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

by

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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 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 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:
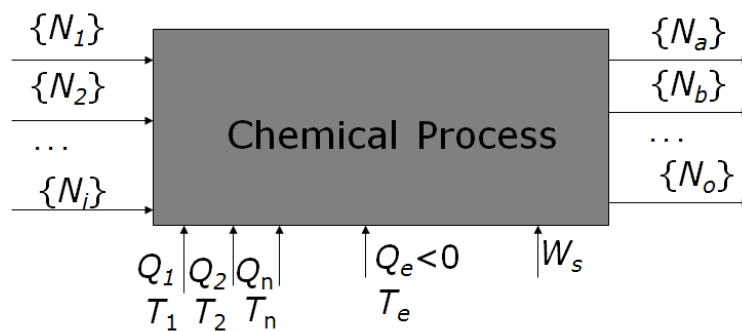

Figure 3.1. Steady Flow System for Applying Material, Energy, and Entropy Relations, Eqs. (3.1) and (3.2).

$$\sum_i N_i h_i(T_i, P_i, \{x\}_i) - \sum_i N_o h_o(T_o, P_o, \{x\}_o) + \sum_s W_s + \sum_b Q_b + Q_e = 0 \qquad (3.1)$$

$$\sum_i N_i s_i(T_i, P_i, \{x\}_i) - \sum_i N_o s_o(T_o, P_o, \{x\}_o) + \sum_b \frac{Q_b}{T_b} + \frac{Q_e}{T_e} + S_{gen} = 0 \qquad (3.2)$$

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. (3.1). 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. (3.1), and the balance of entropy, Eq. (3.2), 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. (3.1) and (3.2) 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 3.1 illustrates a few of these. Others are given in Table 1.1 of Module 1.

Table 3.1 Options for Specifications and Solution Variables for Eqs. (3.1) and (3.2).

Case	Specifications	Solution Variables
A	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}, \{Q_b\}^*, \{T_b\}, T_e, s_{gen}$	Q_e, Q_{bn}
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}
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		

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. (3.2) shows entropy generation means more heat must be removed ($Q_{e\ real} < Q_{e\ rev} < 0$), so Eq. (3.1) 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 ($0 < \Sigma Q_{b\ real} < \Sigma Q_{b\ rev}$).

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 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.
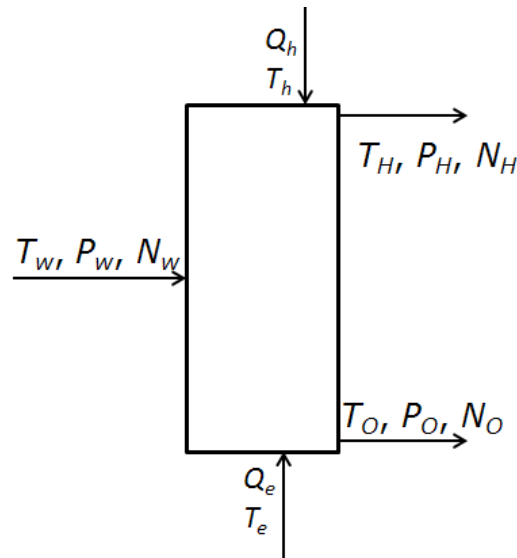

Figure 3.1. Overall Schematic of Process to Thermochemically Decompose Water.

    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:

$$(N_W h_W - N_H h_H - N_O h_O) + Q_h + Q_e = 0 \qquad (3\text{III}.1)$$

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

The basis for s_{gen} is per kmol of Hydrogen produced. With 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 (or diatomic gas) elements set to zero. Thus, Table

3.1 gives the thermodynamic properties of forming H_2O from 1 mole of H_2 and 1/2 mol of O_2 for all species as pure ideal gases and for water as a pure liquid at $T^0 = 298.15$ K and $P^0 = 1$ bar [10]. These properties satisfy the relation $\Delta G_f^0 = \Delta H_f^0 - T^0 \Delta S_f^0$. The estimation of energy efficiencies for Hydrogen manufacture depend on whether the water is gas or liquid; the enthalpy for the former is known as the "lower heating value" whereas the latter is the "higher heating value".

Table 3.1 Standard State Properties of Formation of Water at $T = 298.15$ K and $P^0 = 1$ bar.

Water Phase	ΔH_{Wf}^0, MJ kmol^{-1}	ΔG_{Wf}^0, MJ kmol^{-1}	ΔS_{Wf}^0, MJ kmol^{-1}K^{-1}
Gas	-241.83	-298.13	0.18884
Liquid	-285.83	-306.69	0.06995

The property values for Eqs (3.1) and (3.2) are obtained by adding the effects of changing the species from their standard states to the conditions of the process streams.

