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

Fundamental Thermodynamic Analysis

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

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

	$T_i, P_i, \{N\}$	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_{in} which is solved for

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