Hydrogen and Oxygen from Water

The use of solar energy in a one-step effusional process is considered.

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In recent years there has been a great deal of interest in the use of solar energy to produce hydrogen and oxygen from water. Many studies have been made of thermochemical processes (*1–3*). For various reasons the conclusions of such studies have usually been that low-temperature, multistep processes should be used (*4*). In this article, a one-step, high-temperature process is considered: the effusional separation of the equilibrium components of water substance heated to temperatures in the range 2000° to 3000°K by a concentrating solar collector exemplified by the one at Odeillo–Font Romeu, France (*5*).

The maximum efficiencies of all thermochemical processes can be related to the efficiencies of Carnot engines operating between the same upper and lower temperatures (*6*). It is necessary only to add, conceptually, a reversible fuel cell (*7*) which converts the hydrogen and oxygen to liquid water at the lower temperature, T_L (300°K in this study), performing an amount of electrical work, W, which is given by the Gibbs free energy change, $-\Delta G$, of the reaction. If the reactant and products are in their standards states, 1 atmosphere, the work equivalent to the production of 1 mole of hydrogen and 1/2 mole of oxygen is $-\Delta G$ of the reaction

$$H_2(\mathrm{g},\ 1\ \mathrm{atm},\ T_L) + \tfrac{1}{2}O_2(\mathrm{g},\ 1\ \mathrm{atm},\ T_L) \rightarrow H_2O(\mathrm{l},\ 1\ \mathrm{atm},\ T_L)$$

where g stands for gas and l for liquid.

The efficiency, η_{Carnot}, of a Carnot engine is defined as the work, W, divided by the heat input, Q_H, at the high temperature, T_H, and is given by

$$\eta_{\mathrm{Carnot}} = \frac{W}{Q_H} = \frac{T_H - T_L}{T_H} \qquad (1)$$

Pangborn and Sharer (*6*) show that the heat input at the high temperature required to produce 1 mole of hydrogen and 1 mole of oxygen at a pressure of 1 atm and a temperature T_L from liquid water at the same temperature and pressure, in a reversible process, is given by

$$Q_H = -\Delta G^0_{T_L} \quad T_H - T_L \qquad (2)$$

They also show that, from a thermodynamic standpoint, one should try to operate a thermochemical process at as high an upper temperature as possible, but that, from an operational standpoint, the efficiencies of such processes are also limited by irreversibilities associated with heat transfer and produce separation. The energy-gathering capabilities of the devices themselves also limit efficiencies.

The equilibrium composition of water substance at several temperatures and pressures is shown in Table 1. High temperatures and low pressures favor dissociation. There are substantial amounts of H and H_2, whose molecular weights are low compared with the molecular weights of the other components. Since low pressure both favors dissociation and increases mean free paths, effusion (Knudsen flow diffusional separation) suggests itself (*8*).

When a gas is permitted to effuse through a hole in a thin wall in the Knudsen flow regime—that is, where the diameter of the hole is of the order of magnitude of the mean free path or smaller—the number of molecules of the gas that pass through the hole is proportional to the pressure of the gas and inversely proportional to its molecular weight. It is thus possible to effect a partial separation of a mixture of gases if the components have different molecular weights. The technique is used to separate uranium isotopes, and the separation of two-component, nonreacting isotopic mixtures by porous membranes is well known (*9*). At atmospheric pressure mean free paths are of the order of micrometers; at 0.01 atm, they are of the order of tenths of millimeters. If equilibrium mixtures exemplified by those in Table 1 could be subjected to an ideal effusion process in which the pressure downstream of the orifice was kept very low and the composition of the upstream side was continuously replenished, a substantial separation would result. Subsequent cooling of the effused mixture would bring about recombination of the fragments to form liquid water and excess hydrogen, which could be easily separated. The uneffused mixture would yield an equivalent amount of oxygen. The compositions of the cooled effused products of such idealized separations are given in Fig. 1. The mole fraction of hydrogen in the cooled, condensed effusate, even from an ideal separation at 2100°K and 0.5 atm, for example, would be about 0.026. At 300°K the volume fraction of hydrogen would be 0.97, making for an easy separation from the small volume of liquid water. The uneffused condensate would contain an equivalent amount of gaseous oxygen to be separated from liquid water.

In practice, the mole fractions of hydrogen would be substantially lower. In the first place, it would be neither desirable nor feasible to make the downstream pressure too low. Irreversibilities associated with the effusion process increase with the pressure drop across the membrane. These irreversibilities would ultimately manifest themselves as pump work required to bring the products back up to ambient pressure, or in other related ways. The net effusion rates of the various species would thus be proportional to their partial pressure differences across the membrane. In the second place, hydrogen depletion on the upstream side of the membrane could be minimized only by the pumping and recirculation of very large amounts of uneffused water substance and the use of membranes with very small fractions of open area. Both of these procedures would incur concomitant liabilities.

We cannot now make a comprehensive design of a device for most economically effecting a separation. Such a design would depend on the availability of information which we do not now have—for example, the efficiencies of membranes having various open-area fractions and geometries in effecting separations of complex multicomponent reacting mixtures, and the effective heat transfer coefficients in such systems. Nevertheless, many important features and problem areas of such a process can

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be identified in a simplified sample analysis. To do so is the objective of this article.

Some Preliminary Considerations

A schematic diagram of an apparatus that might be used for achieving such a separation is shown in Fig. 2. We assume that heat transfer is fast enough so that the membrane, which is heated by the sun, and the gases on both sides of it are at the same temperature, T_H. Figure 2 suggests that a very important consideration in the effectiveness with which solar energy can be absorbed by the system will be the amount of heat that is reradiated by the membrane. In low-temperature processes reradiation from the components of a device can be relatively unimportant and is usually ignored. In the process we are examining here, the rate at which we produce hydrogen will be proportional to the membrane's open area for diffusion; the demand is for a large membrane area. But the reradiation loss will be proportional to the effective area of the membrane for radiation. Reradiation losses will be significant because the temperature will be high.

