

Thermochemical Processes for the Production of Hydrogen from Water

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Introduction

A thermochemical hydrogen production process is one which requires only (i.e. mainly) water as a material input and mainly thermal energy, or heat, as an energy input. The output of the process is hydrogen and oxygen and possibly (or probably) some waste heat. The process itself comprises a series of chemical reactions which sum to water decomposition. The products of each reaction must be separated and either recycled or sent to the next reaction. Thermal energy, or heat, is transferred in the process to heat or cool the various reactant and product streams and to provide for the various "heats of reaction." Useful work, or electricity, will be required for pumping and/or operating separation equipment or electrochemical reactions. A "pure" thermochemical process requires only heat as the energy input. A "hybrid" process is one which contains an electrochemical step. In water electrolysis, 80% of the energy input must be in the form of electricity.

The interest in thermochemical processes derives from the potential they offer for lower capital and/or operating costs and higher overall thermal efficiency than water electrolysis. Water electrolysis has been used for some time as an industrial process to produce hydrogen and is especially attractive in areas where electricity is abundant and inexpensive. The thermal efficiency - measured from primary thermal energy source to hydrogen in the pipeline - of the water electrolysis process is in the range of 30-35%. The major determinant is the efficiency of converting heat to useful work (i.e. electricity) which is currently in the range of 35-40%.

The definition of thermal efficiency, η , used here is

$$\eta = \frac{\Delta H_o}{Q_t} \quad 1)$$

$$\text{where } Q_t = q_i + \frac{W_i}{\epsilon} \quad 2)$$

where ΔH_o = enthalpy change upon decomposition of liquid water to hydrogen and oxygen at 25° C and 1 atm. (68.3 kcal/g mole H_2)

Q_t = total thermal energy required by the process

q_i = direct thermal energy input

w_i = direct useful work input

ϵ = efficiency of converting thermal energy to useful work

This definition of η employs the so-called "higher heating value" of hydrogen, but the motivation for its use springs from the fact that liquid water will, in fact, be the material input to the process. End use considerations should not be important in a definition which is meant to focus on the process, as has been argued earlier (1).

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The first paper dealing with the energetics and thermodynamics of thermochemical processes for the decomposition of water was published in 1966 (2). The number of publications on this subject grew rapidly after 1971 with the emergence of an intense worldwide interest in a possible hydrogen economy. The proceedings of The Hydrogen Economy Miami Energy (THEME) Conference (3) contain papers on virtually every aspect of a hydrogen economy including several on thermochemical processing. Two recent review articles, by Braunstein & Bamberger (4) and Chao (5), and a number of other recent papers (6-15) present detailed technical discussions of many aspects of the problem and a long list of references.

Efficiency

Costs, capital and operating, will undoubtedly play the major role in determining what sort of hydrogen production processes become widely used in the future. Thermal efficiency, however, will exert a strong influence on costs and is a reasonable measure to use in the search for "good" thermochemical processes.

The thermodynamic limitation on thermal efficiency, first published in 1966 (2), and verified several times since then, is

$$\eta \leq \left\{ \frac{1}{1 + \frac{q_r}{\Delta H_o} + \left(\frac{W_i}{\Delta H_o} \frac{1 - \varepsilon}{\varepsilon} \right)} \right. \quad 3)$$

$$\left. \frac{\Delta H_o}{\Delta G_o} \frac{T_H - T_c}{T_H} \left[\frac{1}{1 + \frac{1}{\varepsilon} \frac{W_i}{\Delta G_o} \left(\frac{T_H - T_c}{T_H} - \varepsilon \right)} \right] \right\}$$

The derivation leading to this result employs the assumption that all the process thermal energy input, q_i , occurs at the high temperature, T_H , and that all the process heat rejection, q_r , takes place at the heat sink temperature, T_c . ΔG_o is the change in the Gibbs function upon decomposition of liquid water to hydrogen and oxygen at 25° C and 1 atm. (56.7 kcal/g mole H_2).

