

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

by

John P. O'Connell

Department of Chemical Engineering

University of Virginia

Charlottesville, VA 22904-4741

A Set of Energy Education Modules for Chemical Engineering

Sponsored by The Center for Energy Initiatives of

The American Institute of Chemical Engineers

Institute for Sustainability

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 any 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 temperatures, T , pressures, P , and sets of molar or mass amounts for the components, $\{N\}$, along with energy that crosses the boundaries as "shaft work", W_s , and heat, Q . Note that if a stream has both vapor and liquid, its specification must include the amounts of components in the phases. For pure components, this means specifying either T or P , the total flow, N , and the quality or fraction of the system that is vapor, x . For mixtures, defining the state is more elaborate. The balance equations for steady flow processes are:

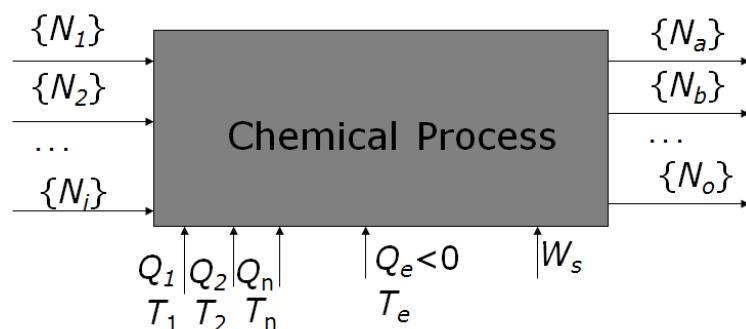


Figure 2.1. Steady Flow System for Applying Material, Energy, and Entropy Relations, Eqs. (2.1) and (2.2).

$$\sum_i N_i h_i(T_i, P_i, \{x\}_i) - \sum_i N_o h_o(T_o, P_o, \{x\}_o) + \sum_s W_s + \sum_b Q_b + Q_e = 0 \quad (2.1)$$

$$\sum_i N_i s_i(T_i, P_i, \{x\}_i) - \sum_i N_o s_o(T_o, P_o, \{x\}_o) + \sum_b \frac{Q_b}{T_b} + \frac{Q_e}{T_e} + S_{gen} = 0 \quad (2.2)$$

Here h is the molar enthalpy, s is the molar entropy, and $\{x\}$ is the set of component mole fractions found from the set of numbers of moles of components, $\{N\}$, in a stream. Kinetic and potential energy differences in the flowing streams have been ignored in Eq. (2.1). The summation \sum_i is over all input streams, i , and the summation \sum_o is over all output streams, o . Consequently, all molar flow numbers, $\{N\}_i$ and $\{N\}_o$, are positive. The summations \sum_s and \sum_b are for the work and heat effects, respectively, associated with external utilities. The species amounts, $\{N\}_i$ and $\{N\}_o$ are related by mass conservation; moles are conserved only in nonreacting systems.

These two relations express the conservation of energy among the forms generally treated in chemical processes, Eq. (2.1), and the balance of entropy, Eq. (2.2), which has entropy conservation for reversible cases ($s_{gen\ rev} = 0$) and positive entropy generation ($s_{gen} > 0$) in real systems. The heat effects, $\{Q_b\}$ and Q_e , are defined to be positive when heat is put in; they cross the outside of the system boundary (surroundings) at temperatures T_b and T_e . A reversible process gives the absolute upper limit, the best case, of the efficiency of energy usage. That is, when $s_{gen} = 0$, the solution to Eqs. (2.1) and (2.2) will give the minimum input shaft work, high-temperature heat, or energy-carrying material, to accomplish a process that does not occur spontaneously.

The two energy/entropy relations force two unknown quantities to be found from the known variable values, while giving consistency among molar flows for all chemical reactions occurring. Thus, many different cases can be set up; Table 2.1 illustrates a few of these relevant to this Module. Others are given in Table 1.1 of Module 1.

Table 2.1 Options for Specifications and Solution Variables for Eqs. (2.1) and (2.2).