We consider first an ideal device which embodies the characteristics of the apparatus shown in Fig. 2. We define the system efficiency of such a device, η_s, as the power equivalent of the hydrogen and oxygen produced divided by the solar energy flux intercepted by the collector. Thus

$$\eta_s = -\frac{\dot{n}_{H_2}\,\Delta G^0_{T_L}}{IA} \tag{3}$$

where $\dot{n}_{H_2}$ is the molar production rate of hydrogen, I is the intensity of the solar radiation, and A is the collector area. The system efficiency is also the product of two efficiencies: the solar collection efficiency, η_c (the fraction of the incident radiation energy which is retained by the device), and the Carnot efficiency given by Eq. 1. The solar collection efficiency depends on the characteristics of the collector and on the radiation characteristics of the membrane material. In a general way it can be represented as

$$\eta_c = \frac{IA\eta_A\alpha - a\epsilon\sigma T_H^4}{IA} \tag{4}$$

where η_A is an efficiency that accounts for energy losses associated with optical deficiencies in the collector, α and ϵ are the appropriate effective absorptance and emittance of the membrane material, σ is the Stefan-Boltzmann constant, and a is the effective radiating area of the membrane. The first term in the numerator is thus the rate at which energy is flowing into the device. The second term is the rate at which energy is being lost by reradiation from the membrane. The denominator is the rate of solar energy flow into the collector. It would be most advantageous but quite unlikely to have a membrane with a high absorptance for solar radiation and a low emittance. Pleating of the membrane would have the effect of making absorptances and emittances approach 1 and the important salutary effect of increasing the effective open area for effusion without increasing by an equivalent amount the effective area from which reradiation losses are incurred.

Table 1. Mole fractions of equilibrium components of water substance.

Component	2000			2200			2400			2600			2800			3000		
	1 atm	0.1 atm	0.02 atm	1 atm	0.1 atm	0.02 atm	1 atm	0.1 atm	0.02 atm	1 atm	0.1 atm	0.02 atm	1 atm	0.1 atm	0.02 atm	1 atm	0.1 atm	0.02 atm
H	0.0001	0.0006	0.0016	0.0007	0.0031	0.0089	0.0028	0.0126	0.0351	0.0092	0.0398	0.1054	0.0249	0.1019	0.2415	0.0578	0.2114	0.4153
H_2	0.0058	0.0124	0.0209	0.0146	0.0306	0.0504	0.0310	0.0629	0.0984	0.0575	0.1088	0.1523	0.0938	0.1566	0.1761	0.1352	0.1811	0.1398
H_2O	0.9896	0.9773	0.9607	0.9725	0.9399	0.8955	0.9380	0.8642	0.7652	0.8766	0.7332	0.5535	0.7800	0.5428	0.2978	0.6440	0.3239	0.1021
O	0.0000	0.0002	0.0004	0.0002	0.0009	0.0027	0.0009	0.0043	0.0121	0.0034	0.0149	0.0401	0.0100	0.0412	0.1004	0.0244	0.0914	0.1866
OH	0.0021	0.0042	0.0075	0.0062	0.0131	0.0218	0.0154	0.0314	0.0498	0.0322	0.0618	0.0882	0.0582	0.0992	0.1148	0.0914	0.1260	0.1010
O_2	0.0024	0.0052	0.0088	0.0058	0.0123	0.0206	0.0119	0.0246	0.0395	0.0213	0.0415	0.0604	0.0336	0.0584	0.0695	0.0470	0.0062	0.0552

Temperature (°K)

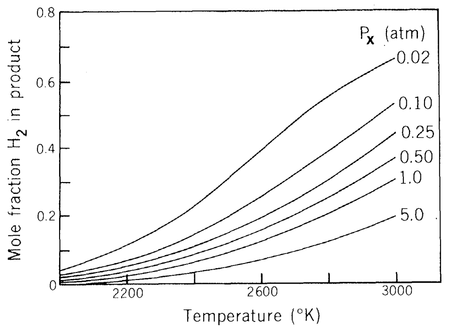
Idealized System Efficiency

It is instructive to examine a simple situation which shows the effect of the operating high temperature on the system efficiency. For this example we assume that η_A, α, and ϵ are all 1. Then

$$\eta_s = \left(\frac{T_H - T_L}{T_H}\right)\left(\frac{IC - \sigma T_H^4}{IC}\right) \tag{5}$$

where $C = A/a$ is the concentration ratio of the device. The system efficiency is plotted as a function of membrane temperature for various concentration ratios in Fig. 3. The uppermost curve in Fig. 3 shows the system efficiency of a pure Carnot machine—one from which reradiation losses have been completely eliminated.

Figure 3 shows that all devices which are characterized by having reradiation losses from the diffusion membrane will have system efficiencies that become maximum at temperatures somewhat below 2300°K. With a particular collector area, the larger the membrane, the lower will be the concentration. Hence, the lower will be the temperature which gives maximum efficiency and the lower will be the system efficiency at any operating temperature. The consideration of efficiency alone suggests that the effective radiating membrane areas should be kept as small as possible—that solar concentrations should be kept as high as possible. But since the rate of hydrogen and oxygen production is also proportional to the membrane's effective effusing area and its permeability, if the area is too small the effusion rate will be too small to absorb the energy influx. If the open-area fraction is too great (or if the holes are too large) effusional separation will be adversely affected. The best operating temperature of a real device will thus depend on a compromise which will be dictated by factors about which



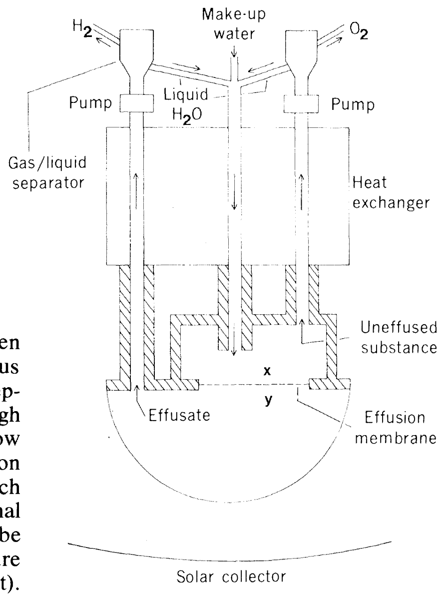
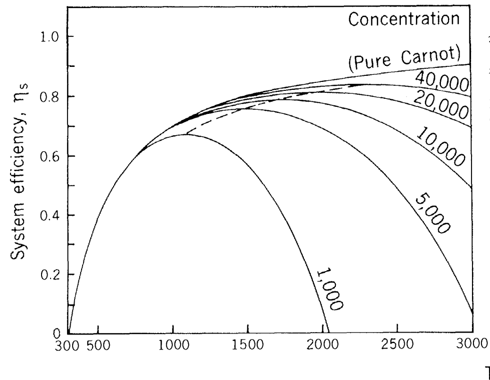


