**"Thermodynamic Analysis of Processes for Hydrogen Generation
by Decomposition of Water"
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Module 4: A Simplified Multisection Process for Thermochemical Hydrogen

Introduction

Module 1 of this series provides the foundation for thermodynamic analysis of processes for energy effects and process constraints. Module 2 provides experience with single-unit processes. Module 3 treats processes for thermochemical decomposition of water for hydrogen manufacture from an overall point of view. The present Module does an analysis of a water decomposition process involving 2 sections that exchange methane and methanol as well as heat. The objective is to gain experience in treating recycles and multiple sections involving reactions that can then be built on in Module 5 that analyzes the 3-section Sulfur-Iodine process.

We first repeat essential elements of Module 1. Figure 4.1 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:
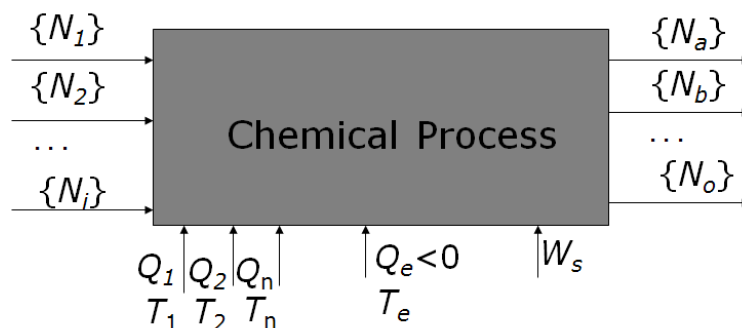

Figure 4.1. Steady Flow System for Applying Material, Energy, and Entropy Relations, Eqs. (4.1) and (4.2).

$$\sum_i N_i h_i(T_i, P_i, \{x\}_i) - \sum_i N_o h_o(T_o, P_o, \{x\}_o) + \sum_s W_s + \sum_b Q_b + Q_e = 0 \qquad (4.1)$$

$$\sum_i N_i s_i(T_i, P_i, \{x\}_i) - \sum_i N_o s_o(T_o, P_o, \{x\}_o) + \sum_b \frac{Q_b}{T_b} + \frac{Q_e}{T_e} + S_{gen} = 0 \qquad (4.2)$$

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. (4.1). 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. (4.1), and the balance of entropy, Eq. (4.2), 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. (4.1) and (4.2) 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 4.1 illustrates the Case to be explored here.

Table 4.1 Option for Specifications and Solution Variables for Eqs. (4.1) and (4.2) of Module 4.

Case	Specifications	Solution Variables
J	$\{T_i\}, \{P_i\}, \{N\}_{i,}^*, \{T_o\}, \{P_o\}, \{N\}_o, \{W_s\}^*, \{Q_b\}, \{T_b\}, T_e, s_{gen}$	Q_e, N_{in}
* Includes all elements of set except $_n$ which is solved for		

Case IV Example.

The Schulten Process, which was investigated for some years before being abandoned because of cost, involves partial oxidation of methane by water to form methanol and product hydrogen in one section, and then regenerating the methane and producing oxygen in a second Section [11]. Figure 4.2 shows a simplified flow diagram and establishes the nomenclature. Note that more chemistry is done in Section 2 than is shown, but that aspect is not needed for the present analysis. The energy necessary for the process is provided by hot Helium entering both Sections, but heat is rejected from only Section 1 because heat is transferred between the Sections to avoid heat rejection from Section 2.

Completing an energy/entropy analysis of this process involves applying Eqs. (4.1) and (4.2) to both sections and using the material and heat transfers that connect the sections. This is the new element of analyzing multisection systems compared to the above treatments. Note that it is assumed that the streams exchanged between the Sections are pure, which means that any reactor recycle and separation devices are within the Section boundaries, while stoichiometry of

the reactions in the sections connects the flows of these streams. This is not a necessary assumption, but significantly simplifies the analysis.

