

Thermodynamics of Multi - Step Water Decomposition Processes

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Processes which convert water into hydrogen and oxygen are of interest for many reasons, including the many advantages accruing to the transport of energy as hydrogen. Hydrogen may be used as a source of thermal or electrical energy, depending on whether it is burned or used in an electrochemical device such as a fuel cell.

Hydrogen is also a key raw material in the chemical process industries and in petroleum refining. It is estimated that by 1975 the total consumption of hydrogen in the U.S. will be at the rate of four trillion cubic feet per year and growing. Gaseous and liquid hydrocarbons are now the principal raw materials for producing large quantities of hydrogen by means of either catalytic steam reforming or partial oxidation. The pressure for inexpensive and plentiful pipeline gas, artificial natural gas, will increase the demand for hydrogen even more. It would clearly be in the interest of conservation of natural resources to develop an economical process to produce hydrogen from water.

A comprehensive study of thermal processes to produce hydrogen from water was performed and reported by General Motors (1,2). A three step process involving either tantalum chloride or bismuth chloride and a four step process using either mercury chloride or vanadium chloride were described. A general discussion of energy requirements for the decomposition of water was published by Funk and Reinstrom (3) and, more recently, a four step thermal process was described by deBeni and Marchetti (4). A review of the current status of electrolytic hydrogen as a fuel has been published by Gregory, et.al. (5).

Second Law Limitations

If one gram mole of water of liquid water at 25°C and 1 atm is converted into one gram mole of hydrogen and one half gram mole of oxygen at 25°C and 1 atm the gibbs function for the system increases by 56.7 kcal, the enthalpy increases by 68.3 kcal and the entropy increases by 39 cal/°K. If the decomposition is done reversibly at 25°C and 1 atm--say in an electrolysis cell--56.7 kcal, the change in the gibbs function, must be supplied as useful work and 11.6 kcal, the difference between the enthalpy change and gibbs function change, must be supplied as heat.

The amount of useful work required may be decreased by operating the single step decomposition at some higher temperature. The amount of energy required as heat will increase by the same amount that the work required is decreased under the best case assumptions of equal specific heats and perfect thermal regeneration of products and reactants.

If the process is depicted on a temperature entropy diagram, the work reduction is equal to the area enclosed when the process loop is closed by allowing the cooler hydrogen and oxygen to form water

reversibly, say in a fuel cell. From this viewpoint the process is a heat engine and is, therefore, limited in efficiency to the "Carnot" efficiency. This second law limitation has been discussed in more detail elsewhere (1,2,3).

It is desirable, of course, to reduce the amount of useful work required to decompose water since such work must be produced from heat in an engine of some sort. A figure of merit, η , may be defined such that

$$\eta = \frac{\Delta H_0}{Q_t} \quad (1)$$

where $\Delta H_0 = 68.3$ kcal

Q_t = total amount of heat required by process which accepts 1 gram mole of liquid water at 25°C and 1 atm and delivers 1 gram mole of hydrogen and 1/2 gram mole of oxygen at 25°C and 1 atm.

Limitations on η resulting from the first and second laws of thermodynamics have already been derived and discussed (3).

The quantity Q_t comprises two terms,

$$Q_t = \left(\frac{W}{\xi} \right) + Q \quad (2)$$

where W = energy as useful work required

ξ = efficiency of converting heat to work

Q = thermal energy required

A 100% efficient electrolyzer operating with a power plant with a ξ of 30% would yield a value for η of 34%. If the electrolyzer had a voltage efficiency of 60% η would drop to 22%.

Multi-Step Processes

If one supposes that water is to be decomposed by heating it and separating the components (i.e., a single step process) the rate of reduction of the change in gibbs function with temperature is approximately equal to the reaction entropy change. As will be shown later, the theoretical work of separation is equal to or greater than the change in the gibbs function.

For a single step process the work requirement simply does not decrease fast enough as the temperature is increased because the entropy change for the reaction is more or less constant and not large. In a multi-step process the reaction entropy change is not fixed and may vary according to the reaction.

Consider the i th reaction in a multi-step process. The work and heat requirements are

$$w(i) = w_0(i) - \Delta s(i) [T(i) - T_0] \quad (3)$$

$$q(i) = q_0(i) + \Delta s(i) [T(i) - T_0] \quad (4)$$

It has been assumed that $\Delta s(i)$, the reaction entropy change, is independent of temperature. The subscript zero refers to conditions at the reference temperature, T_0 , (assumed to be 25°C).

