

"Thermodynamic Analysis of Processes for Hydrogen Generation by Decomposition of Water"

by

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Module 2: Analysis of Single-Unit Processes

Introduction

Module 1 of this series provides the foundation for thermodynamic analysis of processes for energy effects and process constraints. Before evaluating complex systems, experience in more straightforward cases is desirable. The present Module treats systems with a single unit focusing on adiabatic turbines and binary distillation columns. Module 3 shows application of the analysis in an overall perspective to a thermochemical hydrogen process. Module 4 does an analysis of a process involving 2 sections, while Module 5 treats the 3-section Sulfur-Iodine process.

We first repeat essential elements of Module 1. Figure 2.1 illustrates the concept for a steady-flow system, with inlet and outlet streams at specified absolute temperature, pressures, P , and sets of molar or mass amounts for the components, n_i , along with energy that crosses the boundaries as "shaft work", W_s , and heat, Q .

$$\sum_i N_i h_i(T_i, P_i, \mathbf{x}_i) - \sum_i N_o h_o(T_o, P_o, \mathbf{x}_o) - W_s - Q_b = Q \quad (2.1)$$

Analysis of Single-Unit Systems

This Module gives some basic examples of problems that can provide experience in using Eqs. (2.1) and (2.2) as well as quantitative results for N_{gen} , which may not be familiar to learners. It demonstrates a few of the greater variety of situations that can be treated with only a few relations by merely changing specifications. It should be noted that solving the relations can involve different strategies.

Case I Examples Consider an adiabatic turbine that steadily produces work by lowering the pressure on a fluid. We develop the general forms for Eqs. (2.1) and (2.2) and then examine situations of different specifications. The system has single in and out ports, so the molar flows in the streams are the same. There will be a single shaft work mode and no heat effect; thus only cases C, E, and H are relevant. The system with consistent notation is given in Figure 2.2. Eqs. (2.1) and (2.2) then become:

$$N h_i = h_o \quad W_s = Q_e = 0 \quad (2.11)$$

$$N s_i = s_o \quad \frac{Q_e}{T_e} = N s_{gen} = 0 \quad (2.12)$$

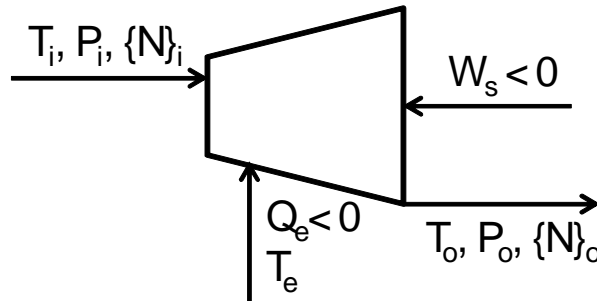


Figure 2.2 Schematic of System for Case I Examples.

For pure nonideal-gas substances, such as steam and refrigerants, tables with values of $h(T, P, \{x\})$ and $s(T, P, \{x\})$ for the inlet and outlet states are usually available. For ideal gases, the fundamental relations are:

$$h_o = h_i^{ig} + \int_{T_i}^{T_o} c_p^{ig} T dT \quad (2.3)$$

$$s_o = s_i^{ig} + \int_{T_i}^{T_o} \frac{c_p^{ig}}{T} dT + R \ln\left(\frac{P_o}{P_i}\right) \quad (2.4)$$

where c_p^{ig} is a constant, polynomial, or other integrable function of T . Use of these relations will affect the form of case E. For multiphase systems

$$h = 1 \quad x^V h^L \quad x^V h^V \quad h^L \quad x^V (h^V - h^L) \quad h^L \quad x^V h^{vap} \quad (2.5)$$

$$s = 1 \quad x^V s^L \quad x^V s^V \quad s^L \quad x^V (s^V - s^L) \quad s^L \quad x^V h^{vap}/T \quad (2.6)$$

where h^L and s^L are the enthalpy and entropy of the saturated liquid, and h^V and s^V are the enthalpy and entropy of the saturated vapor, and h^{VP} is the enthalpy change on vaporization. For this situation, specifying either T or P will determine the values of h^L and s^L and h^V and s^V .

Case I Examples: For the various applicable cases of Table 2.1, the forms to obtain the solution variables are merely rearrangements of Eqs. (2.1) and (2.2). Here we study only cases C and H, though problems for Cases E, F, and G of Table 1.1 of Module 1 are easily formulated. Assuming values for the enthalpy and entropy coefficients can be obtained from a reference or equation of state, the equations for Cases C and H can be solved sequentially.