Fig. 1 (left). Variation of mole fraction of hydrogen in product with reactor temperature at various reactor pressures in an idealized effusional separation. Hydrogen enrichment is greatest at high temperatures and low pressures. The use of low pressures facilitates the fabrication of diffusion barriers since larger holes can be used, but inasmuch as the flow rate through a barrier is proportional to the pressure drop, reactor pressure may not be reduced indefinitely. Moreover, high pressure ratios entail large irreversibilities. Fig. 2 (right). Schematic diagram of a device for using sunlight to decompose and separate water into hydrogen and oxygen. Sunlight is brought to a focus on the membrane to maintain the high reactor temperature. The effusate, enriched in lighter components, and the uneffused material, enriched in heavier components, are both passed through the countercurrent heat exchanger to preheat incoming water. In the heat exchanger and in the separators, liquid water condenses and is separated from hydrogen and oxygen.

we do not now have enough quantitative information. One important problem will be matching the net influx with the rate of product production. The energy matching will, in turn, be determined by the operating temperature and pressure, and the size and open-area fraction of the diffusion membrane.

Another interesting observation made by Pangborn and Sharer (*6*) is illustrated in Fig. 4, in which the thermal effects of operation at various values of $T_{\rm H}$ are plotted. The ordinate gives the heat flow concomitant with the production of hydrogen and oxygen from 1 mole of water. The abscissa gives the membrane temperature, $T_{\rm H}$. The upper curve, $Q_{\rm H}$, is the net solar heat flow into the device. The curve labeled Q'_{300} gives the heat flow into the device from the surroundings when the device is being operated to produce hydrogen and oxygen. It is negative at low temperatures, and heat is thus flowing from the apparatus into the surroundings. At 1761°K, this curve crosses the zero ordinate. At higher membrane temperatures, some heat flows into the device from the ambient-temperature surroundings. When the hydrogen and oxygen are recombined, in a reversible fuel cell, for example, the device rejects heat at the temperature of the surroundings, $T_{\rm L}$, in the amount required by Carnot's principle. This amount of heat, Q_{300}, is given by the lowest curve in Fig. 4. It is always negative, but decreases in magnitude as $T_{\rm H}$ increases, as it should.



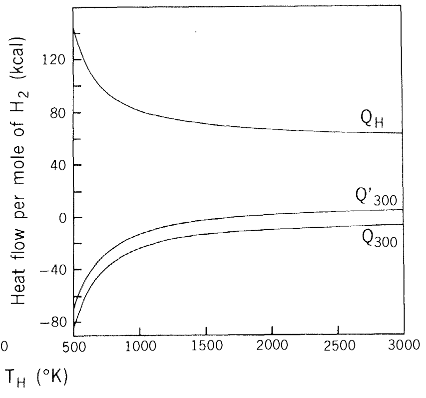


Fig. 3 (left). Variation of ideal system efficiency with temperature at various solar concentration ratios. Since even with an ideal optical system the maximum concentration ratio is about 40,000 (*24*), reradiation from the membrane will cause system efficiencies to become maximum at the low end of our range of interest. The dashed line goes through the efficiency maximum at each concentration. Fig. 4 (right). Heat flows concomitant with the production of 1 mole of hydrogen in an ideal device.

Effusion Membranes

Once the collector area, solar concentration, solar flux intensity, and size, open-area fraction, temperature, and radiational characteristics of the membrane material have been specified, the system efficiency and hydrogen and oxygen production rates are determined. We will then have to operate at mass flow rates and pressures, and with pressure drops across the membrane that can give us this production rate. The collector and membrane characteristics will determine what is technically feasible. Some preliminary exploration we have done suggests that membranes might be made of finely woven iridium cloth (*10, 11*), thoria, or other refractory oxides (*12*) which can be fabricated into "woven" membranes by techniques similar to those used in the manufacture of gas mantles (*13*), or by the electroforming techniques which are used to make fine-mesh screen for the electronics industry (*14*). It might be possible to protect such tungsten or molybdenum screens with sputtered layers of refractory oxides or nitrides (*15*).

In obtaining the results that follow, we have therefore assumed that the membranes would be of woven or electroformed mesh with square holes. Mean free paths were assumed to be those of a one-constituent gas (*16*) at the upstream pressure and temperature for each operating point. Once an open-area fraction and Knudsen number (mean free path/hole width) have been selected, the wire thickness and mesh are uniquely determined by the operating temperature, $T_{\rm H}$, and the pressure of the uneffused gas, $p_{\rm x}$. Available technology looks almost good enough to fabricate membranes having the right geometry with holes substantially smaller than the mean free path, for use at subatmospheric pressures in a range of open-area fractions. Since the effectiveness of the separation will probably decrease as the open-area fraction increases, the selection of the best open-area fraction will depend on experimentally obtained information which is not yet available.

Analysis of the Separation Process

We have constructed a simplified, idealized model to simulate the separation process. Even with this simple model, the interactions between the variables are quite complicated. We therefore devised a program which permitted us to do a set of user-interactive computer experiments (*17*). The objective of these experiments was to determine which sets of operating variables represented stable operating conditions, which did not, how variation of some of the operating conditions affected the others, and about what sorts of wire thicknesses, meshes, and material properties would be necessary for membrane fabrication.