Equation (3) fixes the upper limit on η (when q_r and W_i are 0) such that

$$\eta \leq \left\{ \begin{array}{l} 1.0 \\ \frac{\Delta H_o}{\Delta G_o} \frac{T_H - T_c}{T_H} \end{array} \right. \quad 4)$$

It should be pointed out here that the upper limit on η shown in Equation 4 is 1.0 because it was assumed that q_r , the process heat rejection, could not be negative. If this restriction is removed, which would allow heat to flow into the process from the heat sink at T_c , the upper limit will be given by the lower expression in Equation 4 and will approach 1.2 (i.e. $\Delta H_o/\Delta G_o$), which is exactly the situation for water electrolysis when the process efficiency is based on the "thermoneutral" voltage.

Single Stage Process

The simplest single step process to decompose water is electrolytic. Actual operating data (16) indicate that water electrolysis cells consume 20-27 kw-hr/lb of H_2 generated. The cell efficiency, based on a ΔH_o of 18.1 kw-hr/lb H_2 , is then in the range 66-90%. The simplest conceptual thermal process is to heat the water to a high temperature and separate the hydrogen and oxygen which form in the equilibrium mixture.

The entropy change for water decomposition, after the liquid to vapor phase change has occurred, is approximately 0.01 kcal/g mole °K which is simply too small to achieve a substantial reduction in the work requirement at currently achievable operating temperatures. Another way of saying this is that the equilibrium composition does not shift in favor of H_2 rapidly enough with increasing temperature to suggest that a single step thermal decomposition process offers great promise for the near term. At 2000° K and 1 atm the equilibrium mixture of $H_2O - H_2 - O_2$ contains a mole fraction of H_2 equal to only 0.036 corresponding to only a 3.6% conversion of water. High temperature gas cooled reactors which may be able to provide process heat in the near future are operating in the range of 1200-1300° K (17).

In any direct decomposition process there will be severe practical problems related to the very high temperatures required. Materials of construction, heat exchangers, separation membranes and reaction vessels will present considerable difficulties, but the real and unavoidable drawback has to do with the small entropy increase for the water decomposition reaction. In a practical sense it is not possible to reduce the useful work requirement to zero.

Multistage Processes

As was shown by Funk & Reinstrom (2) and reiterated by Abraham and Schreiner in 1974 (11), it is possible for a multistage process to satisfy the first and second laws of thermodynamics along with the constraint that no useful work be expended in the process. In order to visualize such a situation one should imagine a general thermochemical process comprising an arbitrary number of steps. Each reaction exhibits some change in enthalpy, ΔH , entropy, ΔS , and Gibbs function or free energy, ΔG . If the entire process is operated reversibly at 25° C and 1 atm, the work and heat requirements will be exactly the same as for an ideal electrolysis cell since the work requirement, ΔG , and the heat requirement, $T \Delta S$, are the same for any and all reversible processes. In this sense the reversible constant temperature and pressure thermochemical process is the same as the reversible water electrolysis cell. The work requirement for electrolysis can be reduced by operating at higher temperatures, but by choosing the operating temperatures in the thermochemical process properly it is possible, at least in principle, to reduce the useful work requirement to zero. In the chemical process the work requirement manifests itself mainly in work of separation required in the various reaction steps.

The total process useful work requirement may be reduced by operating some of the reactions at high temperatures and some at low temperatures. If the work requirement for the reaction step is taken to be the change in the Gibbs function for the reaction, the object is to operate those reactions with positive entropy changes at high temperatures. Neglecting the effect of temperature on enthalpy and entropy changes, and realizing that phase changes must be treated with care, the following analysis may be made.

The work and heat requirements for the i th reaction are given by

$$W_i = W_i^{T_o} - \Delta S_i (T_i - T_o) \quad (5)$$

$$q_i = q_i^{T_o} + \Delta S_i (T_i - T_o) \quad (6)$$

where the o subscript refers to a reference or standard temperature, say 25° C.

The effect of the sign of the reaction entropy change is apparent. The total heat and work requirements are obtained by summing, so that

$$W_T = \Delta G_o - \sum_{i=1}^I \Delta S_i (T_i - T_o) \quad (8)$$

Now, suppose that J reactions have positive entropy changes and are operated at high temperatures, T_i and L reactions have negative entropy changes and are operated at T_o . The total work, W_T , will be zero when

$$\sum_{i=1}^J \Delta S_i (T_i - T_o) = \Delta G_o \quad (9)$$

If only one high temperature, say T_H is employed, the result is

$$\sum_{i=1}^J \Delta S_i = \frac{\Delta G_o}{T_H - T_o} \quad (10)$$

In principle, there is no reason why Equations 9 and 10 cannot be satisfied along with

$$\sum_{i=1}^I \Delta S_i = \sum_{j=1}^J \Delta S_j + \sum_{i=J+1}^{J+L} \Delta S_i = \Delta S_o \quad (11)$$

This conclusion cannot be reached for a one step process. In that case, the zero work requirement must be accomplished by a temperature manipulation rather than the selection of a suitable sequence of chemical reaction.

