Availability in Reacting Systems

Introduction

Earlier we worked with the idea that any stream that is out of thermal or mechanical equilibrium with the environment can be thought of as an energy resource. The maximum possible work that can be extracted from such a stream is given by its availability:

$$W_{max} = h_1 - h_0 - T_0(s_1 - s_0) \qquad (1)$$

where the subscript 1 refers to the stream properties and the subscript 0 refers to the properties of the stream at environmental conditions.

A stream of fuel can be thought of in the same way. Here the maximum possible work that can be extracted occurs when the fuel is brought into thermal, mechanical, and *chemical* equilibrium with the surroundings. An example of such a system is an ideal fuel cell that takes in natural gas and air, exhausts CO_2, H_2O, and N_2, and produces electrical work. Equation 1 works just fine for this situation, giving the maximum possible electrical work. The only new things we need to do are (1) learn how to run the equilibrium code to find equilibrium states (and the h and s associated with these), and (2) be able to express h and s for mixtures (something we have already done in Chapter 12 of Çengal and Boles). The operation of the equilibrium code is discussed in a separate handout.

Chemical Availability

There is no new theory here, so let's proceed with an example. Assume you have a process in which a stream of CH_4 (1 kmole/s) is reacted with a stoichiometric stream of air, both at 298 K and 1 atm. Note that it is important to know whether the air is premixed with the fuel (here it is not). Our goal is to compare how much work we can get out of a direct conversion process (like a fuel cell) as opposed to burning the fuel and using the heat in a heat engine.

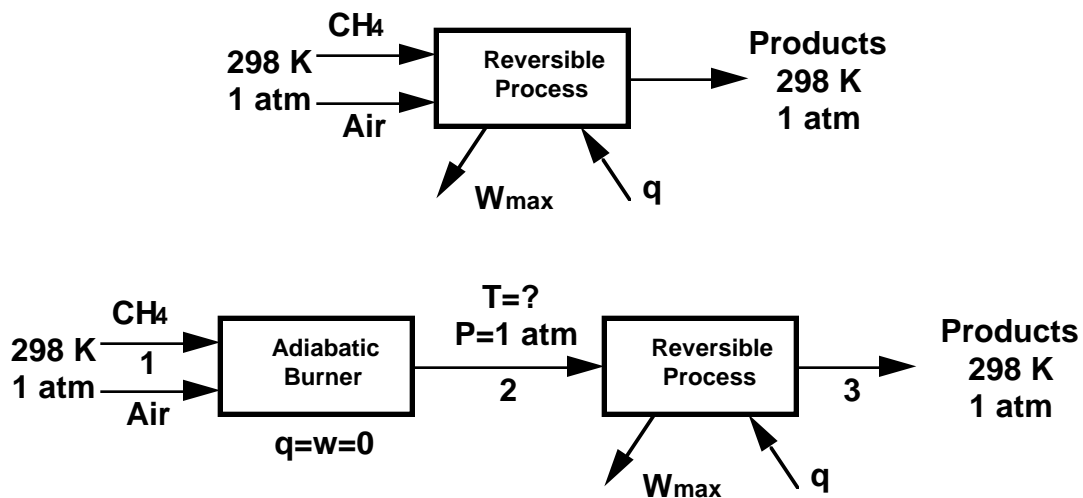The two situations are shown in Figure 1.

Figure 1. Two processes for using chemical energy.

The first process gives the maximum possible work that could be extracted by an ideal fuel cell. In the second process the fuel and air are burned adiabatically to yield a hot product gas. This gas is then run through a reversible process to get the maximum work (*e.g.*, it is used as a heat source for a reversible heat engine). What we will see is that the act of burning the fuel is irreversible and

involves lost work. Thus, the W_{max} for the second process will be less than the first, and this is the sacrifice we make when we burn fuels.

The reaction equation is (we will work on the basis of 1 kmole of CH_4):

$$CH_4 + 2[O_2 + 3.76N_2] \rightarrow CO_2 + 2H_2O + 7.52N_2$$
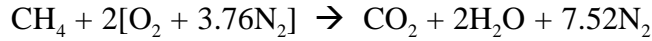
Here, the product list is appropriate for 298 K, but at the high temperature in the second process there will be considerable disassociation, and this must be calculated with the equilibrium code.

