

## CHAPTER 4

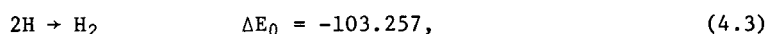
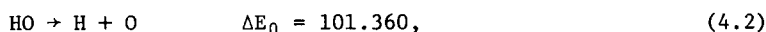
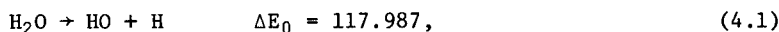
# DIRECT THERMAL DECOMPOSITION OF WATER

### 4-1 INTRODUCTION

When water is heated to a very high temperature, some of the water vapour dissociates into hydrogen and oxygen. If we can separately extract these dissociated products, it may be possible to utilize the reaction for producing hydrogen. The use of this direct thermal splitting of water for hydrogen production utilizing solar energy was suggested by Ford and Kane [1] in 1971. Subsequently, critical comments [2-4] and more detailed conceptual studies [5-8] on such process have appeared in the literature. A generalized conclusion of the literature shows that the major problem area of research and development on the process will be the method of separation of hydrogen and oxygen, and the materials capable of withstanding high temperatures. Various ideas have been proposed in an attempt to solve these problems, and several of them are presently being investigated and are showing some promise. However, our present available information is not enough to make a comprehensive design of a hydrogen production plant by this process, and our present ability is limited to the discussion of feasibility through a simplified thermodynamic consideration. This chapter describes the thermodynamics of the process of direct thermal splitting of water, and examines the related concepts which may make the process practically operable for solar energy utilization.

### 4-2 THERMODYNAMICS OF THE PROCESS

*Dissociation of water.* The simple dissociation of water may be regarded as that it proceeds in two steps. The first step is the dissociation of  $H_2O$  into  $HO$  and  $H$ , and the second one is that of  $HO$  into  $H$  and  $O$ . As the heat source to be considered here is the terrestrial solar thermal energy, the maximum attainable temperature will be lower than 6000 K. In such temperatures ionization of hydrogen and oxygen can be neglected for the first approximation, whereas the association of atomic particles,  $H$  and  $O$ , into molecular particles,  $H_2$  and  $O_2$ , must be taken into account. We thus begin by assuming that the dissociated water vapour system is such that it may be treated with the four reaction equations containing the six gas particle components written by



$$2O \rightarrow O_2 \quad \Delta E_0 = -117.973, \quad (4.4)$$

where  $\Delta E_0$  kcal/mol is the zero point energy change calculated from the zero point energy of the products minus the zero point energy of the reactants referring to their standard states. The values of zero point energy  $E_0$  used in the calculation are the standard state enthalpies at 0 K found in thermochemical tables, and are -60.165, 7.206, 50.617, 57.949, -2.024, and -2.075 kcal/mol for  $H_2O$ ,  $HO$ ,  $H$ ,  $O$ ,  $H_2$ , and  $O_2$ , respectively.

If the partition functions for all components and  $\Delta E_0$  of the reactions are known, the equilibrium constant of each reaction can be determined. The pressure equilibrium constant,  $K$ , of a gas reaction is related to the partition functions for the standard states of unit pressure,  $Q_p$ , and  $\Delta E_0$  by

$$\ln K = -\frac{\Delta E_0}{RT} + \sum b_i \ln Q_p(B_i) - \sum a_i \ln Q_p(A_i), \quad (4.5)$$

where  $R$  is the universal gas constant of 1.987 cal/mol,  $T$  is the absolute temperature, and  $a_i$  and  $b_i$  are the stoichiometric coefficients for the gas particles of  $A_i$  and  $B_i$ .

*Partition functions.* All of the thermodynamic quantities of a gas or a gas mixture can be expressed in terms of the partition function. Therefore, it will be significant to introduce first the partition functions of the six gas particle components in the dissociated water vapour. The definitions of the partition functions may be found in standard texts on statistical mechanics, and the required partition function constants can be taken from the references such as [9] and [10].

For the temperatures being considered here, the partition function  $Q$  is usually separated into a product of the four factors  $Q = Q_t Q_r Q_v Q_e$ , where the factors are the partition functions associated with the translational ( $Q_t$ ), rotational ( $Q_r$ ), vibrational ( $Q_v$ ), and electronic ( $Q_e$ ) energy levels of the gas particle. For the monatomic particles,  $H$  and  $O$ , which have no rotational or vibrational contribution to the partition function,  $Q_r$  and  $Q_v$  take the value unity. Similarly, the electronic contribution to the partition function is negligible for  $H_2O$  and  $H_2$ , and we have  $Q_e = 1$  for these molecules in very good approximation. Thus, the total partition functions are  $Q = Q_t Q_r Q_v Q_e$  for  $HO$  and  $O_2$ ,  $Q = Q_t Q_r Q_v$  for  $H_2O$  and  $H_2$ , and  $Q = Q_t Q_e$  for  $H$  and  $O$ . The logarithms of the approximated total partition functions have been given in reference [11] as

