

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

by

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A Set of Energy Education Modules for Chemical Engineering
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Module 3: The Whole-Process Perspective 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. The present Module treats processes for the thermochemical decomposition of water for hydrogen manufacture from an overall point of view. Module 4 does an analysis of a water decomposition process involving 2 sections that exchange methane and methanol as well as heat, while Module 5 treats the 3-section Sulfur-Iodine process.

We first repeat essential elements of Module 1. Figure 3.1 illustrates the concept for a steady-flow system, with inlet and outlet streams at specified absolute temperature, pressure, 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 3.1. Steady Flow System for Applying Material, Energy, and Entropy Relations, Eqs. (3.1) and (3.2).

$$\sum_i N_i h_i(T_i, P_i, x_i) - \sum_i N_o h_o(T_o, P_o, x_o) - \sum_s W_s - \sum_b Q_b - Q_e = 0 \quad (3.1)$$

$$\sum_i N_i s_i(T_i, P_i, x_i) - \sum_i N_o s_o(T_o, P_o, x_o) - \sum_b \frac{Q_b}{T_b} \quad (3.2)$$

Overall Analysis of Thermochemical Hydrogen Systems

The evaluations of Modules 1 and 2 give the fundamentals and illustrate application of the energy/entropy analysis to single-unit systems. This Module begins the treatment of systems for thermochemical decomposition of water to manufacture Hydrogen. Input high-temperature energy can be from either a nuclear reactor or a solar collector. The specific mechanism can be either as heat or by cooling a high pressure gas, which has an input and an output stream.

The first examples of Case III are those of Narkprasert [5] who applied Eqs. (3.1) and (3.2) to the whole process of H_2O feed, H_2 and O_2 products, with energy from direct heating or from cooling high pressure Helium, and with heat rejection to the environment. The energy requirements vary with inlet and outlet conditions and entropy generation.

Case III Examples. Consider a process to decompose water to make Hydrogen and Oxygen using high temperature heat with no work effect. Figure 3.1 illustrates the system.

Figure 3.1. Overall Schematic of Process to Thermochemically Decompose Water.

Problem 3.1 Comment on the similarities and differences of Case III with Case II of Module 2.

Eqs. (3.1) and (3.2) become:

$$(N_W h_W \quad N_H h_H \quad N_O h_O) \quad Q_h \quad Q_e \quad 0 \quad (3III.1)$$

$$(N_W s_W \quad N_H s_H \quad N_O s_O) \quad \frac{Q_h}{T_h} \quad \frac{Q_e}{T_e} \quad N_H s_{gen} \quad 0 \quad (3III.2)$$

The basis for s_{gen} is per kmol of Hydrogen produced. If a chemical reaction involved, the analysis of the enthalpy and entropy differences becomes more complex.

Typically, the information about property changes for reactions is compiled in Gibbs energy and enthalpy changes of formation of the species in a standard state, with the values of these standard state properties for the atomic (atomic gas) elements set to zero. Thus, Table

3.1 gives the thermodynamic properties of formation from 1 mole of H₂ and 1/2 mol of O₂ for all species as pure ideal gases and for water as a pure liquid at T = 298.15 K and

respectively, and T the temperature of the stream. The reaction changes of a property, where $F = H, G, \text{ or } S$, are given by $F_r^0 = \sum_i \nu_i F_i^0$.

If the thermodynamic properties can be obtained from tables or computation, such as in flowsheeting software like Aspen, the complexities of standard state and correcting for temperature and pressure effects are computed in the background, so these equations become

$$\frac{Q_h}{T_h} = \frac{Q_e}{T_e} + N_H h_H + N_O h_O + N_W h_W \quad (3.8)$$

$$\frac{Q_h}{T_h} = \frac{Q_e}{T_e} + N_H s_{\text{gen}} + N_H s_H + N_O s_O + N_W s_W \quad (3.9)$$

Having this information available will be assumed here.

Problem 3.2A real process will involve compressors and other work machines. Why is there not an explicit term W_s in the above relations?

It is common in energy scenario calculations to obtain an efficiency which is the ratio of the amount of energy, actually enthalpy, obtained from a process to the amount of enthalpy put in. This can be complicated when the energy involves complex reactions, but for water to hydrogen to water, the ratio is merely the standard enthalpy of hydrogen oxidation to water, divided by the heat put into the process. Thus thermal efficiency for this process is

$$H_r^0 / Q_h = 285.8 / Q_h \quad (3.10)$$

where Q_h is in MJ kmol⁻¹.

Numerical Problems for Case B

The properties for the species chosen for this case are given in Table 3.2. Here we will consider Cases A, D, and J.