The maximum work potential is given by equation 1, so we just need to identify values for each term. For the reactants, the value of h is given by:

$$h = \sum N_i \bar{h}_i = \sum N_i (\bar{h}_{f,i}^0 + \bar{h} - \bar{h}_{298})$$ (2)

For the reactants:

Species	kmoles	h_f^0	$h\text{-}h_{298}$	$N_i[h_f^0+(h\text{-}h_{298})]$	s^o	P_I
CH_4	1	-74,850	0	-74,850	186.16	1
O_2	2	0	0	0	205.04	0.21
N_2	7.52	0	0	0	191.61	0.79

So the enthalpy of the reactants is –74,850 kJ/kmole CH_4.

The entropy for the reactants is found from a formula similar to equation 2:

$$h = \sum N_i \bar{s}_i$$ (3)

except now the individual s values are influenced by whether they are in a mixture or not. The equation is:

$$\bar{s}_i = \bar{s}_i^o - R_u \ln \left[\frac{P_i}{P_{ref}} \right]$$ (4)

Since the CH_4 enters as a separate stream, it's partial pressure is 1 atm, and thus s=s°=186.16 kJ/kmole CH_4 (this is the point where it is important to know whether the fuel and air enter as separate streams or are premixed). Since the air is a mixture, we need to correct the O_2 and N_2 values for the mixing. For the O_2 we need to include P_i=0.21 atm and P_{ref}=1 atm, so s=218.02 kJ/kmole O_2. Similarly for N_2, s=193.57 kJ/kmole N_2. Plugging these individual s values in equation 3 gives an overall entropy for the reactants of 2077.85 kJ/mole CH_4.

We could hand calculate the entropy for the products using the equations above, but it is easier to use the equilibrium code. This is run for stoichiometric CH_4/air input as a TP problem with T=298 K and P=1 atm. The result from the code is h=-3017.544 kJ/kg and s=7.2214 kJ/kg-K. These both have to be expressed on a basis of one kmole CH_4. Using the molecular weights in the reaction equation we find that if the reactants contain one kmole CH_4, then the entire reactants (fuel plus air) have a mass of 290.56 kg. Thus, the ratio (290.56 kg products/kmole CH_4) is the conversion factor to put h and s on a kmole CH_4 basis. Applying this, the product properties are h=-876,778 kJ/kmole CH_4 and s=2098.25 kJ/kmole CH_4. Now we are ready to go to equation 1:

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$$W_{max} = (-74,850) - (-876,778) - (298)(2077.85 - 2098.25) = 808,007 \text{ kJ/kmole } CH_4$$

Since the methane flow is 1 kmole/s, the maximum power output from the first configuration is 808.007 MW.

Now we turn to the second configuration. The first task is to find the irreversibility associated with the combustion step. This is given by:

$$i_{comb} = T_o(s_2 - s_1) \tag{5}$$

(Note that here q=0 so this term drops off.) We have already found s_1 (entropy of reactants) above, so we need to get s_2. Running the equilibrium code for stoichiometric CH_4/air as a HP problem with P=1 atm, we get T_2=2226 K, h_2=-257.61 kJ/kg, and s_2=9.8226 kJ/kg-K. Converting both these numbers to a kmole CH_4 basis (as we did above) results in h=-74,850 kJ/kmole CH_4, and s=2854.05 kJ/kmole CH_4. (Surprise! Note that h_2=h_1, which is required for the HP problem.) Going to equation 5, we find that the irreversibility associated with the adiabatic combustion is 231,307 kJ/kmole CH_4, or 231.307 MW. Note that this is not lost heat, since the process is adiabatic. This just means that the very act of burning the fuel, even adiabatically, results in the loss of availability.

Finally, let's get the availability of what's left after the combustion. We will use equation 1. The inlet conditions are those for state 2 just listed above. The outlet conditions are the dead state that was used in the first calculation:

$$W_{max} = (-74,850) - (-876,778) - (298)(2854.05 - 2098.25) = 576,700 \text{ kJ/kmole } CH_4$$

or 576.7 MW. If we add the W_{max} for the second step to the irreversiblity of the first step, we should get the original availability of the fuel and air:

$$231.307 + 576.7 = 808.01 \text{ MW}$$

This compares to 808.007 MW calculated above.

This gives us the comparison between the best fuel cell system possible with the best combustor connected to a reversible heat engine. While the fuel cell could recover 100% of the availability of the fuel stream, the combustor/heat engine combination could, at best, get only 71.4% of the maximum possible work, with 28.6% of the work potential lost due to the irreversibility of the combustion process.

A final note. In these calculations, the code has assumed that the water is always present as water vapor. Somewhat different values would result if liquid water product was assumed. The correct, but more complex, way to do this is to use the dewpoint to decide how the water will divide itself between liquid and vapor, and then calculate h and s treating the water as two separate species.