10.40 Thermodynamics **Fall 2003**

Final Exam

Problem 2

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2. (20 points) MITY Industries is trying to decide where to make its next investments and has been approached by Colossal Technology Inc. (CTI), which claims that it has a new approach for generating motive power from hydrogen that is inherently more efficient than the traditional internal combustion (IC) engines that are in use today in our automobiles and trucks. In their scheme, pressurized pure hydrogen at 500 bar, 25°C is electrochemically oxidized with pure oxygen at 1 bar, 25°C to form water in a Fuel Cell Super Electro Converter (FCSEC) that generates electrical power directly. CTI claims that their concept can produce more power than even the most efficient IC engine using the same H_2 and O_2 feeds because the FCSEC converter is not subject to Carnot limitations. According to CTI, water exits the FCSEC at 1 bar, 25°C,

(a) (12 points) What do you think of CTI's claim? Back up your answer with appropriate thermodynamic analysis and discussion.

(b) (8 points) Pressurized methane, available at 500 bar and 25°C, has also been considered as a transportation fuel. CTI claims that they can chemically reform the methane to hydrogen via steam reforming on the vehicle and then use the FCSEC to produce electricity. Would using methane as a fuel introduce any additional thermodynamic limitations over using pure hydrogen? Explain your answer.

Steam reforming of methane proceeds by two dominant reaction pathways:

$$CH_{4\,(g)} + H_2O_{(g)} = CO_{(g)} + 3H_{2\,(g)}$$
$$CO_{(g)} + H_2O_{(g)} = CO_{2\,(g)} + H_{2\,(g)}$$

Feel free to use the thermochemical and other physical property available in Appendix G and elsewhere in the text.

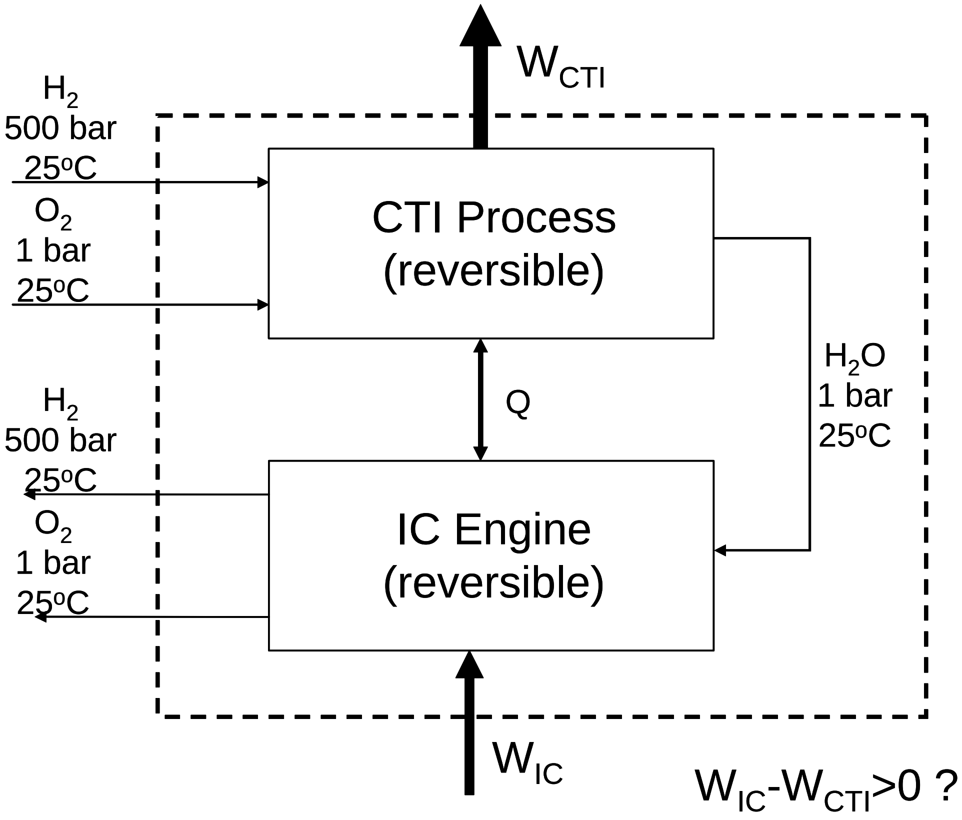
Solution:

(a)

CTI's claim is that they can use their process to produce more power than even the most efficient IC engine using the same feed streams. The solution to this question lies in deciding whether this statement is true or false and then justifying your answer. The phrase "most efficient" indicates that this is a maximum work problem, since the most efficient IC engine is a reversible IC engine. So the question really is, "given the H_2 and O_2 feed streams, is there a reversible process following the CTI method that can be used to produce more work than some other reversible process?" The answer, of course, is no. There are several ways to show this.