Two-Stage Process

Suppose a two-reaction process has been found which requires no useful work. One reaction is operated at T_c and the other at T_H . Choose $T_c = 100^\circ \text{C}$ and $T_H = 950^\circ \text{C}$ and assume that ΔH and ΔS are independent of temperature. For the decomposition of water vapor at 100°C , $\Delta H = 58.1$, $\Delta G = 53.8$, and $\Delta S = 0.0116$, and H_2O is assumed to enter the process in the vapor phase. Since the work required is zero, $\Delta G_c = \Delta G_H = 0$ and

$$\Delta H_H = T_H \Delta S_H \quad (12)$$

$$\Delta H_c = T_c \Delta S_c \quad (13)$$

From Equation 10 it is found that

$$\Delta S_H = \frac{53.8}{950-100} = +0.0633$$

and, from Equation 12

$$\Delta H_H = (1223) (.0633) = +77.4$$

Since the ΔS 's must sum to 0.0116

$$\Delta S_L = -0.0517$$

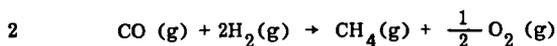
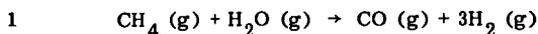
From Equation 13

$$\Delta H_c = (373) (-.0517) = -19.3$$

Abraham and Schreiner (11) indicate that the positive entropy change required for the high temperature reaction (+0.0633) is too large for real substances. Funk and Reinstrom (2) have expressed the opinion that it is unlikely that elements or simple compounds will be found to operate in efficient two-step processes. It is interesting, however, to consider processes which employ the steam-methane reforming reaction. This reaction has a very large entropy change and has been suggested by Schulten as a "good" reaction for thermochemical processes (17).

A two-step process using the steam-methane reforming reaction is shown below

Reaction



Reaction No. 2 is shown to illustrate the point. It is not suggested here that it will "go" as written. The reaction property changes are

Reaction	Temp ° C	ΔH	ΔG	ΔS
1	100	50.2	30.1	+ 0.0541
2	100	7.9	23.7	- 0.0425
1	627	53.6	- 0.4	+ 0.0601

The ΔG for reaction 1 is zero at 621° C. Notice that the work requirement, or at least the free energy change, has been reduced by approximately 30 kcal by raising the operating temperature 527° C. The entropy change for the steam-methane reforming reaction almost satisfies the requirement mentioned earlier. The work of separation for this reaction is high, however, and this is an important quantity in thermochemical processes, as has been described elsewhere (7).

Cycle Evaluation

The complete evaluation of a thermochemical process is a complex and involved task. Experimental data on the reactions describing both equilibrium and kinetic conditions are required. Information dealing with corrosion and materials of construction should be available. Then, from a full mass and energy balance and equipment design or specification the thermal efficiency and capital and operating costs can be determined. Such effort cannot be applied, of course, to every process and an automated procedure for cycle evaluation is necessary. Such a procedure has been developed and is embodied in the HYDRGN computer program, which has been described elsewhere (1). This technique operates in conjunction with a large thermochemical data bank and a program which determines the equilibrium composition of reacting mixtures. It calculates important process conditions such as:

1. Thermodynamic property changes in each step of process, including the heating and cooling steps,
2. Amount of recycle and work of separation (for gas mixtures) as a function of the approach to equilibrium in the chemical reaction steps,
3. Possibilities for thermal energy regeneration and useful work production in the process itself, and
4. An estimate of the overall process thermal efficiency.

The output of the HYDRGN program may be used to generate more detailed mass and

energy balances and may be adapted to a particular process to do parametric studies. This evaluation procedure has been widely used and applied to over 100 processes.