Conceptually, our device is the two-chambered box pictured in Fig. 5a. The effusion membrane is a septum which divides the box into two sides. Water flows into side x through station 1. Side x contains well-stirred, uneffused gas in a state equilibrium at T_H and p_x. Uneffused gas (enriched in oxygen) flows out of x through 4 through a heat exchanger to heat incoming water. Oxygen is separated from the water which has condensed in the heat exchanger. Side y contains effused gas. This too is assumed to be well mixed at T_H. The pressure, p_y, is lower than p_x (*18*). From y the effusate is drawn off through station 3 and flows through the same heat exchanger. Hydrogen is collected from this fraction. Figure 5b gives a set of values for a possible operating condition.

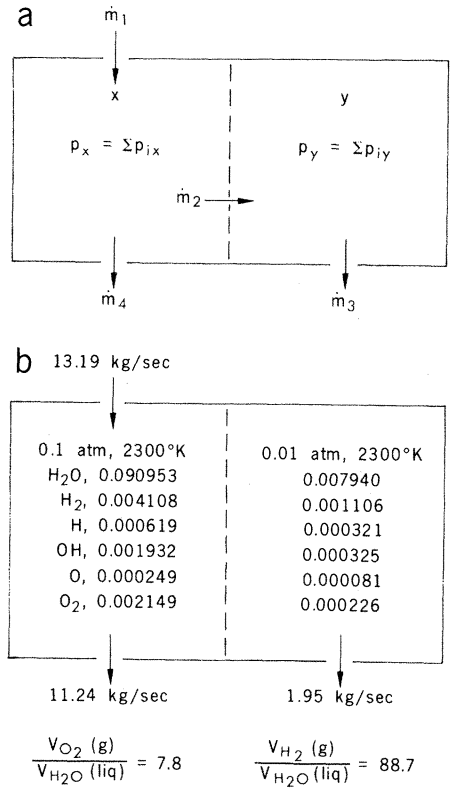


Fig. 5. (a) Schematic representation of the separation process. (b) Flow rates and partial pressures of the components of the uneffused and effused gas at one possible operating condition. The solar concentration ratio is 5000, and with a 2800-m² collector, assuming no irreversibilities or losses, system efficiency is 0.6 and hydrogen production rate is 14 g/sec.

The overall energy balance appropriate to this model has already been presented. Mass conservation requires that the mass flow rates, $\dot{m}$, be related as follows

$$\dot{m}_1 = \dot{m}_4 + \dot{m}_2 \tag{6}$$

$$\dot{m}_2 = \dot{m}_3 \tag{7}$$

The continuity equations for hydrogen and oxygen require that

$$\dot{n}_{OX_1} = \dot{n}_{OX_4} + \dot{n}_{OX_2} \tag{8}$$

$$\dot{n}_{HY_1} = \dot{n}_{HY_2} + \dot{n}_{HY_4} \tag{9}$$

$$\dot{n}_{OX_2} = \dot{n}_{OX_3} \tag{10}$$

$$\dot{n}_{HY_2} = \dot{n}_{HY_3} \tag{11}$$

where the $\dot{n}_{OX}$ and $\dot{n}_{HY}$ are the molar flow rates of oxygen and hydrogen atoms through stations 1 to 4 in whatever molecular species they may be found and are given by

$$\dot{n}_{OX} = \dot{n}_{H_2O} + \dot{n}_{OH} + \dot{n}_O + 2\dot{n}_{O_2} \tag{12}$$

$$\dot{n}_{HY} = \dot{n}_H + 2\dot{n}_{H_2} + 2\dot{n}_{H_2O} + \dot{n}_{OH} \tag{13}$$

Furthermore, the six species H, H_2, H_2O, OH, O, and O_2 flow through the membrane at molar flow rates, $\dot{n}_i$, given by the set of six equations (*19*).

$$\dot{n}_i = \frac{44.63(p_{ix} - p_{iy})a_e f}{(M_i T_H)^{\frac{1}{2}}} \tag{14}$$

where p_{ix} and p_{iy} are the pressures of i in chambers x and y (atmospheres), a_e is the effective area of the membrane for effusion, f is the open-area fraction of the membrane, and M_i is the molecular weight of i. The compositions of the gases in x and y are specified by four independent equilibrium constants, $K(T_H)$ (*20*), which must be satisfied simultaneously in each of the two chambers (eight equations)

$$K_{H_2}(T_H) = \frac{p_{H_2}}{p_H^2} \tag{15}$$

$$K_{H_2O}(T_H) = \frac{p_{H_2O}}{p_H^2 p_O} \tag{16}$$

$$K_{OH}(T_H) = \frac{p_{OH}}{p_O p_H} \tag{17}$$

$$K_{O_2}(T_H) = \frac{p_{O_2}}{p_O^2} \tag{18}$$

and

$$p_x = \Sigma p_{ix} \tag{19}$$

$$p_y = \Sigma p_{iy} \tag{20}$$

Finally, the number ratios of the flow rates of hydrogen atoms to those of oxygen atoms at stations 3 and 4 must be the same as the number ratios in which the atoms are found in y and x. Thus

$$\frac{\dot{n}_{OX_3}}{\dot{n}_{HY_3}} = \frac{p_{H_2Oy} + p_{OHy} + p_{Oy} + 2p_{O_2y}}{p_{HY} + 2p_{H_2y} + 2p_{H_2Oy} + p_{OHy}} \tag{21}$$

$$\frac{\dot{n}_{OX_4}}{\dot{n}_{HY_4}} = \frac{p_{H_2Ox} + p_{OHx} + p_{Ox} + 2p_{O_2x}}{p_{Hx} + 2p_{H_2x} + 2p_{H_2Ox} + p_{OHx}} \tag{22}$$

Results

The number of optional operating variables is large. It would be premature to talk about optimization of the process now since there is still much to be learned about the efficacy of the separation technique and the limitations that radiative, transport, and physical and chemical properties of membrane materials will play. It therefore seems best here to present some sample results. In our studies the 1000-kilowatt solar furnace of the French CNRS (Centre National de la Recherche Scientifique) at Odeillo–Font Romeu (*5*) has served as a guide to what is now available for experimental work. The magnitudes of our flows and our production rates might therefore be ascribed to a facility which is patterned after that prototype.