$$\begin{aligned} \ln Q(H_2O) = & 4 \ln T - 4.1164 - \ln(1 - e^{-5262/T}) - \ln(1 - e^{-2294/T}) \\ & - \ln(1 - e^{-5404/T}) - \ln P, \end{aligned} \quad (4.6)$$

$$\begin{aligned} \ln Q(HO) = & 2.5 \ln T + 1.2787 + \ln(T/26.638 + 1/3 + 1.776/T) \\ & - \ln(1 - e^{-5136/T}) + \ln(1 + e^{-201/T}) - \ln P, \end{aligned} \quad (4.7)$$

$$\ln Q(H) = 2.5 \ln T - 2.9604 - \ln P, \quad (4.8)$$

$$\begin{aligned} \ln Q(O) = & 2.5 \ln T + 0.4939 + \ln(5 + 3e^{-228/T} + e^{-326/T} \\ & + 5e^{-22830/T}) - \ln P, \end{aligned} \quad (4.9)$$

$$\begin{aligned} \ln Q(H_2) = & 2.5 \ln T - 2.6133 + \ln\{T/682.6 + 1/24 + 0.711/T + 104/T^2 \\ & + (T/227.53 + 0.875 + 87.458/T + 6136.3/T^2) \times e^{-171/T}\} \end{aligned}$$

$$+ \ln\{(1 - e^{-6338/T})^{-1} + (360.65/T) \times e^{-6338/T} \times (1 - e^{-6338/T})^{-3}\} - \ln P, \quad (4.10)$$

$$\ln Q(O_2) = 3.5 \ln T + 0.114 - \ln(1 - e^{-2239/T}) + \ln(3 + 2e^{-11340/T} + e^{-18878/T}) - \ln P, \quad (4.11)$$

where P is the pressure and is given in atmospheres.

According to statistical mechanics, the enthalpy H, entropy S, and free energy G per mol of each gas are calculated by the following relations:

$$\frac{H - E_0}{RT} = T \left( \frac{\partial \ln Q}{\partial T} \right)_P, \quad (4.12)$$

$$\frac{S}{R} = \ln Q + T \left( \frac{\partial \ln Q}{\partial T} \right)_P, \quad (4.13)$$

$$G = H - TS. \quad (4.14)$$

Also, the specific heat per mol at constant pressure can be calculated by definition  $C_p = (\partial H / \partial T)_P$ . The equilibrium thermodynamic quantities for the dissociated water vapour are determined by the sum of the contribution from each component proportional to the equilibrium mol fraction, and by the effect of mixing of the components. Hence the equilibrium composition must be calculated.

*Equilibrium composition.* In order to calculate the equilibrium mol fractions of the components, it is necessary to determine the equilibrium constants of  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$ , respectively, for the reaction equations of (4.1), (4.2), (4.3), and (4.4). Putting the pressure  $P$  as unity in Eqs. (4.6) to (4.11) and substituting the results into Eq. (4.5), we have logarithms of the four pressure equilibrium constants as the functions only of temperature. The calculated equilibrium constants are listed as functions of temperature in Table 4.1.

According to the definition of pressure equilibrium constant, we can write

$$K_1 = PX_2X_3/X_1, \quad (4.15)$$

$$K_2 = PX_3X_4/X_2, \quad (4.16)$$

$$K_3 = X_5/PX_3^2, \quad (4.17)$$

$$K_4 = X_6/PX_4^2, \quad (4.18)$$

where X stands for the mol fraction and its subscripts 1, 2, 3, 4, 5, and 6 designate  $H_2O$ ,  $HO$ ,  $H$ ,  $O$ ,  $H_2$  and  $O_2$ , respectively. From the law of partial pressure, and from that the total number of hydrogen atoms is twice that of oxygen, we have

$$\sum_1^6 PX_i = P, \quad (4.19)$$

$$\frac{2X_1 + X_2 + X_3 + 2X_5}{X_1 + X_2 + X_4 + 2X_6} = 2. \quad (4.20)$$

Equations (4.15) to (4.20) are the simultaneous equations of six unknowns for a given temperature and pressure, and the solutions can be obtained by numerical calculation. The mol fractions which have been calculated from the preceding

TABLE 4.1 Logarithms of the Pressure Equilibrium Constants,  $\ln K$ , for the Reactions in Dissociated Water

