

Vm433: Advanced Energy Solutions (Fall 2016)

Project 3: Fuel Cells & Hydrogen Production

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Part A, to be completed **individually**, is due 4 PM, Thur Dec 1, 2016

Part B, to be completed **individually**, is due 4 PM, Thur Dec 8, 2016

Bonus Part C, to be completed **individually**, is due 4 PM, Thur Dec 15, 2016

(v. 11/14/2016) **Start working on the project early!**

The proton exchange membrane (PEM) fuel cell introduced in class is an example of nearly-isothermal electrochemical engine. It takes in hydrogen and air as reactants, and converts them to water in such a way that electrical work is produced by the chemical reaction. By extracting work during the reaction, the high temperatures associated with combustion are avoided, as is entropy generation (irreversibility) associated with those temperatures. As such, the fuel cell offers the potential of high chemical-to-electrical energy conversion and excellent efficiency—if (a) it can be reversibly operated and (b) it can be efficiently supplied with hydrogen fuel.

For this project, you will explore the efficiency potential of reversible hydrogen fuel cells (PEM, as well as Phosphoric Acid, Molten Carbonate, and Solid Oxide), and examine the energy cost of hydrogen production from natural gas via steam methane reforming. The assignment will help you to gain experience working with (a) Gibbs free energy to calculate fuel cell efficiency, and (b) reactive equilibria and equilibrium constants.

SECTION I: MAXIMUM (REVERSIBLE) FUEL CELL EFFICIENCY THE ASSIGNMENT

A. *Part A: To be completed individually, due 4 PM, Thur Dec 1, 2016*

- 1) **10 points.** Modify the MATLAB functions you developed in Project 2 to determine the molar Gibbs free energy G (in kJ/kmol) in the following two cases, each calculated based on (i.e., with reference to) *the standard reference state of 25 °C, 1 atm* (textbook appendix Table A–26):
 - a) G_j for an ideal gas species j , given the gas temperature and (partial) pressure;
 - b) G_{mix} for an ideal gas **mixture**, given the mixture temperature, pressure, and chemical composition (mol%).

Deliverables: The following MATLAB functions (as separate m-files)

- `function [spg] = findSpeciesGibbs(inputs)`
- `function [mixg] = findMixtureGibbs(inputs)`

Decide on the necessary input variables yourselves.

- 2) **20 points.** The *first-law efficiency* η for a reactive, isothermal, isobaric engine is the ratio of engine work output W per unit of heating value HV of the fuel supplied,

$$\eta = \frac{W}{m_{\text{fuel}} HV} = \frac{-\Delta G_{\text{rxn}} - I}{m_{\text{fuel}} HV} \quad (1)$$

This definition applies to fuel cells, which are steady-flow, near-isothermal engines. The power that a fuel cell is capable of producing is limited by the difference in Gibbs free energy of the products versus the reactants supplied to the device, $\Delta G_{\text{rxn}} = G_{\text{Prod}} - G_{\text{React}}$.

Calculate (and plot) the maximum first-law efficiency for a hydrogen-air fuel cell versus temperature T from 25 to 1000 °C. Use dry hydrogen and 100% excess air (consisting 21% O₂, 79% N₂) as the reactants that enter the fuel cell *in separate streams*. Assume that the product stream leaves the fuel cell as an ideal-gas mixture, and the pressure at each electrode is 0.1 MPa.

Consider two ways of defining the fuel heating value HV , which appears in the denominator of the expression for efficiency η (Eq. (1)): (a) constant higher heating value HHV° , versus (b) constant lower heating value LHV° , both at standard reference conditions.

For comparison, **show on the same axes the maximum (Carnot) efficiency for a heat engine** operating between a 25 °C thermal reservoir and a high-temperature reservoir at T (ranging from 25 to 1000 °C).

Deliverables: A MATLAB script named `H2airFCMax1stLawEff.m`, which calls the functions developed in Part 1 above to determine the maximum first-law efficiency for a hydrogen-air fuel cell, as well as calls the basic MATLAB plotting functions to generate the required diagram

- Plot all three maximum efficiency curves (fuel cell: HHV° basis, LHV° basis; Carnot heat engine) on the same set of axes to facilitate comparison of the results
- Do not neglect proper annotation of the figures using functions such as `title`; `xlabel`, `ylabel` (including units in parentheses); `legend` or `gtext`

- 3) **10 points.** The fuel cell operating pressure and the amount of excess air supply are design parameters that may be varied. Operating at higher pressures may be beneficial when the overall reaction leads to mole number decrease (such as hydrogen oxidation to water). However, the issues of cost, gas sealing and membrane mechanical stress limit what is practical. Similarly, operating with higher levels of excess air supplies more oxygen to the cathode, but pumping cost needs to be considered.

Modify the analysis from Part 2 above to calculate (and plot) the maximum fuel cell efficiency (on the LHV° basis) as functions of

- excess air from 100% to 1000% (at 0.1 MPa operating pressure)
- operating pressure from 0.1 to 4 MPa (at 100% excess air)

In both cases, consider fuel cell operation at four temperatures: 80 °C, typical of PEM FC; 220 °C (phosphoric acid fuel cell, PAFC), 650 °C (molten carbonate fuel cell, MCFC), 800 °C (solid oxide fuel cell, SOFC).