A Hybrid Cycle

A good example of a hybrid cycle is the so called hybrid sulfuric acid process now being developed by Westinghouse and NASA. The reactions and their standard state property changes are

Step No.		298° K, 1 atm		
		ΔH^*	ΔG^*	ΔS^{**}
1	$2H_2O(l) + SO_2(g) \rightarrow H_2SO_4(l) + H_2(g)$	13.0	20.2	-.024
2	$H_2SO_4(l) \rightarrow H_2O(l) + SO_2(g) + \frac{1}{2}O_2(g)$	55.3	36.5	.063
<hr/>				
	$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$	68.3	56.7	.039
	* kcal/g mole H_2		** kcal/g mole $H_2^\circ K$	

The first step is accomplished electrolytically and the second, the decomposition of sulfuric acid, is done thermally. Step No. 2 has a large positive entropy change, which is necessary for a good thermochemical process. The work requirement in the first step may be reduced by operating with acid concentrations less than 100%, which has the effect of shifting some of the work requirement into the second step in which thermal energy is the major input. A detailed cost and efficiency estimate has been prepared by Westinghouse and NASA and is presented elsewhere in this symposium.

A Sulfur Cycle

The large entropy changes associated with the decomposition of sulfates and/or SO_3 has led to the generation of a number of processes incorporating such a step (10, 12). One such cycle is

	ΔH^*	ΔG^*	ΔS^{**}
$\frac{1}{4} BaS + H_2O \rightarrow \frac{1}{4} BaSO_4 + H_2$	7.3	1.7	.0187
$\frac{1}{4} BaSO_4 + \frac{1}{2} S \rightarrow \frac{1}{4} BaS + \frac{1}{2} SO_2$	25.6	19.1	.0217
$\frac{5}{2} SO_2 + Fe_2O_3 \rightarrow 2FeSO_4 + \frac{1}{2} S$	-69.4	-37.3	-.1075
$2FeSO_4 \rightarrow Fe_2O_3 + 2SO_2 + \frac{1}{2}O_2$	104.8	73.2	.1061
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$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	68.3	56.7	.039
*kcal/g mole H_2		**kcal/g mole $H_2^\circ K$	298°K, 1 atm

Preliminary estimates indicate that such a cycle could have an efficiency around 40% when the maximum process temperature is 1144° K. A more detailed study is now under way.

A great deal of experimental and theoretical work is now being done by various organizations on a worldwide basis. Table 1 shows some of the processes, cast in terms of the hydrogen and oxygen producing reactions from which they proceed, and the organizations which are doing the research and development. The overall program is broad and a number of avenues - both experimental and theoretical - are being pursued. The results, obtained in the laboratory and from engineering designs, should provide the information necessary to make a realistic evaluation of the true potential of thermochemical processes.

TABLE 1

A Process Classification and Development Scheme

		$\text{H}_2\text{O} + \text{O} \longrightarrow \square + \text{H}_2$	
		$\square \longrightarrow \text{O} + 1/2 \text{O}_2$	
		<u>○</u>	<u>□</u>
		<u>○</u>	<u>Organization</u>
1	CH_4	$(\text{CO} + 2\text{H}_2)$	KFA-Julich, West Germany Lawrence Livermore Laboratory
2	$(\text{SO}_2 + \text{H}_2\text{O})$	H_2SO_4	Westinghouse Hybrid Sulfuric Acid KFA-Julich, West Germany Los Alamos Scientific Laboratory
3	$(3\text{FeCl}_2 + 3\text{H}_2\text{O})$	$(\text{Fe}_3\text{O}_4 + 6\text{HCl})$	IGT GE Euratom-Ispra, Italy RWTH-Aachen, West Germany
4	$1/2 \text{Sn}$	$1/2 \text{SnO}_2$	Gaz de France
5	$1/2 \text{S}$	$1/2 \text{SO}_2$	Los Alamos Scientific Laboratory University of Kentucky
6	$(\text{K}_2\text{Se} + \text{H}_2\text{O})$	$(2\text{KOH} + \text{Se})$	Lawrence Livermore Laboratory
7	Cl_2^*	2HCl	Allison Division, GM Air Products IGT RWTH, Aachen, West Germany
8	$(2\text{Cs} + \text{H}_2\text{O})$	2CsOH	Aerojet General
9	3FeO	Fe_3O_4	IGT RWTH, Aachen, West Germany
10	Hg	HgO	Euratom, Ispra (Mark-1)
11	$1/3 \text{KI}$	$1/3 \text{KIO}_3$	GE
12	SO_2	SO_3	IGT
13	$3/4 \text{Fe}$	$3/4 \text{Fe}_3\text{O}_4$	IGT RWTH, Aachen, West Germany
14	$(\text{SrBr}_2 + \text{Hg})$	$(\text{SrO} + \text{HgBr}_2)$	Euratom, Ispra, Italy