Method 1-Perpetual Motion Machines

Once it is realized that the maximum work comes from a reversible process, we can envision a process in which the 500 bar, 25°C H_2 and 1 bar, 25°C O_2 streams are fed to the reversible CTI process, work is extracted, and then the rejected 1 bar, 25°C H_2O is fed to a reversible, IC engine running backwards that produces 500 bar, 25°C H_2 and 1 bar, 25°C O_2 (see figure below). Any heat rejected from one process is fed to the other (if this restriction bothers you, then you may assume they both interact with a heat reservoir at 25°C).



As the figure shows, if the CTI process is more efficient that the IC engine, then $W_{IC} - W_{CTI} > 0$ and the net effect is produce energy in the universe, or make a perpetual motion machine of the first type. This is impossible. If you are not comfortable with the restriction that the net Q between the processes is zero, but instead imagine each process interacts with a heat reservoir at 25°C, then if $W_{IC} - W_{CTI} > 0$, the net effect is a process that converts heat directly into work, which is a perpetual motion machine of the second type, which is also impossible. The maximum work that can be derived from a given set of feed streams is set by the second law and is independent of the process used. Therefore, CTI's claim is bogus, and there is no way it can be *inherently* more efficient than any other process with the same feed and exit streams.
In reality no process is reversible, and it is possible that their *actual* process is more efficient than an IC engine. However, this was not their claim.

Method 2-Exergy Analysis

In this method, we will perform an exergy analysis to determine if the CTI process is more efficient or not. To begin with, we will expand the H_2 feed from 500 bar to 1 bar using a reversible expander. This will give the maximum work for the expansion, regardless of the process, and will allow us to focus on the conversion of hydrogen to water. Assuming a reversible, isothermal expander operating at 25°C:

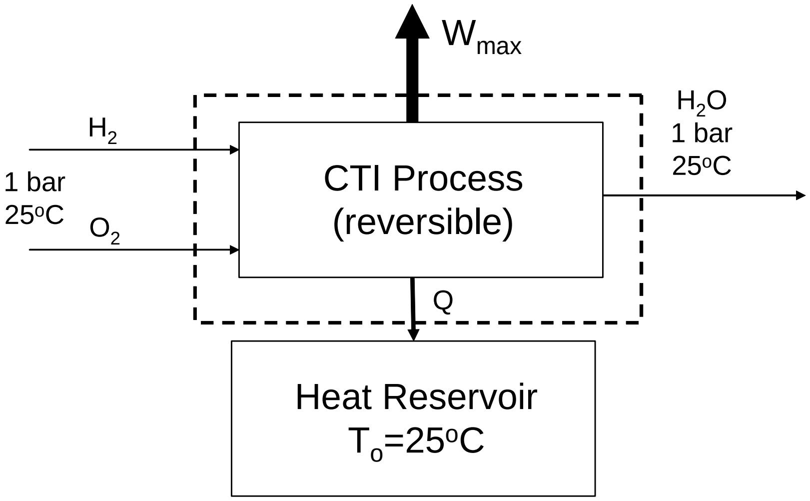
$$\delta W = -P d\underline{V}$$

Integrating, and making an ideal gas assumption for now:

$$W \approx -RT \ln\left(\underline{V}_f \big/ \underline{V}_i\right) = RT \ln\left(P_f \big/ P_i\right) = -15.4 \text{ kJ/mol}$$

To actually evaluate the work from this expansion, we would need an EOS for the hydrogen, but the ideal gas assumption gives us an idea of the work that could be extracted, and frees us to determine the work from the oxidation of hydrogen without worrying about pressure effects.