The total work and heat requirements are obtained by summing (3) and (4) over the I reactions to obtain

$$W = \Delta G_o - \sum_{i=1}^{i=I} \Delta s(i) [T(i) - T_o] \quad (5)$$

$$Q = \sum_{i=1}^{i=I} \Delta s(i) T(i) \quad (6)$$

Another important feature becomes apparent if the process is divided into J reactions which have positive entropy changes and L reactions which have negative entropy changes. To minimize the required work, the first group of reactions should be operated at some high temperature, T_H , and the second group operated at T_o . In this case,

$$W = \Delta G_o - \sum_{j=1}^{j=J} \Delta s(j) [T_H - T_o] \quad (7)$$

As is evident from Eqn. (7), the required work is zero when

$$\sum_{j=1}^{j=J} \Delta s(j) = \frac{\Delta G_o}{T_H - T_o} \quad (8)$$

There is no reason why (8) cannot be satisfied along with

$$\sum_{i=1}^{i=I} \Delta s(i) = \sum_{j=1}^{j=J} \Delta s(j) + \sum_{l=1}^{l=L} \Delta s(l) = \Delta S_o = 39 \frac{\text{cal}}{\text{g mole H}_2\text{-}^\circ\text{K}} \quad (9)$$

This result cannot be obtained for a single step process, in which case the zero work requirement must be accomplished by a temperature manipulation rather than the selection of a suitable sequence of reactions.

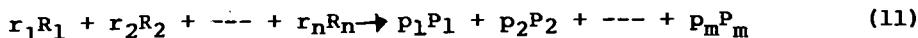
Work of Separation

The theoretical work of separation, ΔG_s , required to separate a mixture of ideal gases into its components is given by

$$\Delta G_s = -RT \sum_k n_k \ln x_k \quad (10)$$

where n_k is the number of moles of the kth component and x_k is the mole fraction of that component.

Fig. 1 shows a reaction process which accomplishes the reaction



The amount of material entering the separator depends on ϵ , the fractional molar conversion of R_1 , which in turn depends on the standard free energy change for the reaction, ΔG_R . Combining the definition of the standard free energy change for a reacting mixture of ideal gases with Eqn. (10) yields

$$\Delta G_s = \Delta G_R - RT \left[\frac{r_1}{\epsilon} \ln x_{R_1} + \frac{r_2}{\epsilon} \ln x_{R_2} + \dots - (\Sigma p - \Sigma r) \ln p^* \right] \quad (12)$$

where
$$x_{R_1} = \frac{r_1(1-\epsilon)}{\Sigma r + \epsilon(\Sigma p - \Sigma r)}, \text{ etc.}$$

and p^* is the operating pressure

Eqn. (12) shows that the theoretical work of separation is greater than standard free energy change for the reaction.

An example of the theoretical work of separation for the vanadium chloride process is shown in Figs. 2 and 3. Fig. 2 is a schematic of the first stage in which there is a gas phase reaction of chlorine with water at 1000°K at 1 atm. Fig. 3 shows the theoretical work of separation and it may be noted that the separation work is increased if the mixture leaves the reaction chamber at less than equilibrium conditions. Fig. 3 is for the separation of all four components and the minimum work requirement is 9.2 kcal per gram mole of hydrogen produced. A similar calculation for the separation of only the HCl and O_2 yields a work requirement of 7.1 kcal.

The Vanadium Chloride Process

The entire vanadium chloride process is shown in Fig. 4. The sums of the enthalpy, entropy, and free energy changes do not exactly equal those for water composition because of questionable thermochemical data.

This process was studied in considerable detail. A plant layout was made assuming a helium cooled nuclear reactor as the heat source. Estimates were made for pumping, heat regeneration, etc. The results are shown in Table 1 and, as can be seen, this process is not as efficient as a water electrolysis plant.

The object here is not to describe an inefficient process - any number of such processes can be easily devised. It is, rather, an attempt to indicate that processes which may be initially attractive can quite quickly lose their appeal when subjected to somewhat more practical considerations of work of separation, thermal regeneration, pumping power, etc. Such a result is not especially surprising in view of the objective, which, in its most fundamental terms, is an attempt to convert heat to useful work more efficiently than in a state of the art power plant.

