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

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Module 1: Fundamentals

Introduction

Hydrogen is being proposed as an important factor in meeting the energy demands of the future global community. While hydrogen is not a fuel, it can serve as an energy carrier and storage for fuel cells that provide stationary and mobile electricity, as well as have chemical value in producing ammonia fertilizer and upgrading heavy oils, coal and biomass [1, 2].

Since, under normal conditions, Nature prefers to combine hydrogen with other atoms, especially to oxidize it to water, energy must be put in to obtain pure hydrogen gas, as described by the Second Law of Thermodynamics. As with all real processes that go against natural tendencies, irreversiblities cause the input energy to always be greater than the energy that might be recovered by oxidizing the hydrogen. The principal engineering issues are how to minimize the extra energy input, and to define the scale of chemical processes and equipment to be constructed for a specific hydrogen technology.

There are three principal methods for obtaining hydrogen involving water: chemical reforming or gasification from water and fossil fuels or biomass, electrolysis of water, and photo-induced or thermochemical decomposition of water [1-3]. Fossil fuels contain carbon along with variable amounts of hydrogen, so carbon dioxide is always produced along with the hydrogen. At present, as much as 95% of the 9 MM tons of hydrogen annually produced in the US is from natural gas, principally methane, via the "water gas" and "water-gas shift" reactions [1]. This process yields four moles of hydrogen and one mole of carbon dioxide from each methane and two water molecules. However, any carbon source can be used in this approach, with the ratio of H_2 to CO_2 reduced as the H content in the fuel decreases. A rough indicator of the H/C ratio is the phase of the fuel; gas has the most H and solid the least. For liquids, the greater the fluidity, the higher the H/C. The decline in fossil fuel resources and the production of carbon dioxide make this approach less attractive over the long run.

In electrolysis, the energy is put in via electron removal and addition at electrodes under electrochemical potentials, basically the reverse operation of a fuel cell. Unfortunately, there are significant losses of useful energy due to irreversible processes in the electrode reactions and to species transport. Photo-induced decomposition uses sunlight energy for either bacteria or

semiconductors to directly produce hydrogen. But the mechanisms are poorly understood and the technology is undeveloped.

Finally, thermochemical decomposition of water uses high temperature heat and closed-cycle processes with added substances to separate the hydrogen and oxygen into the pure components. There are several feasible approaches [2, 3], but most involve costly chemicals and materials of construction, and none have been built and operated at industrial scale.

The intention of the present modules is to give experience in using thermodynamics for process analysis of energy effects and process constraints. Thermochemical decomposition of water to manufacture hydrogen will be the principal illustration, though related units and processes will be examined. The set of modules is comprised of the following components:

Module 1. Fundamentals
Module 2. Analysis of Single-Unit Processes
Module 3. The Whole-Process Perspective for Thermochemical Hydrogen
Module 4. A Simplified Multisection Process for Thermochemical Hydrogen
Module 5. The 3-Section Sulfur-Iodine Process for Thermochemical Hydrogen

Module 1 formulates the thermodynamic relations that will be used in all Modules. The later Modules start with a review of this material and then proceed to example exercises with and without solutions. Module 5 has more extensive problems that to allow individual and group investigation.

Thermodynamics for Process Analysis

Thermodynamic evaluations, using fundamentals and modeling, can provide limited, but vital, information for analysis and design of chemical processes, such as hydrogen production. In particular, best-case energy inputs and outputs, as well as a basis for estimating the inevitable additional energy from irreversible processes, can be obtained. The Laws give always-true relations that constrain processes via mass and energy conservation, entropy generation, and chemical potentials for phase and reaction equilibria. Models then provide values for these nonmeasurable, or conceptual, properties in terms of measurables, such as temperature, pressure, and composition.