Case	Specifications	Solution Variables
C	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}^*, \{Q_b\}, \{T_b\}, T_e, Q_e$	W_{sn}, s_{gen}
D	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}, \{Q_b\}, \{T_b\}, T_e$	Q_e, s_{gen}
E	$T_i, P_i, \{N\}_i, P_o, \{N\}_o, \{W_s\}, \{Q_b\}, \{T_b\}, T_e, Q_e$	T_o, s_{gen}
F	$T_i, P_i, \{N\}_i^*, P_o, \{N\}_o, \{W_s\}, \{Q_b\}, \{T_b\}, T_e, Q_e, s_{gen}$	T_o, N_{in}
H	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}^*, \{Q_b\}, \{T_b\}, T_e, Q_e, s_{gen}$	T_o, W_{sn}

* Includes all elements of set except $_n$ which is solved for

Note again that 2-phase systems require a specification of the relative amounts of the phases, such as by the quality, x^v , in a pure component system.

Some generalizations about effects of changing specified variables can be made for closed and for single-unit open systems. For example, we can state the consequences of $s_{gen} > 0$, *i.e.*, of putting in irreversibilities while keeping the same flow conditions. For work-absorbing devices, such as heat pumps, Eq. (2.2) shows entropy generation means more heat must be removed ($Q_{e\ real} < Q_{e\ rev} < 0$), so Eq. (2.1) gives more work input ($W_{s\ real} > W_{s\ rev} > 0$). For devices that produce work, such as heat engines, real systems yield less work ($W_{s\ rev} < W_{s\ real} < 0$) and less heat is put in ($0 < \sum Q_{b\ real} < \sum Q_{b\ rev}$).

Analysis of Single-Unit Systems

This Module gives some basic examples and problems that can provide experience in using Eqs. (2.1) and (2.2) as well as quantitative results for s_{gen} , which may not be familiar to learners. It demonstrates a few of the great 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 only 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:

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

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

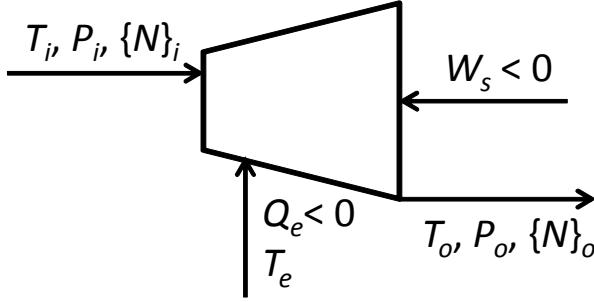


Figure 2.2 Schematic of System for Case I Examples.

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:

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

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

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

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

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

where h^L and s^L are the enthalpy and entropy of the saturated liquid, h^V and s^V are the enthalpy and entropy of the saturated vapor, and Δh^{vap} 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 differences 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?

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

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

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

Table 2.I1 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.I2 gives specific problems for cases IH 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 signs of s_{gen} and W_s , as well as the limitation of adiabatic ($Q_e = 0$), other values are normally not rounded.

Table 2.I1 Specific Problems for Case IC with Helium. Eqs. (2.3) and (2.4) used with T_i , 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.**

Problem #	T_i , K	P_i , bar	N , kmol	T_o , K	P_o , bar	$h_o - h_i$, MJ kmol $^{-1}$	$s_o - s_i$ MJ kmol $^{-1}$ K $^{-1}$	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		

Problem #IC.1 solution. This is the reversible case because of the choice of outlet state.

$$s_{gen} = s_o - s_i = c_p \ln(T_o/T_i) - R \ln(P_o/P_i) = 0.0208 \ln(342.8/800) - 0.008314 \ln(12/100) = 0 \quad (2.IC1.1)$$

$$W_s = N(h_o - h_i) = Nc_p(T_o - T_i) = 5(20.8)(342.8 - 800)/1000 = -47.5 \quad (2.IC2.1)$$

Problems 2.1 Complete Table 2.I1 for problems IC.1 to IC.4.