Numerical Problems for Case I

Case IC For a turbine with the heat rejection and states of all streams fully specified, what are the entropy generated and the work effect?

$$W_s = N(h_o - h_i) - Q_e \quad (2.IC1)$$

$$s_{gen} = N(s_o - s_i) - Q_e/NT_e \quad (2.IC2)$$

For adiabatic, the terms Q_e disappear and so the value of T_e is irrelevant. The desired variables are computed directly.

Table 2.11 gives specific problems for Case IC for both reversible and real systems where the fluid is Helium with $c_p^{ig} T = \frac{5}{2}R = 20.8 \text{ kJ kmol}^{-1}\text{K}^{-1}$, with Problem #1 fully worked out. Table 2.12 gives specific problems for cases using steam, with Problem #1 fully worked out. The effect of s_{gen} on T_o and W_s are shown in Figure 2.1. Note that while most of the input numbers can be rounded, because there are constraints on the sign and W_s , as well as the limitation of adiabatic ($Q_e = 0$), other values are normally not rounded.

Table 2.11 Specific Problems for Case IC with Helium. Eqs. (2.3) and (2.4) used with P_i, T_o, P_o , with $c_p = 0.0208 \text{ MJ kmol}^{-1}\text{K}^{-1}$ to obtain $h_o - h_i$ and $s_o - s_i$. Bold = Specified Italic = Solved.

							$s_o - s_i$	W_s , MJ	s_{gen} , MJ kmol ⁻¹ K ⁻¹
IC.1	800	100	5	342.8	12	9.51	0.000	-47.5	0
IC.2	800	100	5	435.9	12	7.57	0.005		
IC.3	800	100	5	342.8	6.58	9.51	0.005		
IC.4	800	100	5	332.1	1	9.73	0.020		

Case H: For an adiabatic turbine with a fully specified input stream, outlet pressure, and entropy generation, what are the outlet temperature (or quality) and work? Assume tabulated values of h and s are available, such as for steam.

$$s_o = s_i + s_{gen} \quad (2.IH1)$$

$$W_s = N(h_o - h_i) \quad (2.IH2)$$

The desired variable T_o or x_o , is embedded in h_o . This Case can be solved for both reversible ($s_{gen} = 0$) and real ($s_{gen} > 0$) specifications.

Table 2.12 Case IH with steam. Bold = Specified Italic = Solved. $Q_e = 0$. Properties from [10].

Problem #	T_i , K	P_i , bar	h_i , MJ kmol ⁻¹	s_i , MJ kmol ⁻¹ K ⁻¹	N , mol	P_o , bar	s_{gen} , MJ kmol ⁻¹ K ⁻¹	s_o , MJ kmol ⁻¹ K ⁻¹	T_o , K	h_o , MJ kmol ⁻¹	W_s , MJ
IH.1	600	9	56.05	0.131	3	1.2885	0.000	0.131	380	48.39	-23
IH.2	600	9	56.05	0.131	3	0.90	0.000				
IH.3	600	9	56.05	0.131	3	0.90	0.003				
IH.4	600	9	56.05	0.131	3	0.90	0.005				
IH.5	600	9	56.05	0.131	3	0.90	0.01				
IH.6	600	9	56.05	0.131	3	0.90	0.015				
IH.7	600	9	56.05	0.131	3	0.90	0.019				
IH.8	600	9	56.05	0.131	3	0.50	0.017				
IH.9	800	100	62.04	0.033	20	0.90	0.117				

Problem IH.1 solution

$s_o = 0.131 + 0 = 0.131$ For these values of s_o and P_o searching the NIST tables yields

$$T_o = 380 \text{ K and } h_o = 45.39 \text{ MJ kmol}^{-1} \quad (IH.1.1)$$

$$W_s = 3(48.39 - 56.05) = -23 \text{ MJ} \quad (IH.2.1)$$

Problems 2.2 Complete Table 2.12 for problems #IH.2 to #IH.9. Show the variations of outlet temperature and work as a function of entropy generated for problems #IH.2 to #IH.7.

Problems #IH.2 to #IH.7 show entropy generation increases the outlet temperature and decreases the work produced. Problems #IH.7-9 show that **more** work can be obtained even with increased entropy generation, if there is a sufficient increase in T_i (raises h_i and, especially, lowers s_i) or decrease in P_o (raises s_o).

Problem 2.3 Write the relations for Case IE: what are the outlet state and entropy generated for an adiabatic turbine with a fully specified input stream, outlet pressure, and work effect?

Problem 2.4 Write the relations for Case IF: what are the outlet state and required input moles for an adiabatic turbine with specified input and output streams, work, and entropy generated?

Case II Examples Consider a distillation column that steadily puts in high temperature heat and removes low temperature heat, with no work effect. We separate a two-component feed into liquid mixtures dominated by the light component in the distillate and by the heavy component in the bottom product. We develop the general forms for Eqs. (1) and (2) and then examine situations of different specifications and solution variables.