For the electrochemical fuel cell used in the CTI process, an exergy analysis or our analysis from Problem Set 11, Problem #2 tells us that the maximum work that can be derived from the isothermal oxidation of H_2 and O_2 is equal to $\Delta\underline{G}_{rxn}$:



$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

$$W_{\max} = \Delta\underline{B} = \Delta\underline{H}_{rxn} - T_o \Delta\underline{S}_{rxn} = \Delta\underline{G}_{rxn}$$

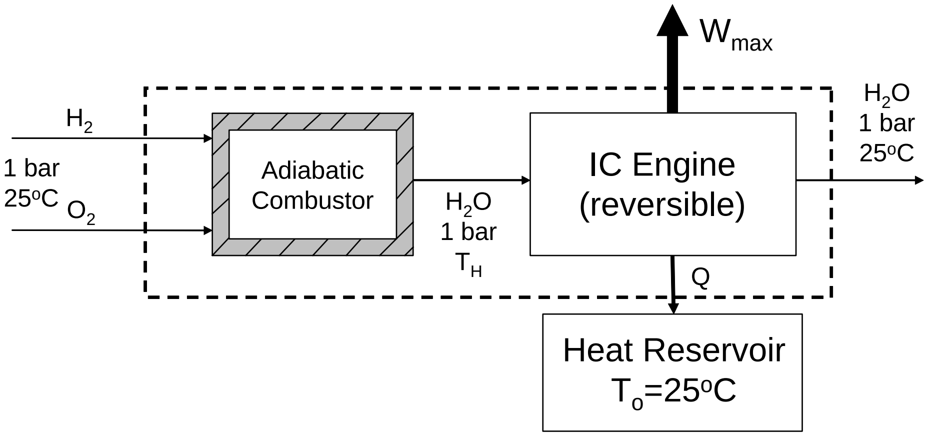
$$\Delta\underline{G}_{rxn} = \sum_i \upsilon_i \underline{G}_{f,i}$$

Luckily for us, the information in Appendix G is given at the same conditions as in our problem, so we can evaluate $\Delta\underline{G}_{rxn}$ directly:

$$\Delta G_{rxn,\ 25^o C} = -228.8 \text{ kJ/mol} - \left[(0) + \tfrac{1}{2}(0)\right] = -228.8 \text{ kJ/mol}$$

$$W_{\max} = N \Delta\underline{G}_{rxn} = N\left(-228.8 \text{ kJ/mol}\right)$$

Let us compare the maximum work from the CTI process to that from an IC engine. An IC engine works by combusting fuel and then converting the heat of the combustion products into work. In order to derive maximum work, we will assume that these are Carnot IC engines (see figure below).



Performing a first law analysis around the Adiabatic Combustor:

$$d\underline{U} = 0 = \cancel{\delta Q} + \cancel{\delta W} + H_{in}\delta n_{in} - H_{out}\delta n_{out}$$

$$\delta n_{H_2} = \delta n_{H_2O} = \tfrac{1}{2}\delta n_{O_2} = \delta n$$

$$0 = \left[\tfrac{1}{2}H_{O_2}\left(T_o\right) + H_{H_2}\left(T_o\right) - H_{H_2O}\left(T_H\right)\right]\delta n$$

Moving the enthalpy term for $H_2O(T_H)$ to the other side and subtracting $H_{H_2O}\left(T = T_o\right)$ from both sides, we have:

$$\underbrace{H_{H_2O}\left(T_H\right) - H_{H_2O}\left(T_o\right)}_{\Delta H_{adib}} = \underbrace{\tfrac{1}{2}H_{O_2}\left(T_o\right) + H_{H_2}\left(T_o\right) - H_{H_2O}\left(T_o\right)}_{\Delta H_{rxn}\left(T_o\right)}$$

In other words, all the energy from the combustion of hydrogen to water goes to heat the product gases. An entropy balance gives similar results (we will find this useful later):

$$d\underline{S} = 0 = \cancel{\frac{\delta Q}{T}} + S_{in}\delta n_{in} - S_{out}\delta n_{out}$$

$$\underbrace{S_{H_2O}\left(T_H\right) - S_{H_2O}\left(T_o\right)}_{\Delta S_{adib}} = \underbrace{\tfrac{1}{2}S_{O_2}\left(T_o\right) + S_{H_2}\left(T_o\right) - S_{H_2O}\left(T_o\right)}_{\Delta S_{rxn}\left(T_o\right)}$$