Deliverables: Two required diagrams (varying %excess air and operating pressure), generated by the same MATLAB script named `H2airFCMax1stLawEff.m` as Part 2 above

- For each diagram, plot all four maximum efficiency curves (at 80, 220, 650, and 800 °C) on the same set of axes to facilitate comparison of the results
- Do not neglect proper annotation of the figures using functions such as `title`; `xlabel`, `ylabel` (including units in parentheses); `legend` or `gtext`

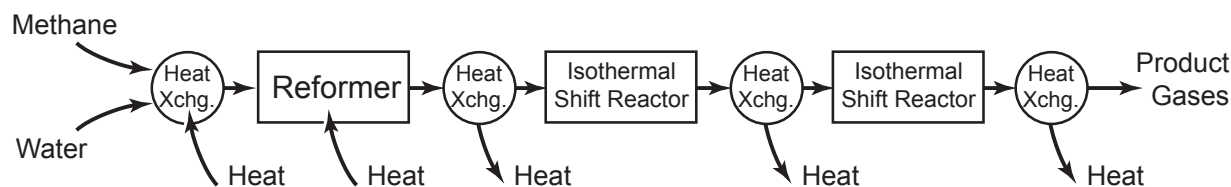


Fig. 1. Methane reforming system with two isothermal (high- and low-temperature) shift reactors.

SECTION II: HYDROGEN PRODUCTION VIA STEAM-METHANE REFORMING THE BACKGROUND

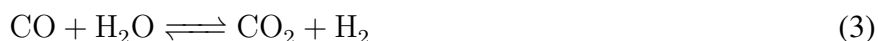
A big challenge to widespread use of hydrogen fuel cells is this: While our surroundings contain lots of water, which is the stable oxide of hydrogen, our surroundings do not contain lots of molecular hydrogen for fuel cell consumption. At present, hydrogen is produced most cost-effectively from fossil fuels. This process, when involving the simplest hydrocarbon, is called steam-methane reforming (SMR):



If you can get the proper conditions to “move” the reaction to the right-hand side—a matter of reactive equilibrium—then you can generate two to three moles of hydrogen per mole of methane fuel (and water) invested.

There remains a problem, however: SMR also yields substantial quantity of carbon monoxide, which is unacceptable for the operation of lower-temperature fuel cells. This is because CO preferentially adsorbs onto platinum catalyst sites on the anode side, thereby *poisoning* the catalyst and prevent hydrogen molecules from reaching it. This problem is more serious the lower the fuel cell operating temperature. So PAFC (~200 °C operating temperature) requires hydrogen fuel supply with less than 0.5 mol% CO in it, whereas PEMFC (<100 °C operation) can tolerate at most 0.001% CO (10 parts per million, or ppm) at the anode. Therefore, the co-production of one CO molecule for every three H₂ from steam-methane reforming (right-hand side of reaction (2)) is unacceptable.

Luckily (for us) a catalyst that enables reaction (2) to reach chemical equilibrium almost always drives reaction (3), called the water-gas shift reaction (WGS), to equilibrium, too:



Again, if you can get the proper conditions to “move” this reaction to the right-hand side—again, a matter of reactive equilibrium—then the CO content might be reduced and the problem of catalyst poisoning averted.

Figure 1 shows a typical methane reforming system consisting of a reforming reactor, two shift reactors, and heat exchangers between them to heat or cool the process stream. In the first reactor (the “reformer”), methane and steam are supplied and reactions (2) and (3) are driven to equilibrium. This takes place over nickel catalyst at an elevated temperature, typically around 800 °C. The process is endothermic; this means the reformer has to be heated to keep its temperature at 800 °C while the chemical species equilibrate. (Upstream of the reformer, methane and water have to be mixed and heated to the reformer operating temperature.)

As your analysis in this section will show, the process stream exiting the reformer is H₂-rich, but also contains an excessive amount of CO—way too much for direct supply to PEMFC or PAFC. However, your analysis will also show that the equilibrium CO content can be shifted downward by cooling via the second heat exchanger. We want to be careful, though, not to reverse the SMR reaction (i.e., re-generate methane and steam), but only to drive the WGS equilibrium (reaction (3)) to the right-hand side.

In industrial practice, this is accomplished by choosing the shift reactor catalysts that promote WGS equilibrium while blocking methane formation (reverse-SMR). The first shift takes place over iron-chromium catalyst at a relatively high temperature of 400–500 °C. This is followed by further gas cooling

before the process stream passes over copper catalyst in a second, lower-temperature reactor (200–250°C). At this point, the equilibrium CO content should have dropped to ~ 1 mol%, almost low enough to meet the needs of the phosphoric acid fuel cell. (For ppm-level CO mole fraction appropriate for PEMFC application, a final CO removal step via selective catalytic oxidation or methanation reaction would be required, which we will not consider in this assignment.)