References

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Acknowledgment

This work was done at the Allison Division of General Motors and was partially supported by U.S. Army Engineer Reactors Group, Fort Belvoir, Virginia. Permission to publish these results is gratefully acknowledged.

Table 1
Vanadium Chloride Process Data Tabulation

Parameter	Units	Systems				Remarks
		2000	2000	1500	1500	
Maximum helium temperature	F	2000	2000	1500	1500	
Minimum helium temperature	F	37	37	67	67	
Helium system pressure	atm	10	1	10	1	He pressure drop equals 10 psi in all cases
Process heat input	kcal	155	155	475	475	
Total heat rejected	kcal	312	382	698	998	Includes unrecovered shaft work
Total heat regenerated	kcal	262	262	872	872	
Helium flow	$\frac{\text{moles}}{\text{mole H}_2}$	113	113	383	383	
Helium pumping power	kcal	3	24	14	105	100% efficiency
Separation work (VCl ₄ and He)	kcal	18	18	23	23	
Total separation work	kcal	33	33	38	38	4 stages plus VCl ₄ and He separations
Shaft work input	kcal	69	90	90	18	Separation work at 50%; pump work at 100% efficiency
Thermal power	kcal	230	300	296	600	30% efficient (Heat to work)
Total reactor thermal power	$\frac{\text{kcal}}{\text{mole H}_2}$	385	455	770	1075	Process heat plus shaft work
Figure of Merit, η	%	18	15	9	6	$\frac{\Delta H_O}{Q_t}$