The principal approach of open-system thermodynamics uses balance equations about "black-box" units with only flows of material, and their accompanying energies and entropies, to account for the effects of interactions of the system with its surroundings. In addition, the streams can be constrained to phase and reaction equilibrium conditions which can be solved for. Thus, no details of the process, such as equipment or internal stream flows, need to be included; only streams and energies crossing the boundary of the defined system are used. The balance equations force the heat, work, and material interactions of the process unit to obey the Laws, and quantitative results are reliable to the extent that the properties are accurate. A main goal is to determine the process configurations for minimum energy requirements for specified sets of constraints by imposing reversibility. In addition, the impacts of irreversibilities characterized by rates of entropy generation, or other measures [4], can be determined. Besides this design activity, the relations allow analysis of entropy generation for processes developed with process simulation software, determine consistency among solution properties, and compare results from different property models [5].

Fundamental Thermodynamic Analysis

Thermodynamics offers many ways, both rigorous and approximate, to evaluate the utilization of energy flows for open systems, as described in chemical engineering texts [6, 7]. The basic analysis here is described in [6]. Figure 1.1 illustrates the concept for a steady-flow system, with inlet and outlet streams at specified absolute temperatures, T, and pressures, P, as well as sets of molar or mass amounts for the components, $\{N\}$, and 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 both the phases. For pure components, this means either T or P, the total flow, N, and the quality or fraction of the system that is vapor, x, would specified. For mixtures, defining the state is more elaborate.
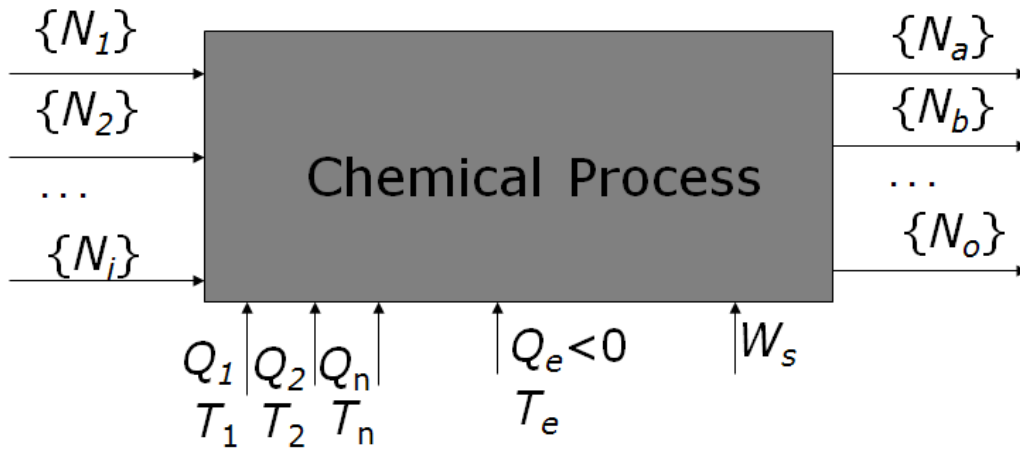

Figure 1.1. Steady Flow System for Applying Material, Energy, and Entropy Relations, Eqs. (1.1) and (1.2).

The balance equations for steady flow processes are:

$$\sum_i N_i h_i(T_i, P_i, \{x\}_i) - \sum_i N_o h_o(T_o, P_o, \{x\}_o) + \sum_s W_s + \sum_b Q_b + Q_e = 0 \qquad (1.1)$$

$$\sum_i N_i s_i(T_i, P_i, \{x\}_i) - \sum_i N_o s_o(T_o, P_o, \{x\}_o) + \sum_b \frac{Q_b}{T_b} + \frac{Q_e}{T_e} + S_{gen} = 0 \qquad (1.2)$$

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. (1.1). 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. (1.1), and the balance of entropy, Eq. (1.2), 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. We distinguish Q_e as the total heat discharged or rejected (< 0) by the system to the process environment at T_e. If an amount of heat is transferred over a range of temperature such as in a heat exchanger with a single phase fluid, the log mean temperature should be used. 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. (1.1) and (1.2) will give the minimum input shaft work, high-temperature heat, or energy-carrying material, to accomplish a process that does not occur spontaneously.