> *Problem 4.1* Comment on how realistic is the assumption of pure streams. If it is unrealistic, what changes should be made to Eqs. (4.IV1) - (4.IV.4)?

The characterization of Section 1 involves the equations of Case J. The basis chosen is 1 kmol of hydrogen produced. For this idealized process, the mass balances yield relations for the moles of the species: $N_H = 1 = N_W = N_M = N_A = 2N_O$. Further, the streams are all pure, so composition is not relevant.

$$N_H(h_W + h_M - h_H - h_A) + N_1(h_{1i} - h_{1o}) + Q_{21} + Q_e = 0 \qquad (4.\text{IV}1)$$

$$N_H(s_W + s_M - s_H - s_A) + N_1(s_{1i} - s_{1o}) + \frac{Q_{21}}{T_{21}} + \frac{Q_e}{T_e} + N_H s_{gen1} = 0 \qquad (4.\text{IV}2)$$

The analysis of Section 2 is similar.

$$N_H(h_A - 0.5h_O - h_M) + N_2(h_{2i} - h_{2o}) - Q_{21} = 0 \qquad (4.\text{IV}3)$$

$$N_H(s_A - 0.5s_O - s_M) + N_2(s_{2i} - s_{2o}) - \frac{Q_{21}}{T_{21}} + N_H s_{gen2} = 0 \qquad (4.\text{IV}4)$$

Note that the sign on Q_{21} in Eqs. (4.IV3) and (4.IV4) must be negative to be consistent with Eqs. (4.IV1) and (4.IV2). Helium can be considered an ideal gas under these conditions, so its enthalpy and entropy differences can be computed with Eqs. (4.3) and (4.4).

$$(h_o - h_i)^{ig} = \int_{T_i}^{T_o} c_p^{ig}(T)dT \qquad (4.3)$$

$$(s_o - s_i)^{ig} = \int_{T_i}^{T_o} \frac{c_p^{ig}(T)}{T}dT - R\ln\left(\frac{P_o}{P_i}\right) \qquad (4.4)$$

where $c_p^{ig}(T)$ is a constant, polynomial, or other integrable function of T.

Table 4.1 lists all the 26 variables of Eqs. (4.IV1) - (4.IV4), of which 22 can be independent and 4 can be solved for. Typically, the solution variables are N_1, N_2, Q_e, and Q_{21}.

Table 4.1 Variables of Case IV Examples.

Process Stream Variables	$T_W, P_W, T_H, P_H, T_A, P_A, T_M, P_M, T_O, P_O, N_1, N_2$
Helium Stream Variables	$T_{1i}, P_{1i}, T_{1o}, P_{1o}, T_{2i}, P_{2i}, T_{2o}, P_{2o}$
Heat and Entropy Variables	$Q_{21}, T_{21}, Q_e, T_e, s_{gen1}, s_{gen2}$