Next, we move on to the reversible IC engine, and perform a maximum work/exergy calculation:

$$W_{\max} = \Delta\underline{B} = \Delta\underline{H} - T_o\Delta\underline{S}$$

$$W_{\max} = \left[\left(H_{H_2O}\left(T_H\right) - H_{H_2O}\left(T_o\right)\right) - T_o\left(S_{H_2O}\left(T_H\right) - S_{H_2O}\left(T_o\right)\right)\right]N$$

$$W_{\max} = \left[\Delta H_{rxn} - T_o\Delta S_{rxn}\right]N = N\Delta G_{rxn}$$

$$W_{\max} = N\left(-228.8 \text{ kJ/mol}\right)$$

This is the exact same value as for the CTI process, so CTI's claim must be false.

(b)
From our analysis in part (a), the most direct way to determine how using methane instead of H_2 as the feed for the CTI process is to determine how this affects the overall $\Delta\underline{G}_{rxn}$ for the process. The overall reaction in the steam reforming process is:

$$CH_{4\,(g)} + 2H_2O_{(g)} = CO_{2\,(g)} + 4H_{2\,(g)}$$

The hydrogen is then fed to the CTI process to produce fuel. We expect that the steam reforming step will require energy in order to make hydrogen, so that the overall efficiency of the process will suffer.

$$W_{\max} = \Delta\underline{G}_{overall} = \Delta\underline{G}_{CH_4 \to H_2} + \Delta\underline{G}_{H_2 \to H_2O}$$

$$\Delta G_{CH_4 \to H_2} = -394.6 \text{ kJ/mol} - \left[-50.87 \text{ kJ/mol} + 2\left(-228.8 \text{ kJ/mol}\right)\right]$$

$$\Delta G_{CH_4 \to H_2} = 113.87 \text{ kJ/mol}$$

So we see that the steam reforming step does have a positive ΔG_{rxn}, meaning that it requires energy. Since each mole of CH_4 supplied contributes 4 moles of H_2, the net result is a reduction in W_{max} of 113.87/4 or 28.5 kJ/mol H_2.

Furthermore, energy will be required to separate the products of steam reforming, H_2(g) and CO_2(g), since only pure H_2(g) can be fed to the FCSEC. Assuming that the gaseous products of steam reforming can be treated as ideal gases:

$$\Delta G_{separation} = -RT\sum_i x_i \ln x_i = -8.314\left(\text{J}/\text{mol}\cdot\text{K}\right)\left(298 \text{ K}\right)\left[0.8 \ln\left(0.8\right) + 0.2 \ln\left(0.2\right)\right]$$

$$\Delta G_{separation} = 1.24 \text{ kJ}/\text{mole CH}_4 \text{ or } 0.31 \text{ kJ}/\text{mole H}_2$$

The energy required to reversibly separate the gases is negligible compared to the energy required for steam reformation. In the end, for each mole of H_2 sent to the FCSEC, 28.8 kJ is required to produce the H_2 from CH_4 using steam reforming. In reality, this energy would likely come from burning additional CH_4 in order to generate heat to supply the steam reforming reaction.

For the entire process, per mole of CH_4:

$$W_{\max} = \Delta\underline{G}_{overall} = \left(113.87 \text{ kJ/mol CH}_4\right) + \left(1.24 \text{ kJ/mol CH}_4\right) - \left(4\ \frac{\text{moles H}_2}{\text{mole CH}_4}\right)\left(228.8 \text{ kJ/mol H}_2\right)$$

$$W_{\max} = -800.1 \text{ kJ/mole CH}_4$$

Compared to the maximum work that could be obtained from directly combusting methane and then separating the CO_2 and H_2O streams:

$$W_{\max} = \Delta G_{rxn} - \Delta G_{sep} = -800.1 \text{ kJ/mol CH}_4$$

We see that the difference is equivalent to the price of steam reforming and separating the product gases. If we were to extract energy from recombining CO_2 and H_2O in both processes, we would see that they are still equivalent, and W_{max} = –801.3 kJ/mol