Once the intensity of solar radiation, the effective optical characteristics and sizes of the collector and membranes, and the membrane temperature have been specified, the system efficiency and hydrogen production rate of this (reversible) device have been determined. No other inputs such as pressures, hole sizes, or open-area fractions enter into the calculations of the system efficiency or hydrogen production rate. Other inputs enter subsequent calculations to determine what combinations (if any) of these variables lead to physically possible operating conditions (*21*).

In Figs. 6 to 10, the results of three sets of idealized computer experiments are presented. Although a flat membrane might be used, a puckered or pleated one increases the ratio of the effective effusing area to the reradiating area. In these experiments the total membrane area for diffusion is ten times the radiation area, and the hole size is one-tenth the mean free path. The collector efficiency, absorptance, and emittance are 1. The intensity of solar radiation is 0.1 watt per square centimeter. The collector area is 2800 square meters. The open area fraction is 0.1 in sets I and II and 0.01 in set III. The pressure ratio, p_y/p_x, is 0.1. Effective membrane radiating areas are 0.56 m² in sets I and III and 0.28 m² in set II, which correspond to concentration ratios of 5,000 and 10,000. The corresponding overall efficiencies and hydrogen production rates, which depend on the operating temperature but not on the pressure, are given in Fig. 6.

Once an operating temperature and x-side pressure have been chosen, we have used all of our degrees of freedom; the operating state of the device has been fixed. Figure 7 shows how the fraction of the mass of water being fed which must be effused ($\dot{m}_3/\dot{m}_1$) varies with temperature at various operating pressures. It is analogous to the distillate fraction from a single-stage fractionation. All of these curves have positive slopes. This means that, at any particular pressure, the higher we make the temperature, the greater we can make the "distillate" fraction and the lower we make the "bottom" (oxygen-containing) fraction because higher temperatures increase the extent of dissociation. The temperatures at which the isobars cross the horizontal axis are limiting low temperatures. As these temperatures are approached, the fraction drawn off (distillate fraction) approaches zero. Since the amount drawn off cannot approach zero, the feed rate required to maintain steady operation approaches infinity. The composition of the material on side x cannot provide us with a composition which, when effused through the membrane, will give us the required hydrogen production rate, no matter how fast we replenish it.

Figure 8 shows the mass flow rates into the reactor, $\dot{m}_1$, for various operating pressures and temperatures. At high temperatures, low feed rates can provide the reactor with a sufficiently dissociated working fluid that the material which effuses (even with the low pressure drops associated with low reactor pressures) is sufficiently enriched in hydrogen to maintain the required hydrogen production rate. As the temperature is reduced, the working substance is less dissociated; feed rate must be increased to prevent depletion of the relatively low concentrations of light components on side x. Eventually, as the temperature is reduced further still, mass flow through the membrane cannot be made high enough at the lower pressures to produce the requisite amount of hydrogen, no matter how high the flow rate of water substance into the reactor. Thus, very low pressures permit us to operate with low pumping rates at high temperatures, but at low temperatures the low pressures cannot be used because the flow rates through membranes will be too low.

Higher solar concentrations (compare sets I and II) give higher overall efficiencies at a particular temperature but engender the use of either higher operating temperatures or finer membranes. If smaller open-area fractions are required (compare sets I and III), higher temperatures and finer membranes will be required.

Figure 9 shows the mole fraction of gaseous hydrogen in the condensed, effused product. It increases with decreasing reactor pressure, but is relatively insensitive to reactor temperature. Since a mole fraction of hydrogen greater than 0.07 gives a volume fraction greater than 0.99, there will be very little liquid water (on a volume basis) to be separated from the product at any operating condition. These curves end at the temperature below which the operation is not possible.

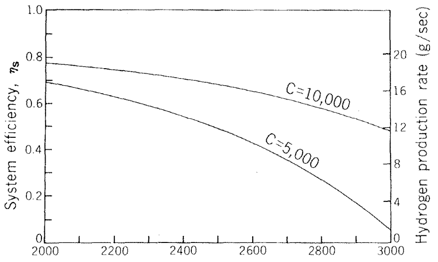


Fig. 6. System efficiencies and hydrogen production rates for sets I and III (C = 5000) and set II (C = 10,000).

Figure 10 shows corresponding operating temperatures and pressures at various values of $\dot{m}_3/\dot{m}_1$. Also shown are lines of constant wire thickness and mesh which would make membranes with square holes having side lengths one-tenth of the mean free paths (Knudsen numbers of 10).

Reference to Fig. 10a, for example, shows that 10-μm wire, woven into a 684-cm^{-1} mesh membrane, would be required for a diffusion membrane with a projected area of 0.56 m^2 operating at a temperature of 2400°K and a pressure of 0.055 atm, with one-tenth the mass of water being fed to the reactor being effused through the membrane. The mole fraction of hydrogen collected in the condensed product would be about 0.11 (Fig. 9a). The hydrogen production rate would be about 13 g/sec (Fig. 6) and the overall efficiency of the process would be about 0.55 (Fig. 6).