The species of a process to be analyzed are not normally ideal gases. In the absence of tabulated information such as steam tables, the effect of nonideality may be taken into account by residual properties, h^r and s^r computed from an equation of state suitable for the species. One set of formal relations for residual properties is:

$$h^r(T,P) \equiv h(T,P) - h^{ig}(T,P) = \int_0^P (v - T\tfrac{\partial v}{\partial T}|_P)dP \tag{3.3}$$

$$s^r(T,P) \equiv s(T,P) - s^{ig}(T,P) = \int_0^P (\tfrac{R}{P} - \tfrac{\partial v}{\partial T}|_P)dP \tag{3.4}$$

For the system of Figure 3.1, and using the standard state properties of the formation (not decomposition) reaction and residuals, Eqs. (3.1) and (3.2) become:

$$Q_h + Q_e = (N_H h_H^r + N_O h_O^r - N_W h_W^r) + \tag{3.5}$$
$$\left[N_H(h_H^{ig} - h_H^0) + N_O(h_O^{ig} - h_O^0) - N_W(h_W^{ig} - h_W^0) \right] + N_H \Delta H_r^0$$

$$\frac{Q_h}{T_h} + \frac{Q_e}{T_e} + N_H s_{gen} = (N_H s_H^r + N_O s_O^r - N_W s_W^r) + \tag{3.6}$$
$$\left[N_H(s_H^{ig} - s_H^0) + N_O(s_O^{ig} - s_O^0) - N_W(s_W^{ig} - s_W^0) \right] + N_H \Delta S_r^0$$

where the subscripts are $_H$ for Hydrogen, $_o$ for Oxygen, and $_w$ for water.

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:

$$(h^{ig} - h^0) = \int_{T^0}^T c_P^{ig}(T)dT \tag{3.7a}$$

$$(s^{ig} - s^0) = \int_{T^0}^T \frac{c_P^{ig}(T)}{T}dT - R\ln\left(\tfrac{P}{P^0}\right) \tag{3.7b}$$

Thus, the property differences $(h_H^{ig} - h_H^0)$ and $(s_H^{ig} - s_H^0)$ of Eqs. (3.5) and (3.6) can be found from Eqs. (3.7a) and (3.7b) with T^0 and P^0 the standard state temperature and pressure,

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

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

$$Q_h + Q_e = N_H h_H + N_O h_O - N_W h_W \tag{3.8}$$

$$\frac{Q_h}{T_h} + \frac{Q_e}{T_e} + N_H s_{gen} = N_H s_H + N_O s_O - N_W s_W \tag{3.9}$$

Having this information available will be assumed here.

> *Problem 3.2* A real process will involve compressors and other work machines. Why is there not an explicit term of 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 values involve 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, Q_h. Thus thermal efficiency for this process, η, is

$$\eta \equiv -\Delta H_r^0 / Q_h = 285.8 / Q_h \tag{3.10}$$

where Q_h is in MJ kmol^{-1}.

Numerical Problems for Case III

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** (*l*)	**0.4**	**-287.2**	**-0.169**
H$_2$ (H)	**1**	**386.15** (*g*)	**4.0**	**-7.32**	**-0.023**
O$_2$ (O)	**0.5**	**346.57** (*g*)	**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:

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

$$Q_h = N_H h_H + N_O h_O - N_W h_W - Q_e \tag{3.IIIA2}$$

Table 3.3 gives problems to evaluate heat effects when efficiencies from different s_{gen} values.

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

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

$$Q_e = \frac{1[-7.32-942(-0.0023)]+0.5[-25.99-942(-0.0007)]-1[-287.2-942(-0.169)+1(0)]}{(1-942/313)}$$

$$= \text{-66} \tag{3.IIIA1.1}$$

$$Q_h = 1(-7.32) + 0.5(-25.99) - 1(-287.2) - (-66) = 333 \tag{3.IIIA2.1}$$

> *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}	η T_h = **942** K T_e = **313** K	η T_h = **1000** K T_e = **313** K	η T_h = **942** K T_e = **300** K	η T_h = **1000** K T_e = **300** 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

$$\eta = (285.8/333)100 = 86\% \tag{3.IIIA4.1}$$

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 IIID: 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. Eqs. (3.8) and (3.9) can be combined and rearranged to find the desired variables.

$$Q_e = N_H h_H + N_O h_O - N_W h_W - Q_h \tag{3.IIID1}$$

$$s_{gen} = \left(N_H s_H + N_O s_O - N_W s_W - \frac{Q_h}{T_h} - \frac{Q_e}{T_e}\right)/N_H \tag{3.IIID2}$$

Table 3.5 gives problems to evaluate the heat rejection and entropy generated for different heat inputs.