Problems #IC.2 and #IC.3 show how the results change with outlet state. Problem #IC.4 shows that changing several variables simultaneously can lead to unexpected results (W_s is more negative even as s_{gen} increases, as long as T_o and P_o are lowered enough at the same T_i and P_i).

Case IH: 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^V_o , is embedded in s_o . This Case can be solved for both reversible ($s_{gen} = 0$) and real ($s_{gen} > 0$) specifications.

Table 2.I2 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	<i>0.131</i>	<i>380</i>	<i>48.39</i>	-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

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

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

Problems 2.2 Complete Table 2.I2 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 raises the outlet temperature and decreases the work produced. Problems #IH7-9 show that increased work can be obtained even with increased entropy generation, if there is a sufficient increase in P_i and 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, to 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 for one of the components that involves the stream compositions. Present analyses will specify the compositions, though this is not necessary.

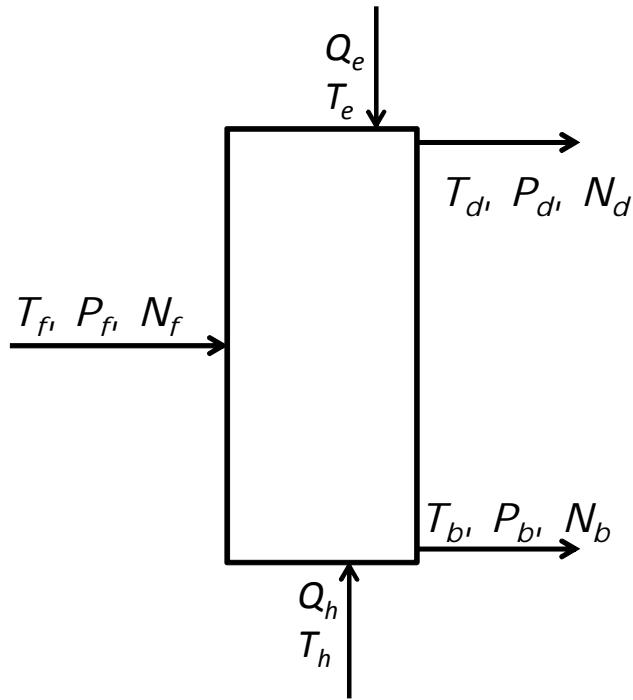


Figure 2.3 Schematic of System for Examples II.

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

$$N_d(h_f - h_d) + N_b(h_f - h_b) + Q_h + Q_e = 0 \quad (2.II2)$$

$$N_d(s_f - s_d) + N_b(s_f - s_b) + \frac{Q_h}{T_h} + \frac{Q_e}{T_e} + (N_d + N_b)s_{gen} = 0 \quad (2.II3)$$

Here, the stream enthalpies and entropies are assumed to be accessible from mixture models.

The only cases of interest among those in Table 1 are Cases A and D, solved by rearranging Eqs. (2.II2) and (2.II3). Case D can be solved sequentially, but Case A involves combining the equations to eliminate the unknown Q_h . The basis for s_{gen} is per kmol of feed.

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).

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

$$\begin{aligned} s_f &= x_{1f}s_{1f}^0 + (1 - x_{1f})s_{2f}^0 - R[x_1(\ln x_1) + (1 - x_1)\ln(1 - x_1)] \\ &= 0.5(-0.00907) + 0.5(-0.00489) - 0.0 - 0.008314[0.5 \ln(0.5) + 0.5 \ln(0.5)] \\ &= 0.003671 \end{aligned} \quad (2.II4b.1)$$