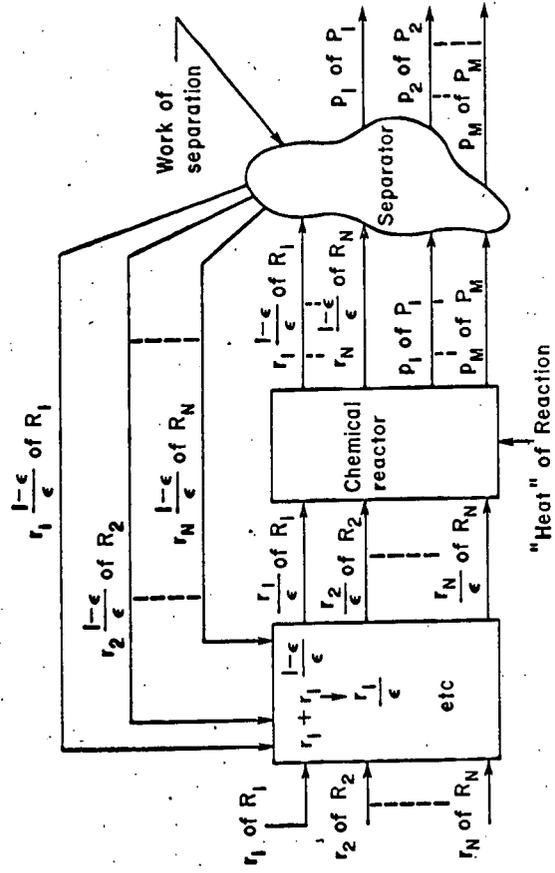


Fig. 1 Overall Reaction Process

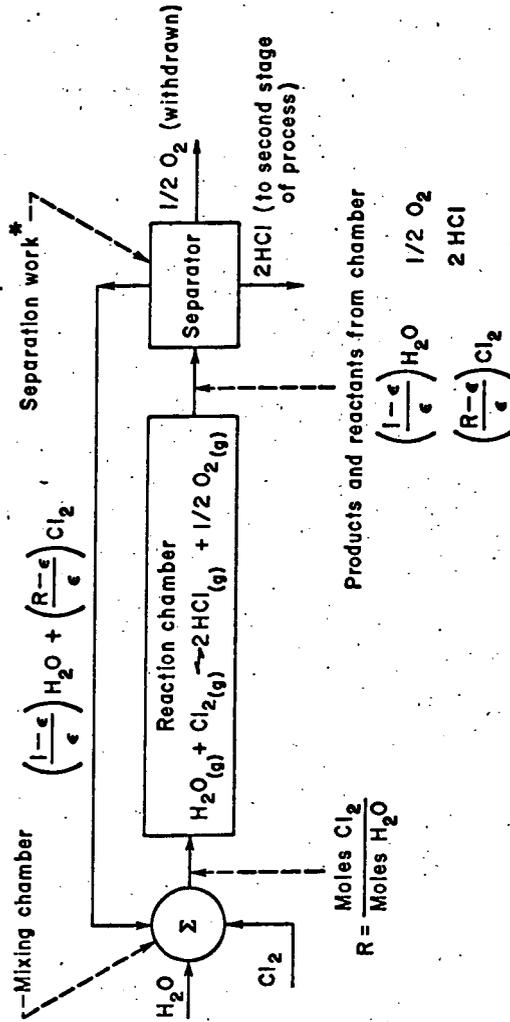


Fig. 2 First Stage of the Vanadium Chloride Process

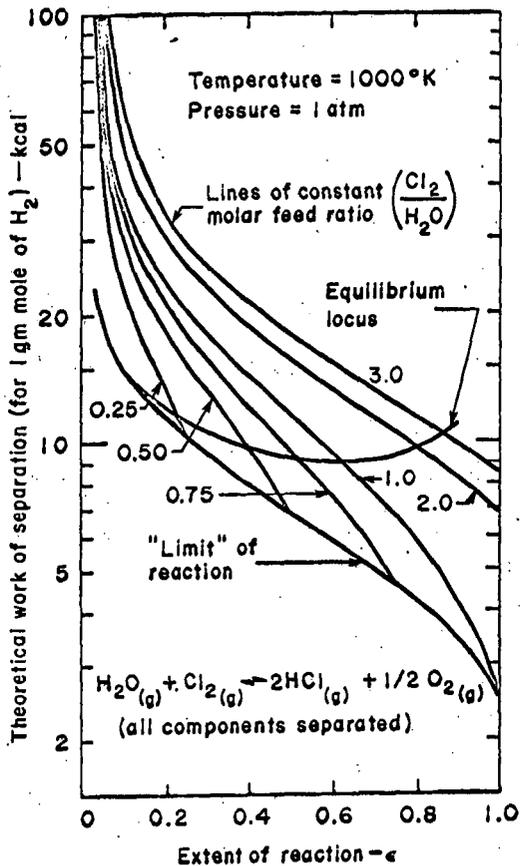
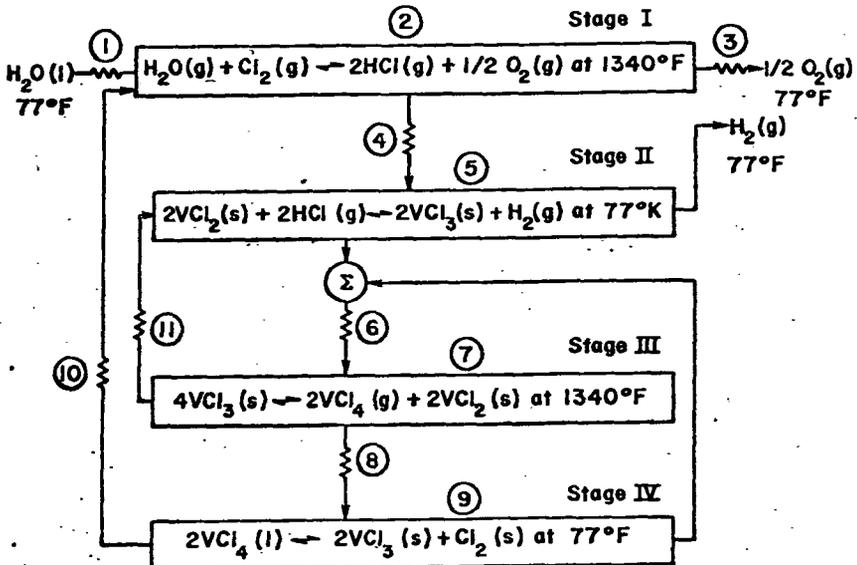


Fig. 3 Theoretical Work of Separation



Enthalpy, entropy, and free energy tabulation
(values in kilocalories)

Step	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	Σ
ΔH	16.7	15.8	-2.7	-10.1	-18.0	72.5	83.0	-65.2	2.0	6.1	-26.7	73.4
ΔS	45.7	18.5	-4.6	-17.4	-45.4	123.6	77.8	-119.0	4.7	10.4	-46.0	48.3
ΔG	-36.0	-2.7	19.1	69.9	-0.5	138.9	5.2	139.0	0.6	-41.7	53.9	59.9

Fig. 4 Vanadium Chloride Process