T(K)	H <sub>2</sub> O → H <sub>2</sub> +O	HO → H+O	2H → H <sub>2</sub>	2O → O <sub>2</sub>
1000	-45.91015	-39.62788	39.79906	45.15716
1100	-40.34330	-34.85006	34.93147	39.62685
1200	-35.69561	-30.85870	30.86473	35.01211
1300	-31.75621	-27.47341	27.41512	31.10244
1400	-28.37426	-24.56518	24.45124	27.74730
1500	-25.43899	-22.03927	21.87664	24.83621
1600	-22.86720	-19.82454	19.61890	22.28625
1700	-20.59518	-17.86649	17.62254	20.03396
1800	-18.57331	-16.12269	15.84438	18.02993
1900	-16.76237	-14.55961	14.25028	16.23516
2000	-15.13095	-13.15035	12.81289	14.61841
2100	-13.65357	-11.87315	11.51002	13.15436
2200	-12.30937	-10.71014	10.32352	11.82230
2300	-11.08111	-9.64658	9.23836	10.60511
2400	-9.95438	-8.67013	8.24200	9.48852
2500	-8.91709	-7.77044	7.32390	8.46050
2600	-7.95899	-6.93874	6.47512	7.51092
2700	-7.07134	-6.16753	5.68804	6.63109
2800	-6.24662	-5.45041	4.95612	5.81359
2900	-5.47839	-4.78181	4.27372	5.05201
3000	-4.76101	-4.15693	3.63594	4.34078
3100	-4.08961	-3.57159	3.03851	3.67507
3200	-3.45990	-3.02210	2.47768	3.05063
3300	-2.86810	-2.50524	1.95017	2.46372
3400	-2.31090	-2.01816	1.45308	1.91106
3500	-1.78534	-1.55831	0.98381	1.38971
3600	-1.28881	-1.12346	0.54008	0.89708
3700	-0.81896	-0.71160	0.11985	0.43086
3800	-0.37369	-0.32092	-0.27872	-0.01104
3900	0.04886	0.05019	-0.65728	-0.43048
4000	0.45041	0.40319	-1.01732	-0.82913
4100	0.83247	0.73939	-1.36016	-1.20853
4200	1.19644	1.05998	-1.68703	-1.57003
4300	1.54356	1.36604	-1.99903	-1.91488
4400	1.87499	1.65855	-2.29715	-2.24422
4500	2.19176	1.93841	-2.58232	-2.55909
4600	2.49482	2.20643	-2.85536	-2.86042
4700	2.78505	2.46337	-3.11705	-3.14907
4800	3.06324	2.70992	-3.36807	-3.42585
4900	3.33013	2.94670	-3.60909	-3.69147
5000	3.58639	3.17429	-3.84069	-3.94661
5100	3.83265	3.39324	-4.06342	-4.19189
5200	4.06948	3.60403	-4.27778	-4.42787
5300	4.29741	3.80712	-4.48424	-4.65508
5400	4.51693	4.00294	-4.68324	-4.87402
5500	4.72850	4.19188	-4.87517	-5.08512
5600	4.93255	4.37431	-5.06041	-5.28882
5700	5.12947	4.55056	-5.23932	-5.48550
5800	5.31962	4.72096	-5.41220	-5.67553
5900	5.50335	4.88579	-5.57937	-5.85924
6000	5.68098	5.04533	-5.74111	-6.03696

equations are listed in Table 4.2.

The molecular weight,  $M$ , of the dissociated water is the sum of the molecular weight of each component multiplied by its mol fraction:

$$M = 18.016X_1 + 17.007X_2 + 1.008X_3 + 16.000X_4 + 2.016X_5 + 31.999X_6, \quad (4.21)$$

where the coefficients are the molecular weights in g/g-mol. The total number of molecules resulting from the thermal dissociation of 1 g-mol of water is calculated from  $N = 18.016/M$ . Therefore, the concentration of each component in an isobaric dissociation system is

$$N_i = \frac{18.016}{M} X_i, \quad (4.22)$$

where  $N_i$  is the concentration of the component designated by the subscript  $i$ , which corresponds to that of  $X_i$ , and the unit is in moles. Figure 4.1 illustrates the calculated molar concentrations for the pressure of 0.1, 1, and 10 atmospheres.

The calculated results shown in Table 4.2 and Fig. 4.1 indicate that the dissociated products increase with increasing temperature. For pressure of 1 atm, for example, about 1 per cent of water vapour is dissociated at 2000 K, and it reaches 36 per cent at 3000 K. Another important indication of the calculated results, which can also be intuitively expected from Le Chatlier's law, is that the dissociated products increase with decreasing pressure. It may be pointed out as a rule of thumb for the temperatures lower than 3000 K over a range of pressure from 0.01 to 100 atmospheres that, roughly twofold of water vapour dissociates when the total pressure is decreased by an order of magnitude.