*Reverse the $\text{H}_2 + 1/2\text{O}_2$

References

1. Funk, J. E., Conger, W. L., and Carty, R. H., "Evaluation of Multi-Step Thermochemical Processes for the Production of Hydrogen from Water," THEME Conf. Proc., Miami Beach, Fla., pp. S11-11, March, 1974.
2. Funk, J. E. and Reinstrom, R. M., "Energy Requirements in the Production of Hydrogen from Water," I & EC Proc. Res. and Dev., Vol. 5, No. 3, pp. 336-342, July, 1966.
3. Proceedings of The Hydrogen Economy Miami Energy (THEME) Conference, University of Miami, Miami Beach, Fla., March 18-20, 1974.
4. Bamberger, C. E. and Braunstein, J., "Hydrogen: A Versatile Element," Amer. Sci., Vol. 63, No. 4, pp. 438-447, July-August, 1975.
5. Chao, R. E., "Thermochemical Water Decomposition Processes," I & EC Proc. Res. and Dev., Vol. 13, No. 2, pp. 94-101, June, 1974.
6. Marchetti, C., "Hydrogen Energy," Chemical Economy and Engineering Review, Chemical Economy Research Institute (Japan), January, 1973.
7. Funk, J. E., "Thermodynamics of Multi-Step Water Decomposition Processes," Proc. Sym. on Non-Fossil Chemical Fuels, ACS 163rd National Meeting, Boston, Mass., pp. 79-87, April, 1972.
8. Funk, J. E., "The Generation of Hydrogen by the Thermal Decomposition of Water," Proc. 9th IECEC, San Francisco, Calif., August 26-30, 1974.
9. Funk, J. E., Conger, W. L., Carty, R.M., and Barker, R.E., "Thermochemical Production of Hydrogen from Water," Proc. British Nuclear Energy Soc. Int'l. Conf. on the High Temp. Reactor and Proc. Applic., London, England, November 26-28, 1974.
10. Bowman, M. G., "Fundamental Aspects of Systems for the Thermochemical Production of Hydrogen from Water," Proc. First National Topical Meeting on Nuc. Heat Applic., Los Alamos, New Mexico, October 1-3, 1974.
11. Abraham, B. M. and Schreiner, F., "General Principles Underlying Chemical Cycles which Thermally Decompose Water into the Elements," I & EC Fund, Vol. 13, No. 4, pp. 305-310, 1974.
12. Soliman, M. A., Carty, R. H., Conger, W. L. and Funk, J. E., "New Thermochemical Cycles for Hydrogen Production," Canad. Jour. Chem. Eng., Vol. 53, pp. 164-169, April, 1975.
13. Chao, R. E., "Thermochemical Hydrogen Production: An Assessment of Nonideal Cycles," Ind. Eng. Chem. Process Des. Dev., Vol. 14, No. 3, pp. 276-279, 1975.
14. Bamberger, C. E., et al., "Thermochemical Decomposition of Water Based on Reactions of Chromium and Barium Compounds," Science, Vol. 189, pp. 715-716, Aug. 29, 1975.
15. Funk, J. E., "Thermochemical and Electrolytic Production of Hydrogen from Water," Introduction to Hydrogen Energy, T.N. Vezerglu, Ed., Int. Assn. Hyd. Energy, pp. 19-49, Sept. 1975.

16. Michael, J. W., et al., "Hydrogen and Other Synthetic Fuels,"
TID 26136, UC-80, September, 1972.
17. Proceedings - British Nuclear Energy Soc. Int'l. Conf. on the High
Temp. Reactor and Proc. Applic., London, England, November 26-28,
1974.