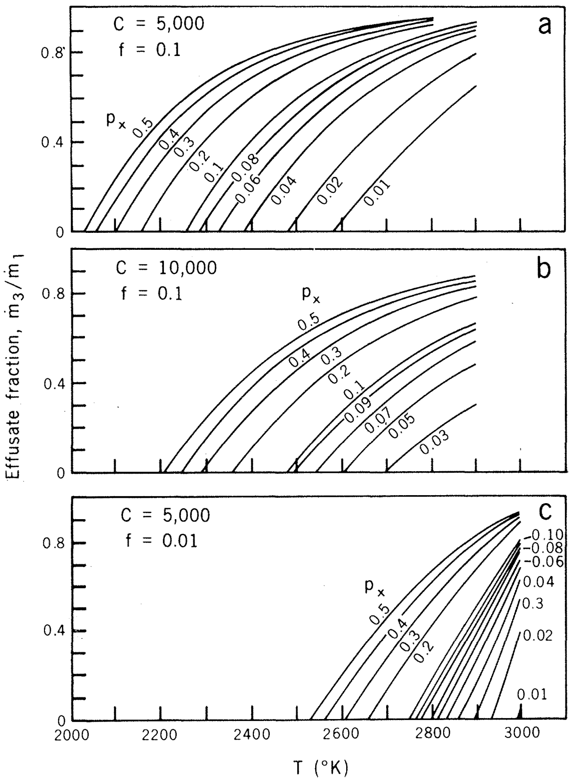
If the operating temperature were raised to 2500°K, 0.45 of the feedwater would be effused (Fig. 10a) and only about one-third as much water would have to be fed to the system as at 2400°K (Fig. 8a). The mole fraction of hydrogen in the condensed product would go down very slightly (Fig. 9a), the hydrogen production rate would go down to about 12 g/sec (Fig. 6), and the overall efficiency would go down to about 0.5 (Fig. 6). Even if a finer membrane could be made, so that operation at 2400°K and 0.2 atm were possible, the hydrogen production rate and overall efficiencies, being independent of pressure, would be the same as they were in the first example, 0.61 of the feedwater would be collected as effusate, but the pumping rate would be about the same. There would thus be no advantage in seeking a finer membrane in this case, unless it was required to achieve a good separation.

Figures 7c, 8c, 9c, and 10c illustrate the situation that would prevail if a smaller open-area fraction (0.01) were required for suitable separation. A membrane made of 10-μm wire woven into a 900-cm^{-1} mesh would have an open-area fraction of 0.01 and would permit operation at temperatures as low as 2650°K at a pressure of 0.26 atm with $\dot{m}_3/\dot{m}_1 = 0.1$. The overall efficiency would be about 0.39. The mole fraction of hydrogen in the condensate would be about 0.17, the hydrogen production rate would be about 9 g/sec, the oxygen production rate would be about 72 g/sec, and the rate of water flow to the reactor would be about 4 kg/sec.

A membrane having the same total area, open-area fraction, and hole size, made with 50-μm wire, would have a mesh of 180 cm^{-1}, but it would require operation at a pressure of about 0.055 atm at a temperature of about 2850°K. The overall efficiency would now be about 0.20 and the hydrogen production rate about 5 g/sec. The mole fraction of hydrogen in the condensate would be 0.39, corresponding to a volume ratio of hydrogen to water of about 900, but because of the high temperature required, the feed rate would have to be only about 750 g/sec.

Discussion

The foregoing examples suggest that the effusional separation of hydrogen and oxygen from water at high temperatures, using solar energy, is a tantalizing possibility. In this article we have, as have the advocates of other types of processes, made optimistic, idealizing assumptions. To have done otherwise at this stage in its development would not have been fair to this idea. We have neglected irreversibilities associated with the effusion process as well as those associated with internal heat transfer processes. While the latter can, in principle if not in practice, be made vanishingly small, the former cannot. The irreversibilities associated with the effusion process will result ultimately in lost work, which will be (at least) equal to the entropy change associated with the separation process multiplied by the ambient temperature. We have not computed them here because their computation requires a more detailed model and more information than we now have (*22*). In practice, they might become disappointingly large, especially if high pressure ratios and mass flow rates through the membrane are required. At this time, the points made by Shinnar (*23*) in response to Wentorf and Hanneman (*1*) and Chao (*3*) are most pertinent. Irreversibilites are the most dominant factors in determining



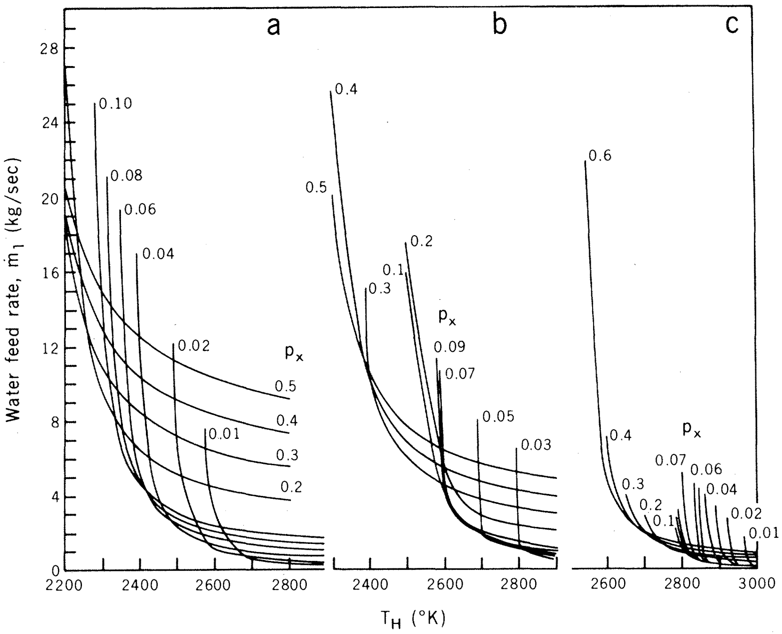
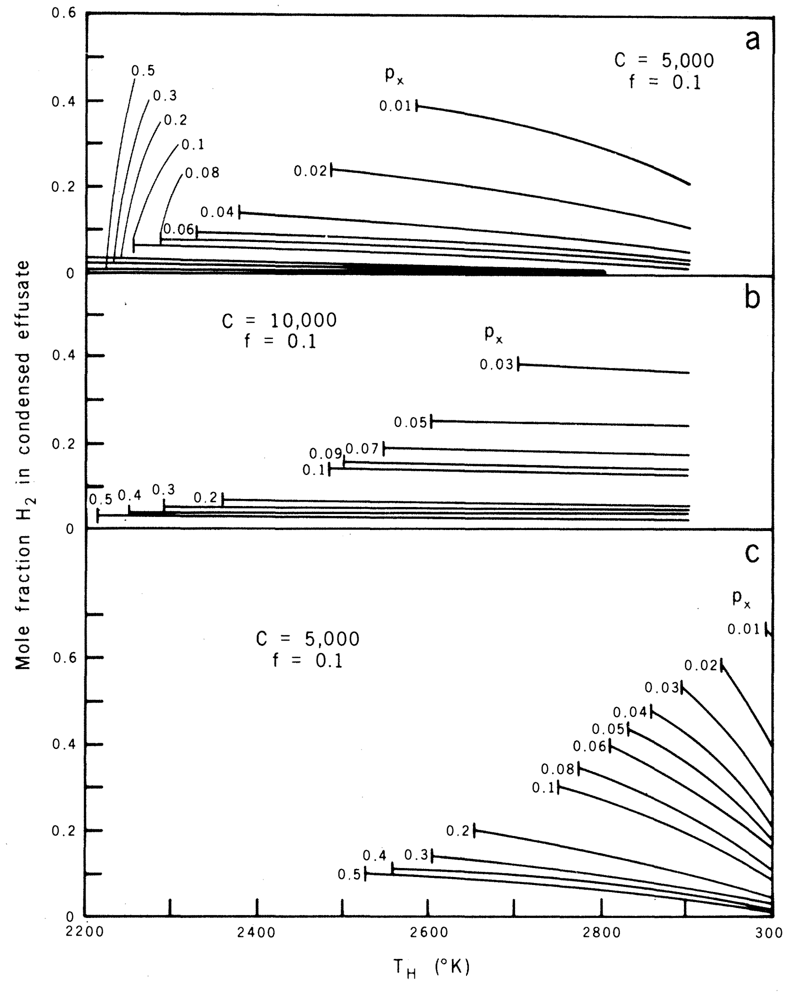