  The shaft work is usually in the form of electricity for pumps, compressors, and turbines and is positive for work put in across the system boundary. Here, it is not the traditional *Pv* work associated with expanding or contracting the system boundary, since that work cannot occur steadily. The choice of boundary locations is made on the basis of convenience, known device efficiencies, and available property estimates. Thus the boundary of a system may be drawn so that all work devices are inside the system and so are unseen in the diagrams. Such devices may be driven by a stream that enters and leaves the system at different conditions, such as by steam or high-pressure helium from a nuclear reactor, or by heats that cross the boundary at different temperatures to run a heat engine. As long as the specifications of the work devices are consistent with the boundary-crossing flows, the process results will also be consistent. In particular, as shown below, it can be quite convenient to do analyses that avoid details of particular pieces of equipment, while connecting to real process flows. In any case, the location of the system boundaries will determine if W_s is explicit in the energy balance, Eq. (1.1), though it never appears in the entropy equation, Eq. (1.2).

  These equations for a steady-flow system must be computed in relation to a basis chosen to represent the system. Here we will use a defined amount of the desired product, e.g., per kmol of H_2 product, though production rate per unit of time, e.g., kmol per hour, can also be chosen.

  Note that this model-free analysis does not expose locations within a process where heat would need to flow up a temperature gradient. This must be found from a "pinch analysis" [8], though "exergy" analyses also can be used [9]. However, this involves treating the specific process units, which we wish to avoid. In any case, since complex processes normally have the possibility of temperature crossover, real energy requirements will be different, leading to lower efficiencies than those found here, and process design must find where pinches appear. This may require ultimate adjustment of the process flows, but once the present analysis is set up, that aspect can be done easily.

  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. The result is that many different cases can be set up; Table 1 illustrates a few of these. Table 2 lists the common practical applications of the cases.

  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. (1.2) shows that entropy generation means more heat must be removed ($Q_{e\ real} < Q_{e\ rev} < 0$), so Eq. (1.1) 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 ($W_{s\ rev} < W_{s\ real} < 0$) while less heat is put in ($0 < \Sigma Q_{b\ real} < \Sigma Q_{b\ rev}$).

Table 1.1. Some Options for Specifications and Solution Variables for Eqs. (1.1) and (1.2).

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}
B	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}^*, \{Q_b\}, \{T_b\}, T_e, s_{gen}$	Q_e, W_{sn}
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}
G	$T_i, P_i, \{N\}_i, P_o, \{N\}_o, \{W_s\}, \{Q_b\}, \{T_b\}, T_e, s_{gen}$	Q_e, T_o
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}
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.

Table 1.2. Practical Applications of the Cases in Table 1.

Case	Common Practical Application
A	Heat effects on a distillation column (Design or Analysis)
B	Work and heat rejection of a turbine, compressor, or pump (Design)
C	Work and irreversibility of a turbine, compressor, or pump (Analysis)
D	Heat rejection and irreversibility of a turbine, compressor, pump, or distillation column (Design or Analysis)
E	
F	
G	
H	
J	

Problem 1.1 Complete Table 1.2 for Cases E - J.

For complex open systems, the interplay among the work, heat, and stream flows and conditions can prevent simple generalizations. Yet in cases where energy or high-energy substances are produced, entropy generation handles all of the effects of irreversibilities. These can be cataloged as energy costs: (A) putting in more energy by increasing input heat (more positive Q_b), higher h_i (usually by higher T_i), and/or greater $\{N_i\}$, and (B) taking out more energy, either by more heat output (more negative Q_e), higher h_o (usually by higher T_o), and/or greater $\{N_o\}$, which must be consistent with $\{N_i\}$. Thus, to obtain the same power from a real steam power cycle, irreversibility (positive entropy generation) requires more input heat to produce more steam or the input heat must be at a higher temperature (and/or pressure). In addition, either the temperature of the outlet heat is higher, or more heat must be removed.

For a process producing a given amount of hydrogen from input energy carried by helium at a given pressure and temperature from a nuclear plant, if s_{gen} is increased, the solution to Eqs. (1.1) and (1.2) means more He flow or higher energy conditions and more heat rejection.

Problem 1.2 Extend Tables 1.1 and 2.1 to other cases. Comment on their expected usefulness in real engineering work.

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