The strategy of solving the relations is the same as Case IIIJ of Module 3. First combine Eqs. (4.3) and (4.4) to eliminate Q_{21} and find N_2, then solve (4.3) for Q_{21}. Follow this by combining Eqs. (4.1) and (4.2) to eliminate Q_e and find N_1, then solve (4.1) for Q_e. For this procedure, Eqs. (4IV.1) to (4IV.4) become:
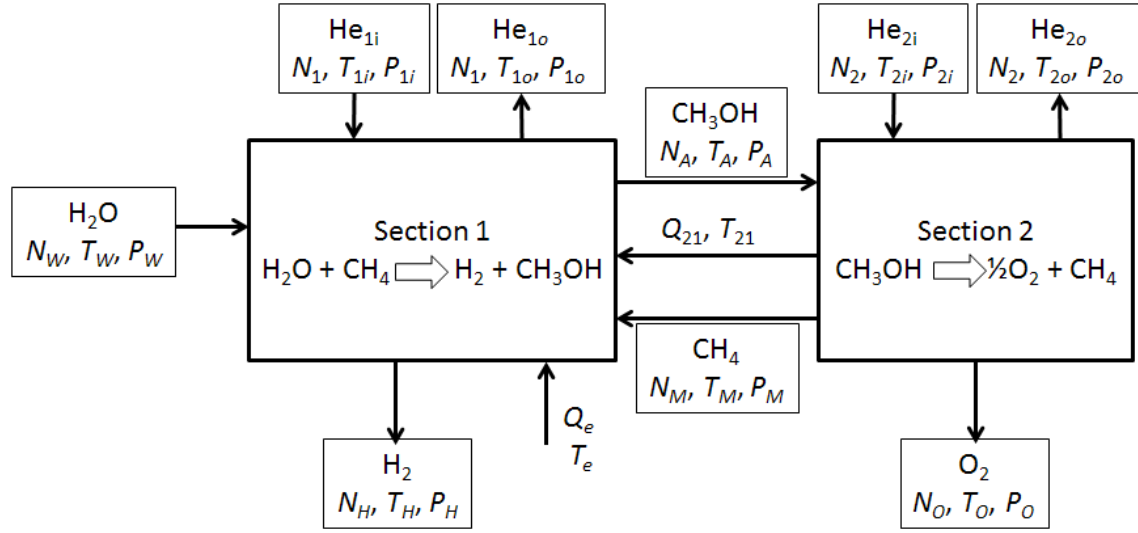
Figure IV.1. Simplified Schematic Diagram of Schulten Process for Thermochemical Decomposition of Water to Manufacture Hydrogen. Subscripts for species are A = Methanol, H = Hydrogen, M = Methane, O = Oxygen, W = Water. Subscripts for Helium streams are $1i$ = input to Section 1, $1o$ = output from Section 1, $2i$ = input to Section 2, $2o$ = output from Section 2; other subscripts are e = environmental; 21 = from Section 2 to Section 1.

$$N_2 = \frac{[N_A(h_A - T_{21}s_A) - N_M(h_M - T_{21}s_M) - N_O(h_O - T_{21}s_O)] - T_{21}N_W s_{gen2}}{c_p^{ig}(T_{o2} - T_{i2}) - T_{21}c_p^{ig}\ln(T_{o2}/T_{i2})} \qquad (IVJ.4)$$

$$Q_{21} = (N_A h_A - N_M h_M - N_O h_O) + N_2 c_p^{ig}(T_{i2} - T_{o2}) \qquad (IVJ.3)$$

$$N_1 = \frac{[N_M(h_M - T_e s_M) + N_W(h_W - T_e s_W) - N_H(h_H - T_e s_H) - N_A(h_A - T_e s_A)] + Q_{21}(1 - T_e/T_{21}) - T_e N_W s_{gen1}}{c_p^{ig}(T_{o1} - T_{i1}) - T_e c_p^{ig}\ln(T_{o1}/T_{i1})} \qquad (IVJ.2)$$

$$Q_e = -(N_M h_M + N_W h_W - N_H h_H - N_A h_A) - Q_{21} - N_1 c_p^{ig}(T_{i1} - T_{o1}) \qquad (IVJ.1)$$

The problems below illustrate the results for varying degrees of irreversibility via values of s_{gen1} and s_{gen2}. Alternative problems include specification of stream conditions, which may include mixtures passing between systems, and solving for s_{gen1}, s_{gen2}, Q_e, and Q_{12}.

Numerical Problems for Case IV.
    The properties for the species chosen for this case are given in Table 4.2.

Table 4.2 Properties for Components in Water Decomposition via the Schulten process [10, 11].
Bold = **Specified**; *Italic* = *Solved.* Properties for W, H, and O are the same as in Table 3.2.