Fig. 7 (left). Variation of effused fraction, $\dot{m}_3/\dot{m}_1$, with temperature for various upstream pressures. (a) Set I: C = 5000; f = 0.1. (b) Set II: C = 10,000; f = 0.1. (c) Set III: C = 5000; f = 0.01. Fig. 8 (right). Variation of the feed rate of water to the reactor with temperature for various upstream pressures. (a) Set I. (b) Set II. (c) Set III.



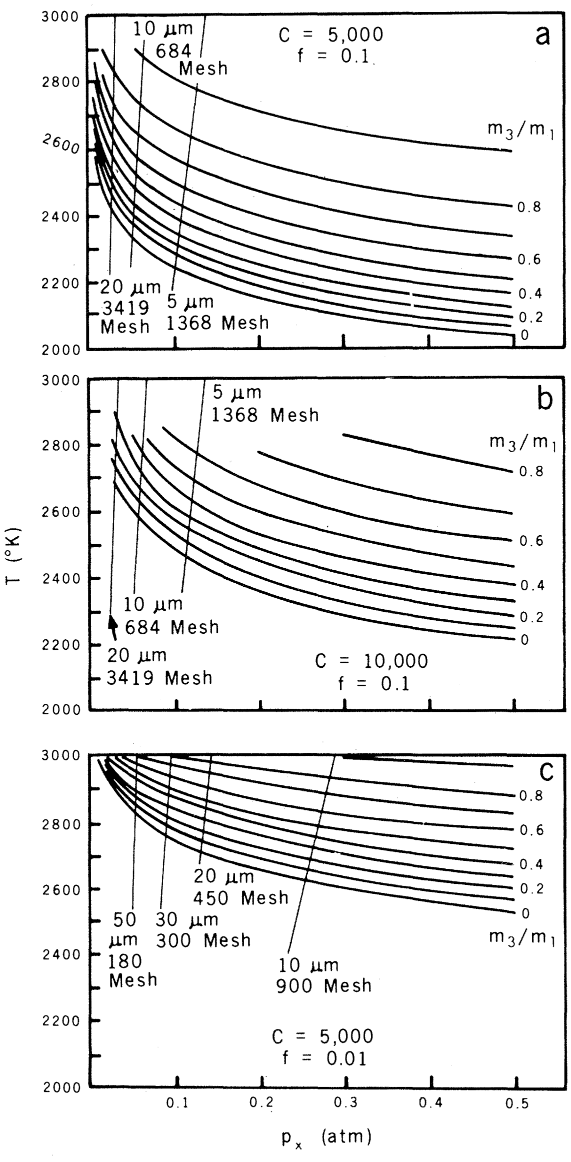


Fig. 9 (left). Variation of the mole fraction of hydrogen in the cooled product with reactor temperature for various upstream pressures. These lines terminate at the lowest temperature at which the system can operate. (a) Set I. (b) Set II. (c) Set III. Fig. 10 (right). Temperature and pressure regimes in which the system functions with various effused fractions ($\dot{m}_3/\dot{m}_1$). Wire diameters and meshes of screen-like membranes which have hole widths equal to one-tenth of the mean free paths in these temperature-pressure regimes are also shown.

the economic feasibility of any such proposed system and should be kept in mind in the evaluation of all such processes. However, the mechanics of this one-step process are quite simple. These losses are not likely to be as great as they will be for multistep processes. It may be that clever design and arrangements of components will permit us to reduce reradiation losses, making this portion of our analysis unduly pessimistic. The idea is worthy of further consideration and may even acquire economic and social value in the future.

Summary

The limitations of thermochemical energy storage devices are the limitations of Carnot devices. Entropy production entailed in product separation further limits the efficiency of thermochemical processes. Thus, high upper temperatures and few reaction steps are desirable. In this article, the one-step effusional separation of water into hydrogen and oxygen is considered. Membrane materials, design, and fabrication techniques are suggested. A parametric analysis of the process suggests that the idea is a tantalizing possibility.