Table 3.5 Specific Problems for Case IIID. **Bold** = **Specified**; *Italic = Solved.* The temperatures for the heat transfers are set at T_e = **313K** and T_h = **942K**

Problem #	Q_h, MJ	Q_e, MJ	s_{gen}, MJ kmol^{-1} K^{-1}
IIID.1	**800**	*-533*	*1.00*
IIID.2	**600**		
IIID.3	**400**		
IIID.4	**300**	*-33*	*-0.07*

For problem #IIID.1, Eqs. (IIID.1) and (IIID.2) become

$$Q_e = 1(-7.32) + 0.5(-25.99) - 1(-287.2) - 800 = -533 \tag{3.IIID1.1}$$

$$s_{gen} = [1(-0.023) + 0.5(-0.007) - 1(-0.169) - (\tfrac{800}{942} + \tfrac{-533}{313})]/1 = 1.00 \tag{3.IIID2.1}$$

Problem IIID.4 is evaluated similarly.

Problems 3.5 Complete Table 3.5 for problems #IIID.2 - #IIID.3.

Note that $s_{gen} < 0$ for the smallest heat input, Q_h = 300, so the process is not feasible; there is not enough energy put into the process. For Problems IIID.1 to IIID3, $s_{gen} > 0$, so they are feasible.

Case IIIJ. The energy for a thermochemical process from a nuclear plant can be provided via pressurized Helium that is cooled as its energy is used for the decomposition. Thus, the block diagram is as in Figure 3.2.

The forms of Eqs. (3.1) and (3.2) become, for this case with the notation of Figure 3.2 and $N \equiv N_i = N_o$:

$$N = \frac{[N_W(h_W - T_e s_W) - N_H(h_H - T_e s_H) - N_O(h_O - T_e s_O)] - T_e N_H s_{gen}}{c_p^{ig}(T_o - T_i) - T_e c_p^{ig} \ln(T_o/T_i)} \tag{3.11}$$

$$Q_e = (N_W h_W - N_H h_H - N_O h_O) + N c_p^{ig}(T_o - T_i) \tag{3.12}$$

Helium can be considered an ideal gas under these conditions, so its enthalpy and entropy differences can be computed with Eqs. (3.7a) and (3.7b).

Table 3.6 gives problems to evaluate the required Helium flow and heat rejection for different entropy generation values.
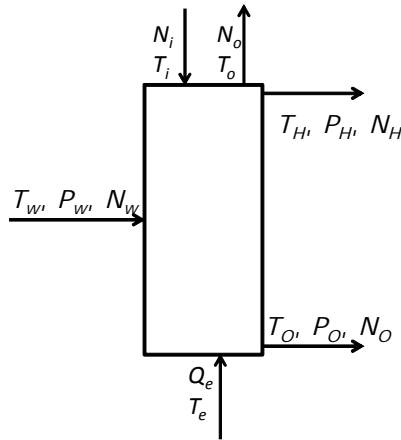
Figure 3.2. Schematic for Thermochemical Decomposition with Energy Supplied By High-Temperature Gas.

Table 3.6 Specific Problems for Case IIIJ. **Bold** = **Specified**; *Italic = Solved.* The Helium states are set at T_i = **1100** K, P_i = **40** bar, T_o = **800**K, P_o = **38** bar along with $c_p^{ig}(T) = \frac{5}{2}R = 0.0208$ MJ kmol^{-1} K^{-1} and T_e = **313** K.

Problem #	s_{gen}, MJ kmol^{-1} K^{-1}	N, mol	Q_e, MJ
IIIJ.1	**0**	*53.4*	*-66*
IIIJ.2	**0.25**		
IIIJ.3	**0.5**		
IIIJ.4	**0.75**		

For Problem IIIJ.1, Eqs. (3.11) and (3.12) become:

$$N = \frac{1[-287.2-313(-0.169)]-1[-7.32-313(-0.023)]-0.5[-25.99-313(-0.007)]-313(0)}{0.0208(800-1100)-313(0.0208)\ln(800/1100)} = 53.4 \text{ kmol} \qquad (3.\text{IIIJ}11.1)$$

$$Q_e = 1(-287.2) - 1(-7.32) - 0.5(-25.99) + 53.4(0.0208)(800-1100) = -66 \text{ MJ} \quad (3.\text{IIIJ}12.1)$$

Problems 3.6 Complete Table 3.6 for problems #IIIJ.2 - #IIIJ.4.

Note that the result for Q_e for Problem #IIIJ.1 is the same as for Problem #IIIA.1 as it must. The moles of Helium, and therefore the heat rejected, rises dramatically with small amounts of irreversibilities.

References
[5] O'Connell, J.P., Narkprasert, P., Gorensek, M.B., Process model-free analysis for thermodynamic efficiencies of sulfur– processes for thermochemical water decomposition, Int. J. Hydrogen Energy, 2009, 34, 4033-4040.
[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).