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

$$\begin{aligned} Q_e &= \frac{N_d[(h_d - h_f) - T_h(s_d - s_f)] + N_b[(h_b - h_f) - T_h(s_b - s_f)] + T_h(N_b + N_d)s_{gen}}{(1 - T_h/T_e)} \\ &= \frac{1[(-0.0346 - (-0.821)) - 383(-0.000098 - 0.003671)]}{(1 - 383/300)} \\ &\quad + \frac{+1[(-0.137 - (-0.821)) - 383(-0.000357 - 0.003671)] + 383(1 + 1)0}{(1 - 383/300)} \\ &= -15.98 \text{ MJ} \end{aligned} \quad (2.IIA1.1)$$

$$Q_h = 1[-0.0346 - (-0.821)] + 1[-0.137 - (-0.821)] - (-15.98) = 17.45 \text{ MJ} \quad (2.IIA2.1)$$

Problem IIA.9 is solved similarly. Note that the heat rejected in this case is not much less than for IIA.1, but the heat in is much lower because the significantly higher enthalpy of the feed brings in energy with the material, not by heat transfer.

Since the separation is considered complete, there is very little difference between the input and output heats because the inlet and outlet stream enthalpies are nearly equal. Problem IIA.7 is evaluated similarly. The increase in pressure leads to a higher temperature and thus, different heat effects.

Problem 2.5 Complete Table 2.II1 for problems #II.3 - #II.6 and #II.8 - #II.9.

Problems # IIA1-3 show effects on the heat input and output from different entropy generation and #IIA.4-6 and #IIA.8-9 show effects of different inlet and outlet state conditions. Problem #IIA.7 shows that for a high energy feed, the distillate must be cooled and the reboiler heat is significantly reduced.

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.

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

$$s_{gen} = \left[N_d(s_d - s_f) + N_b(s_b - s_f) - \frac{Q_h}{T_h} - \frac{Q_e}{T_e} \right] / (N_d + N_b) \quad (2.IID2)$$

Table 2.II2 Specific Problems for Case IID. **Bold** = Specified; *Italic* = Solved. Properties from Table 2.II.1.

Problem #	T_f , K	P_f , bar	h_f , MJ kmol $^{-1}$	s_f , MJ kmol $^{-1}$ K $^{-1}$	N_d , kmol	T_d , K	P_d , bar	h_d , MJ kmol $^{-1}$	s_d , MJ kmol $^{-1}$ K $^{-1}$	
IID.1	365	1	-0.82	0.00367	1	353	1	-0.0346	-0.000098	
IID.2	365	1	-0.82	0.00367	1	353	1	-0.0346	-0.000098	
IID.3	365	1	-0.82	0.00367	1	353	1	-0.0346	-0.000098	
IID.4	365	1	-0.82	0.00367	1	353	1	-0.0346	-0.000098	
IID.5	430.5	5	10.66	0.03127	1	353	1	-0.0346	-0.000098	
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 $^{-1}$
IID.1	300	-18.53	383.8	20	1	383	1	-0.137	-0.000357	0.00049
IID.2	300		383.8	25	1	383	1	-0.137	-0.000357	
IID.3	300		383.8	30	1	383	1	-0.137	-0.000357	
IID.4	300		383.8	35	1	383	1	-0.137	-0.000357	
IID.5	300	-27.99	452	20	1	451.5	5	13.360	0.031890	0.00872

For Problem #IID.1, Eqs. (IID.1) and (IID.2) become

$$Q_e = 1[-0.0346 - (-0.82)] + 1[-0.137 - (-0.82)] - 20 = -18.53 \quad (2.IID1.1)$$

$$s_{gen} = \frac{[1(-0.0000978 - 0.00367) + 1(-0.000357 - 0.00367) - (\frac{20}{384} - \frac{-18.53}{300})]}{(1 + 1)} \quad (2.IID2.1)$$

$$= 0.00047$$

In this problem, there is very little entropy generated because the temperatures are close. Problem IID.5 is evaluated similarly; the column pressure (the feed and bottoms) lead to a significantly higher reboiler temperature and thus to higher entropy generation.

Problems 2.7 Complete Table 2.II2 for problems #IID.2 - #IID.4.

Reference

[10] Lemmon, E.W., McLinden, M.O., Friend, D.G., "Thermophysical Properties of Fluid Systems" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, (retrieved July 12, 2011).