

Surroundings



Reminder: for an ideal gas $U=f(T)$ only and $U \neq f(p,V)$

Solution:

This is a highly irreversible change (i.e. an explosion!). However, we can approximate this by a reversible process.

First let's explore the state change (which does not depend on whether or not the change is reversible):

We know that $\Delta U=0$ (isolated system \rightarrow no W or Q).

If $U=f(T)$ and $\Delta U=0$, then $\Delta T=0$

Therefore, we have the final T and V but we need P , we need an EOS!

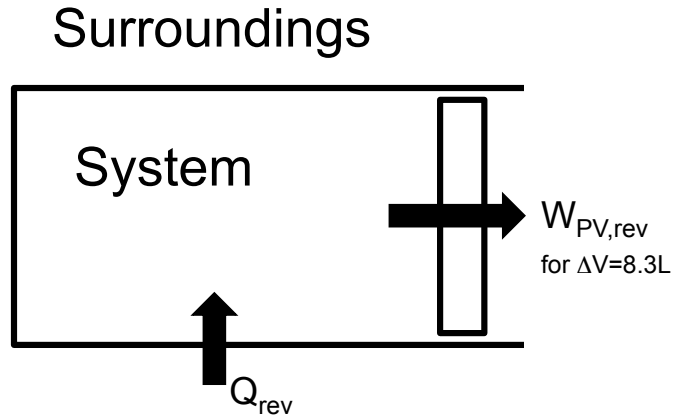
$$PV=nRT$$

From the ideal gas law for $\Delta T=0$

$$\text{We have } p_1 V_1 = p_2 V_2$$

Therefore, for a doubling of the volume, the pressure drops by half $\rightarrow p_2 = 1.5 \text{ bar}$

We now know the initial and final states! So, we can design a reversible process to go from the 1st to the 2nd stage:



Remember, $DU = 0 = Q_{rev} + W_{rev} \rightarrow Q_{rev} = -W_{rev} = \int_{V_I}^{V_F} P dV = nRT \int_{V_I}^{V_F} \frac{dV}{V} = nRT [\ln(V)]_{V_I}^{V_F} = nRT \ln\left(\frac{V_F}{V_I}\right)$

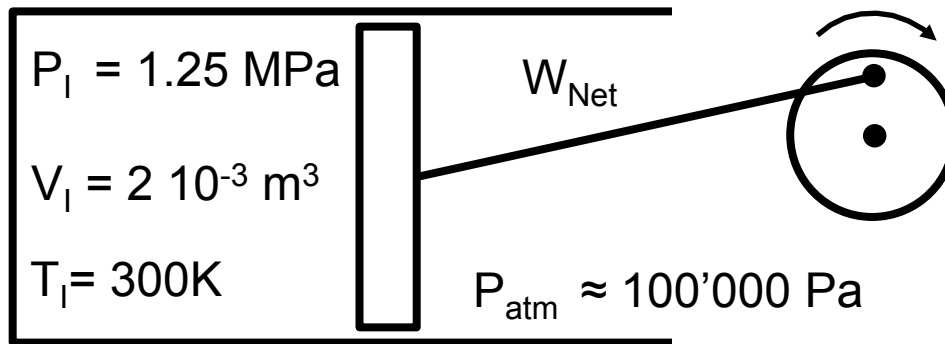
Remember that $\Delta S_{system} = S_2 - S_1 = \int_{S_1}^{S_2} \frac{dQ_{rev}}{T_{system}}$

Here $T = \text{cst} \rightarrow \Delta S_{system} = \frac{1}{T_{system}} \int_{S_1}^{S_2} dQ_{rev} = \frac{Q_{rev}}{T_{system}} = nR \ln\left(\frac{V_F}{V_I}\right) =$

$1 \text{ mol} \left(8.314 \frac{\text{J}}{\text{mol K}} \right) \ln(2) = 5.8 \text{ J/K}$

Problem 3

In order to properly understand PV work, let's calculate the work done in a single reversible expansion stroke of a piston. In this case, the gas is air and it is assumed that it acts ideally. The expansion occurs until the gas inside the cylinder is at atmospheric pressure. You can assume that the piston and cylinder are perfectly isolating.