THE ASSIGNMENT (CONTINUED)

A. *Part B: To be completed individually, due 4 PM, Thur Dec 8, 2016*

- 4) **10 points.** Calculate, from first principle (i.e., beginning from the Gibbs free energy of reaction from Part 2 above), and plot the equilibrium constants K_P for the steam-methane reforming and water-gas shift reactions as functions of temperature T from 25 °C to 1200 °C.

Hint: You can use the equilibrium constants tabulated at the back of the textbook (appendix Table A–28) to help debug your analysis.

Deliverables: A MATLAB script named `KpSMRWGS.m`, which calls the functions developed in Part 1 above to determine the equilibrium constants K_P for the SMR and WGS reactions, as well as calls the basic MATLAB plotting functions to generate the required diagram

- To facilitate comparison of the results, plot $\log_{10} K_P$ versus T on the same axes (use the semilogy function) for both reactions, over the range of $K_P = 10^{-3}$ to $K_P = 10^{+3}$ (i.e., from $\log_{10} K_P = -3$, negligible reaction, to $\log_{10} K_P = +3$, near-complete reaction)
- Do not neglect proper annotation of the figures using functions such as `title`; `xlabel`, `ylabel` (including units in parentheses); `legend` or `gtext`

- 5) **20 points.** Plot the equilibrium mole fractions of chemical species involved in steam-methane reforming (SMR, reaction (2)) as functions of temperature from 25 °C to 1200 °C. Start with 3:1 molar ratio of steam to methane being fed to the reformer. This is the case in industrial practice to avoid elemental carbon formation and deposition.

Do not consider the WGS reaction here in Part 5, just the SMR reaction. As is done throughout this project, consider the equilibrium chemical species to exist as an ideal-gas mixture.

Deliverables: A MATLAB script named `equilMolFracSMR.m`, which solves for the equilibrium mole fractions of chemical species in the SMR reaction, as well as calls the basic MATLAB plotting functions to generate the required diagram

- If the equilibrium composition is pressure-dependent, plot the results at three different operating pressures—0.1, 1 and 10 MPa—to examine the effects
- Do not neglect proper annotation of the figures using functions such as `title`; `xlabel`, `ylabel` (including units in parentheses); `legend` or `gtext`

- 6) **10 points.** Next, plot the equilibrium mole fractions of species involved in water-gas shift (WGS, reaction (3)) as functions of temperature from 25 °C to 1200 °C.

This time, do not consider the SMR reaction, just the WGS reaction. However, use the same *atom ratios* as Part 5—ones which correspond to a 3:1 molar ratio of steam to methane, even though methane does not feature in the water-gas shift. (For the purpose of this analysis, you may assume that all the methane has been reformed to CO and/or oxidized to CO₂.)

Deliverables: A MATLAB script named `equilMolFracWGS.m`, which solves for the equilibrium mole fractions of chemical species in the WGS reaction, as well as calls the basic MATLAB plotting functions to generate the required diagram

- If the equilibrium composition is pressure-dependent, plot the results at three different operating pressures—0.1, 1 and 10 MPa—to examine the effects
- Do not neglect proper annotation of the figures using functions such as `title`; `xlabel`, `ylabel` (including units in parentheses); `legend` or `gtext`

B. Bonus Part C: To be completed individually, due 4 PM, Thur Dec 15, 2016

- 7) **Up to 20 bonus points.** Building on your scripts from Parts 4–6 above, analyze the performance of the typical methane reforming system described in the background and shown in Figure 1.

Take operating pressure to be 0.1 MPa. Start with 3:1 molar ratio of steam to methane being fed to the reformer, which is assumed to be an isothermal reactor at 800 °C. Assume that the shift reactor inlet temperatures are 400 °C and 220 °C, respectively.

- Find the gas stream composition (mole fractions) exiting the reformer, and determine the heat transfer required to maintain the 800 °C isothermal condition (in kJ per kg of reactants). If the heat required were supplied by burning methane, how much fuel needs to be combusted per unit of fuel supplied to the reformer?
- If the shift reactors are isothermal as well (Fig. 1), find the mole fractions of chemical species leaving the high-temperature (400 °C) and low-temperature (220 °C) reactors, as well as the amounts of heat transfer needed to maintain the isothermal conditions (kJ per kg reactants).

Hint: Your analysis in Part 5 should indicate that at 0.1 MPa, 800 °C, the SMR reaction has destroyed essentially all of the methane supplied. This means that in calculating the gas compositions in Part 6, only the WGS equilibrium needs to be considered.

Deliverables: A MATLAB script named `methaneReformingSystem.m`, which solves for and reports the required compositions and heat transfer terms (use standard `fprintf` commands to format and display your results on the screen).

ANALYSIS REQUIREMENTS AND HINTS

See requirements and hints laid out in Project 1 description.

DELIVERABLES

A formal write-up is not necessary for this assignment. Please turn in a folder containing the MATLAB scripts and functions listed in the assignment.

Your grade will be assigned based on the analysis approach (whether the code makes sense), the numerical results, and its presentation quality (whether the figures are formatted neatly and professionally), as well as the performance of the code when exercised in real time (none of the calculations should take more than a few seconds on a standard-issue laptop).