Table 3.2 Properties for Water Decomposition **Bold = Specified** *Italic = Solved*.

Species	N, kmol	T, K	P, MPa	h^* , MJ kmol ⁻¹	s^* , MJ kmol ⁻¹ K ⁻¹
H ₂ O (W)	1	275.00 <i>(l)</i>	0.4	-287.2	-0.169
H ₂ (H)	1	386.15 <i>(g)</i>	4.0	-7.32	-0.023
O ₂ (O)	0.5	346.57 <i>(g)</i>	0.4	-25.99	-0.007

*Reference [5]. The reference states for $h^0, s = 0$ here are different from Table III.1.

Case IIIA For a specified separation and entropy generation, what are the heat effects? Both real and reversible systems can be evaluated for this case.

Eqs. (3.7) and (3.8) can be combined and rearranged to find the desired variables, as for Eqs. (2.IIA1) and (2.IIA2) of Module 2:

$$Q_e = \frac{N_H(h_H - T_h s_H) + N_O h_O + T_h s_O + N_W h_W + T_h s_W - T_h N_H s_{\text{gen}}}{1 - T_h/T_e} \quad (3.IIIA1)$$

$$Q_h = \dots \quad (3.IIIA2)$$

Table 3.3 gives problems to evaluate heat effects when efficiencies from different values.

Table 3.3 Specific Problems for Case IIIA. **Bold = Specified Italic = Solved.** The temperatures for the heat exchanges are set at $T_e = 313\text{K}$ and $T_h = 942\text{K}$

Problem #	S_{gen} MJ kmol ⁻¹ K ⁻¹	Q_h , MJ	Q_e , MJ
IIIA.1	0.00	333	-66
IIIA.2	0.25		
IIIA.3	0.50		
IIIA.4	0.75		

For Problem IIIA.1, Eqs. (3.IIIA1) and (3.IIIA2) become

$$Q_e = \frac{1 \cdot 7.32 \cdot 942 + 0.0023 \cdot 0.5 \cdot 25.99 \cdot 942 + 0.0007 \cdot 1 \cdot 287.2 \cdot 942 + 0.169 \cdot 1 \cdot 0}{1 \cdot 942/313} = -66 \quad (3.IIIA1.1)$$

$$Q_h = 1 \cdot 7.32 + 0.5 \cdot 25.99 + 1 \cdot 287.2 + 66 + 333 \quad (3.IIIA2.1)$$

Problems 3.3 Complete Table 3.3 for problems #IIIA.2 - #IIIA.4. Plot the heat effects as a function of S_{gen} .

The solutions to Problems IIIA.1- IIIA.4 show that as S_{gen} is increased, the heat input and output both increase in magnitude, demonstrating that irreversibilities cause more energy to be required for a process, with the extra energy being rejected to the environment. The results are linear in S_{gen} .

Table 3.4 gives problems to evaluate efficiencies from different Helium conditions.

Table 3.4 Specific Problems for Efficiencies from Case IIIA with Varying Heat Exchange Temperatures. **Bold = Specified Italic = Solved.**

Problem #	S_{gen} MJ kmol ⁻¹ K ⁻¹	$T_h = 942\text{K}$ $T_e = 313\text{K}$	$T_h = 1000\text{K}$ $T_e = 313\text{K}$	$T_h = 942\text{K}$ $T_e = 300\text{K}$	$T_h = 1000\text{K}$ $T_e = 300\text{K}$
IIIA.5	0	86%	88%	87%	89%
IIIA.6	0.25				
IIIA.7	0.5				
IIIA.8	0.75				

For Problem IIIA.5, Eq. (3.10) becomes

$$285.8/333100 = 86\% \quad (3.IIIA4.1)$$

Input to these problems comes from the solutions to Problems IIIA.1 - IIA.4 and similar ones.

Problems 3.4 Complete Table 3.4 for problems #IIIA.6 - #IIIA.8. Comment on the effects of changing Helium conditions.

Case IID For a specified separation and input heat, what is the heat removal and the entropy

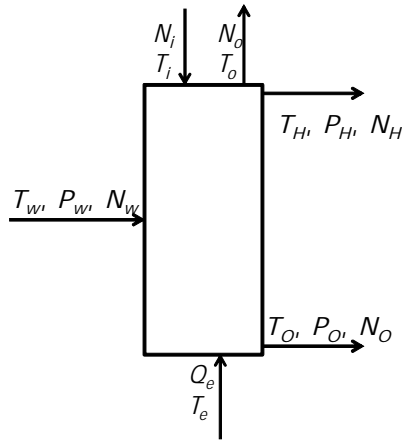


Figure 3.2. Schematic for Thermochemical Decomposition with Energy Supplied By