The system has a single in-port (feed) and two out-ports (distillate and bottoms), so the molar flows in the streams must be obtained from a material balance. This system, with consistent notation, is shown in Figure 2.3. The overall material balance relation is:

$$N_f - N_d - N_b = 0 \quad (2.II1)$$

There is also another material balance one of the components that involves the stream compositions. Present analyses will specify the compositions, though this is not necessary.

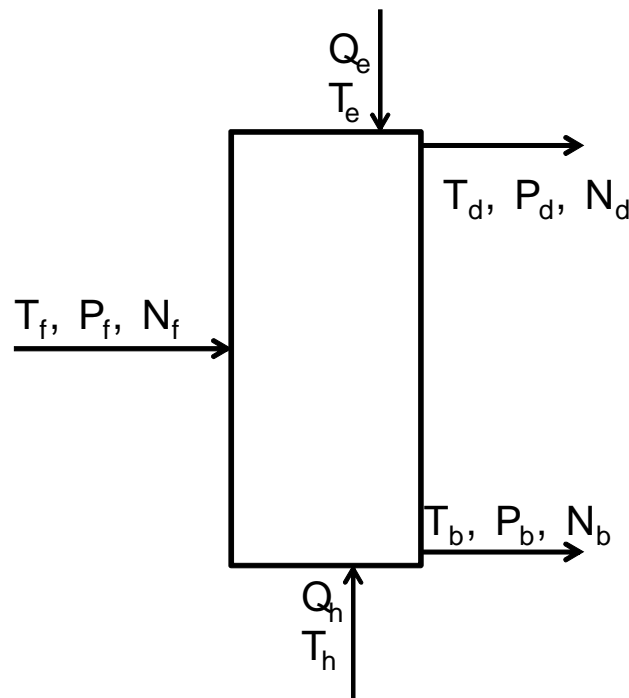


Figure 2.3 Schematic of System for Examples II.

Eqs. (2.1) and (2.2) then become:

$$N \quad (2.II2)$$

Problem #	T _e , K	Q _e , MJ	T _h , K	Q _h , MJ	N _b , kmol	T _b , K	P _b , bar	h _b , MJ kmol ⁻¹	S _b , MJ kmol ⁻¹ K ⁻¹	S _{gen} , MJ kmol ⁻¹ K ⁻¹
IIA.1	300	-15.98	383.8	17.45	1	383	1	-0.137	-0.000357	0.000
IIA.2	300		383.8		1	383	1	-0.137	-0.000357	0.001
IIA.3	300		383.8		1	383	1	-0.137	-0.000357	0.003
IIA.4	300		383.8		1	383	1	-0.137	-0.000357	0.003
IIA.5	300		383.8		1	383	1	-0.137	-0.000357	0.003
IIA.6	300		410		1	383	1	-0.137	-0.000357	0.003
IIA.7	300		400		1	383	1	-0.137	-0.000357	0.003
IIA.8	300		410		1	383	1	-0.137	-0.000357	0.003
IIA.9	300	-11.65	452	3.66	1	451.5	5	13.36	0.003189	0.000
IIA.10	300		383.8		1	383	1	-0.137	-0.000357	0.003
IIA.11	300		383.8		2	383	1	-0.137	-0.000357	0.003

In these problems, the feed properties are computed first from Eqs. (2.II.4).

$$h_f = x_{1f} h_{1f}^0 + (1 - x_{1f}) h_{2f}^0 = 0.5(3.40) + 0.5(1.76) = 0.821 \quad (2.II4a.1)$$

$$s_f = x_{1f} s_{1f}^0 + (1 - x_{1f}) s_{2f}^0 - R[x_1(\ln x_1) + (1 - x_1) \ln(1 - x_1)] \\ = 0.5(0.00907) + 0.5(0.00489) - 0.0[0.5 \ln(0.5) + 0.5 \ln(0.5)] \\ = 0.003671 \quad (2.II4b.1)$$

Then the heats are computed from Eqs. (2.IIA1) and (2.IIA2).

$$Q_e = N_d [(h_d - h_f) + T_h (s_d - s_f)] - N_b [h_b - h_f + T_h (s_b - s_f)] - T_h N_b N_d s_f \quad (2.IIA1.1)$$

Problem 2.6 Plot the effects of s_{gen} on Q_e and Q_h for a set of fixed column specifications.

Case IID For a specified separation and input heat, what is the heat removal and the entropy generated? Only real systems, not reversible, can be evaluated for this case.

$$Q_e = N_d(h_d - h_f) + N_b h_b - h_f \quad Q_h \quad (2.IID1)$$

$$S_{gen} \quad (2.IID2)$$