References and Notes

→ R. H. Wentorf, Jr., and R. E. Hanneman, *Science* **185**, 311 (1974).
2. J. Funk and R. Reinstrom, *Ind. Eng. Chem. Prod. Res. Dev.* **5** (No. 3), 336 (1966); A. Broggi, G. DeBeni, D. VanVelzen, paper presented at the First World Hydrogen Energy Conference, Miami Beach, Fla., 1 to 3 March 1976.
3. R. E. Chao, *Ind. Eng. Chem. Prod. Res. Dev.* **13** (No. 2), 94 (1974).
4. Such conclusions have usually been based on unnecessarily restrictive assumptions, which implied that continuous extraction of products from the reaction site would not be used. Wentorf and Hanneman (*1*) recognized this.
5. F. Trombe, A. Le Phat Vinh, C. Royere, in *Large Scale Energy Test Facilities, Proceedings of the NSF International Seminar*, H. C. Connell, Ed. (New Mexico State University, Las Cruces, 1974), p. 139.
6. J. B. Pangborn and J. C. Sharer, in *Hydrogen Energy*, T. N. Veziroglu, Ed. (Plenum, New York, 1975), part A, pp. 449–475.
7. B. M. Abrahani and F. Schreiner, *Ind. Eng. Chem. Fundam.* **13** (No. 4), 305 (1974).
8. J. D. Henry, Jr., in *Chemical Engineers Handbook*, R. H. Perry and C. H. Chilton, Eds. (McGraw-Hill, New York, ed. 5, 1973), pp. 17–44.
9. S. Villani, *Isotope Separation* (American Nuclear Society, Hinsdale, Ill., 1976).
10. Iridium might be resistant to chemical attack by water substance in the temperature range of interest (R. Yu and E. A. Fletcher, unpublished results).
11. The catalog of the Unique Wire Weaving Company, Inc., lists a specially woven tungsten cloth with 10 by 472 wires per centimeter and a stock stainless steel cloth with 157 by 984 wires per centimeter.
12. S. J. Schneider [*Natl. Bur. Stand. (U.S.) Monogr. 68* (1963)] suggests a number of possibilities, such as zirconia, urania, and yttria.
13. R. Diver and E. A. Fletcher, unpublished results; R. Diver, thesis, University of Minnesota (1977).
14. A 1975 price schedule of the Buckbee-Mears Company lists electroformed mesh of 787 wires per centimeter made of 6.35-μm wires to give an open-area fraction of 0.22. This mesh is 2.5 to 5 μm thick.
15. The suggestion that sputtering might be used to protectively coat refractory metals such as tungsten and molybdenum for this purpose was first made to us by W. G. Shepherd.
16. J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1949), p. 20.
17. The program is designed for on-line user interaction with the computer. It is described in R. Moen, thesis, University of Minnesota (1976).
18. Actually, additional dissociation which occurs as the effusate passes through the membrane to side y tends to reduce the temperature on side y. The overall energy balance appropriate to this model has already been presented. We cannot now make a detailed energy balance across the membrane because we do not know enough about the magnitudes of pertinent transport coefficients and reactions rates. The assumption that the effused gas is in a state of chemical equilibrium at T_H and p_y implies that chemical reaction rates and heat transfer rates are both very high.
19. L. Loeb, *The Kinetic Theory of Gases* (McGraw-Hill, New York, 1934), p. 302.
20. The tabulated equilibrium constants given by V. N. Huff, S. Gordon, and V. E. Morrell [*Natl. Advis. Comm. Aeronaut. Rep. 1037* (1951)] were fitted to polynomials in T for these calculations.
21. If the open area of the membrane is too small, for example, to permit the flow of enough effusate to yield the amount of hydrogen required by the energy balance, the system will not be stable. The membrane will overheat and be destroyed.
22. An estimate of the irreversibility associated with the separation process may be made by calculating the entropy change (ΔS) associated with it. There are many ways the reactor might be run, and many different avenues of heat transfer within the reactor and separator which might be selected. Since all of the governing equations are linked, each of these requires a separate, iterated, time-consuming solution. However, we can use the example of Fig. 5b to illustrate how this problem may be handled. The overall system efficiency, with irreversibilities neglected, is 0.58. If the effusion barrier permits the flow of gas, carrying its energy, but not the flow of heat, the effused gas, finding itself at a lower pressure, will dissociate some more, reducing its temperature from 2300° to about 2265°K, and will acquire a composition corresponding to chemical equilibrium at its new temperature and pressure. The entropy produced by the separation process can be calculated from the difference between the entropies of the two product streams, the entropy of the reactant stream, and the concomitant heat flow into the reactor. For the example given, this comes to 68.62 calories per degree Kelvin per mole of hydrogen produced. The lost work, $T_L\Delta S$, is 68.62 × 300 calories. Thus, at this operating condition, the production of 1 mole of hydrogen, equivalent to 56.69 kilocalories of work, entails the irrevocable loss of 20.59 kilocalories, even for the otherwise reversible process. The maximum overall efficiency is thus reduced from 0.58 to 0.37. If the device were made to operate with a smaller pressure drop (it was 90 percent in this example), the loss would be smaller.
23. R. Shinnar, *Science* **188**, 1036 (1975).
24. J. A. Duffie and W. A. Beckman, in *Solar Energy Thermal Processes* (Wiley, New York, 1974), p. 178.
25. We thank R. S. Fletcher, who conducted a literature search for us while she was on sabbatical leave from Metropolitan Community College, Minneapolis, and was a constant source of enthusiastic encouragement. W. G. Shepherd stimulated many lively discussions and, with G. W. Fornell, helped us get funding from the University of Minnesota. R.L.M. was supported by a Solar Energy Traineeship grant to the University of Minnesota from the National Science Foundation.

Secondary Sewage Treatment Versus Ocean Outfalls: An Assessment

Charles B. Officer and John H. Ryther

About one-third of the population of the United States lives or works close to estuarine and coastal waters (*1*). Understandably, there is concern about disposal of municipal and industrial wastes in the waterways adjacent to the larger metropolitan coastal communities—concern about how much and what types of waste can be assimilated by these waters and about what corrective actions should be taken to improve their quality.

These are not easy problems to solve. They require appropriate contributions from the marine sciences of physical oceanography, biology, chemistry, and geology as well as the related branches of civil engineering. The Environmental Protection Agency, under the terms of its enabling legislation, has taken the position that the solution shall be in the construction of secondary sewage treatment facilities (*2*). However, environmental scientists and engineers alike have argued that secondary treatment of wastewater is unneeded and ineffective if discharges are made into open coastal waters, where there is adequate mixing, dilution, and advection to prevent oxygen depletion, eutrophication, and other adverse effects resulting from high concentrations of organic wastes (*3–6*).

Generally, there is agreement among environmentalists and the practitioners of waste disposal that untreated sewage should not be discharged into harbors, estuaries, or other confined coastal ma-