Species	N, kmol	T, K	P, MPa	h, MJ kmol^{-1}	s, MJ kmol^{-1} K^{-1}
H$_2$O (W)	**1**	**275.00 (l)**	**0.4**	**-287.20**	**-0.1690**
H$_2$ (H)	**1**	**386.15 (g)**	**4.0**	**-7.32**	**-0.0230**
O$_2$ (O)	**0.5**	**346.57 (g)**	**0.4**	**-25.99**	**-0.0070**
CH$_4$ (M)	**1**	**491*(g)**	**2.8**	**22.26**	**0.0992**
CH$_4$O (A)	**1**	**620* (g)**	**10.6**	**49.03**	**0.0993**

*Temperature not given in [11]; estimated. Values of h and s from [10].

Table 4.3 shows problem specifications for decomposing water by the Schulten process, with the streams and properties of Table IV.2 and $T_e = 313K$, and $T_{21} = 491$ K.

Table 4.3 Specific Problems for Case IIIJ. **Bold** = **Specified**; *Italic* = *Solved.* The Helium states are set at $T_{i1} = T_{i2} = 1100K$, $T_{o1} = T_{o2} = 800K$, and $P_{i1} = P_{i2} = P_{o1} = P_{o2} = 68$ **bar** along with $c_p^{ig}(T) = \frac{5}{2}R = 0.0208$ MJ kmol^{-1} K^{-1}

Problem #	s_{gen1}, MJ kmol^{-1} K^{-1}	s_{gen2}, MJ kmol^{-1} K^{-1}	N_1, kmol	N_2, kmol	Q_{21}, MJ	Q_e, MJ
IV.1	**0.0**	**0.0**	*66.1*	*-12.7*	*-39.5*	*-66.0*
IV.2	**0.5**	**0.5**				
IV.3	**1.0**	**1.0**				
IV.4	**0.5**	**1.0**				
IV.5	**1.0**	**0.5**				

For Problem IV.1, Eqs. (IVJ.1) - (IVJ.4) become:

$$N_2 = \frac{1[49.03-491(0.09934)]-1[22.26-491(0.09918)-0.5[-25.99-491(-0.007)]-491(1)0}{0.0208(800-1100)-491(0.0208)\ln(800/1100)} = -12.7 \quad \text{(IV.J4.1)}$$

$$Q_{21} = 1(49.23) - 1(22.26) - 0.5(-25.99) + (-12.7)(0.0208)(1100 - 800) = -39.5 \quad \text{(IV.J3.1)}$$

$$N_1 = \frac{1[22.26-313(0.09918)]+1[-287.2-313(-0.169)]-1[-7.32-313(-0.023)-1(49.03-313(0.09934))]+126(1-313/491)-313(1)0}{20.8(800-1100)-313(20.8)\ln(800/1100)} = 66.1 \quad \text{(IV.J2.1)}$$

$$Q_e = -[1(22.26) + 1(-287.2) - 1(-25.99) - 1(49.03) - 126 - (-12.7)(20.8)(1100 - 800) = 66.0 \quad \text{(IV.J1.1)}$$

Note that the Helium flow into Section 2 is negative. This is unphysical, but is a result of assuming a reversible process with the given stream conditions. Negative Helium flow does not occur for processes with irreversibilities.

Problems 4.2 Complete Table 4.3 for problems #IV.2 - #IV-5.

Note that both the heat effects and the Helium requirements increase with irreversibility, and the amounts for each section, as well as the heat exchanged between sections, depend on the entropy generated in the sections, while the heat rejection and total Helium flow depend only on the total entropy generated.

Problem 4.3 Verify that the total Helium flows and heats rejected in Problems #4.1 - #4.5 are consistent with the overall analyses of Problems #III.1 - III.5 of Module 3.

References
[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).
[11] Funk, J.E., Eisermann, W., "An Exergetic/Energetic/Economic Analysis of Three Hydrogen Production Processes: Electrolysis, Hybrid, and Thermochemical," Alternative Energy Sources: Proceedings of the Miami International Congress on Energy and the Environment, 1982, 8, 3285-3320.