Recall that for an ideal gas where c_p and c_v are constant

$$P_1 V_1^k = P_2 V_2^k \text{ or } PV^k = \text{constant with } k = c_p/c_v \approx 1.4 \text{ for air}$$

Calculate W_{Net} , as well as T_{final} and V_{final} of the gas.

Solution:

First let's calculate the total work done by the gas (eq. 1.4):

$$W_{\text{tot}} = \int_{V_I}^{V_F} P dV$$

Here P , V and T are all changing. However, $PV^k = A$ (we are calling the constant A):

$$W_{\text{tot}} = \int_{V_I}^{V_F} P dV = A \int_{V_I}^{V_F} \frac{dV}{V^k} = -\frac{A}{k-1} \left[\frac{1}{V^{k-1}} \right]_{V_I}^{V_F} = \frac{A}{k-1} \left[\frac{1}{V_I^{k-1}} - \frac{1}{V_F^{k-1}} \right]$$

Knowing that:

$$P_I V_I^k = P_F V_F^k = A \rightarrow \frac{1}{V^k} = \frac{P}{A} \rightarrow \frac{1}{V^{k-1}} = \left(\frac{P}{A} \right)^{\frac{k-1}{k}} \text{ Let's use this relation in the equation above:}$$

$$W_{tot} = \frac{A}{k-1} \left[\left(\frac{P_I}{A} \right)^{\frac{k-1}{k}} - \left(\frac{P_F}{A} \right)^{\frac{k-1}{k}} \right]$$

Now let's take $\left(\frac{P_I}{A} \right)^{\frac{k-1}{k}}$ out of the bracket:

$$W_{tot} = \frac{A}{k-1} \left(\frac{P_I}{A} \right)^{\frac{k-1}{k}} \left[1 - \left(\frac{P_F}{P_I} \right)^{\frac{k-1}{k}} \right]$$

Let's use $P_I V_I^k = A$

$$W_{tot} = \frac{P_I V_I^k}{k-1} \left(\frac{P_I}{P_I V_I^k} \right)^{\frac{k-1}{k}} \left[1 - \left(\frac{P_F}{P_I} \right)^{\frac{k-1}{k}} \right]$$

Simplify:

$$W_{tot} = \frac{P_I V_I^k}{k-1} \frac{1}{V_I^{k-1}} \left[1 - \left(\frac{P_F}{P_I} \right)^{\frac{k-1}{k}} \right] = \frac{P_I V_I}{k-1} \left[1 - \left(\frac{P_F}{P_I} \right)^{\frac{k-1}{k}} \right]$$

If we plug in the numbers:

$$W_{tot} = \frac{1'250'000 \times 2 \cdot 10^{-3}}{1.4 - 1} \left[1 - \left(\frac{100'000}{1'250'000} \right)^{\frac{0.4}{1.4}} \right] = 3213 \text{ J}$$

To this, we need to subtract the work needed to push back the atmosphere:

$$W_{PV} = \int_{V_I}^{V_F} P_{atm} dV = P_{atm} (V_F - V_I)$$

We need to calculate V_F :

$$P_I V_I^k = P_F V_F^k \rightarrow V_F = \left(\frac{P_I V_I^k}{P_F} \right)^{1/k} = \left(\frac{1250000 (2 \cdot 10^{-3})^{1.4}}{100000} \right)^{1/1.4} = 0.01215 \text{ m}^3 = 12.15 \text{ l}$$

$$W_{PV} = P_{atm} (V_F - V_I) = \frac{100'000(12.15 - 2)}{1000} = 1015 \text{ J}$$

Therefore the net work produced is:

$$W_{net} = W_{tot} - W_{PV} = 3213 - 1015 = \mathbf{2198 \text{ J}}$$