The same pressure-equilibrium relations apply for reduced water partial pressure. It then can be suggested to use a diluent inert gas to obtain a low water partial pressure without making the total pressure too low. However, the inert diluent may not be helium since it seems to be difficult to separate hydrogen from helium. Even if we reduce the total pressure or the water partial pressure to about 0.1 atm, the theoretical equilibrium conversion of water to hydrogen at 2000 K is only a few per cent. This might lead one to think that a direct thermal decomposition requires extremely high temperature such as 3000 to 4000 K. But it is possible to obtain substantial amount of hydrogen at temperatures considerably lower than 2000 K by removing the dissociated products, hydrogen and oxygen, continuously from the dissociation site. As shown later, this comparatively low temperature process requires a large amount of work input.

*Net energy requirements.* It is now possible to estimate the net amount of energy required by the process to produce hydrogen from water. We consider the case of an isobaric and isothermal process, and the energy is calculated for the reactant,  $H_2O$ , 1 g-mol at 298 K.

According to the elementary thermodynamics, enthalpy, entropy, and free energy of the dissociated water vapour are given by

$$H_r = \sum_1^6 N_i H_i, \quad (4.23)$$

$$S_r = \sum_1^6 (N_i S_i - R N_i \ln X_i), \quad (4.24)$$

$$G_r = H_r - T S_r, \quad (4.25)$$

where the subscript  $r$  designates the reactant  $H_2O$ , and the second term in the parentheses in Eq. (4.24) means the entropy of mixing of dissociated components.

TABLE 4.2 Mol fraction of the components in the dissociated water vapour.

MOL FRACTIONS AT P= 0.1000ATM						
T(K)	H <sub>2</sub> O	HO	H	O	H <sub>2</sub>	O <sub>2</sub>
1000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1500	0.99930	0.00008	0.00000	0.00000	0.00043	0.00019
2000	0.97727	0.00452	0.00058	0.00015	0.01236	0.00512
2500	0.88627	0.04597	0.02351	0.00825	0.08382	0.03217
3000	0.32170	0.12723	0.21637	0.09206	0.17760	0.06506
3500	0.02183	0.06746	0.54285	0.26158	0.07882	0.02746
4000	0.00057	0.01384	0.64464	0.32141	0.01503	0.00451
4500	0.00002	0.00315	0.66175	0.33092	0.00331	0.00085
5000	0.00000	0.00093	0.66523	0.33268	0.00095	0.00021
MOL FRACTIONS AT P= 1.0000ATM						
T(K)	H <sub>2</sub> O	HO	H	O	H <sub>2</sub>	O <sub>2</sub>
1000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1500	0.99968	0.00004	0.00000	0.00000	0.00020	0.00009
2000	0.98955	0.00211	0.00013	0.00003	0.00560	0.00239
2500	0.91130	0.02306	0.00530	0.00184	0.04258	0.01593
3000	0.64372	0.09286	0.05932	0.02451	0.13349	0.04611
3500	0.23103	0.14890	0.26026	0.12043	0.18117	0.05821
4000	0.02808	0.08611	0.51155	0.25194	0.09462	0.02770
4500	0.00194	0.02788	0.62208	0.31135	0.02926	0.00750
5000	0.00016	0.00893	0.65276	0.32694	0.00915	0.00207
MOL FRACTIONS AT P= 10.0000ATM						
T(K)	H <sub>2</sub> O	HO	H	O	H <sub>2</sub>	O <sub>2</sub>
1000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1500	0.99985	0.00002	0.00000	0.00000	0.00009	0.00004
2000	0.99517	0.00098	0.00003	0.00001	0.00270	0.00111
2500	0.95926	0.01105	0.00116	0.00040	0.02053	0.00759
3000	0.83048	0.05087	0.01397	0.00570	0.07404	0.02495
3500	0.56321	0.12442	0.07593	0.03449	0.15421	0.04774
4000	0.24746	0.16973	0.22875	0.11105	0.18919	0.05382
4500	0.06163	0.13004	0.42423	0.21296	0.13605	0.03509
5000	0.01022	0.06603	0.55873	0.28255	0.06705	0.01542
MOL FRACTIONS AT P= 100.0000ATM						
T(K)	H <sub>2</sub> O	HO	H	O	H <sub>2</sub>	O <sub>2</sub>
1000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1500	0.99993	0.00000	0.00000	0.00000	0.00004	0.00002
2000	0.99776	0.00046	0.00001	0.00000	0.00126	0.00052
2500	0.98120	0.00520	0.00025	0.00009	0.00969	0.00356
3000	0.92109	0.02525	0.00312	0.00127	0.03696	0.01231
3500	0.78449	0.07184	0.01832	0.00826	0.08973	0.02736
4000	0.56944	0.13703	0.06520	0.03145	0.15371	0.04317
4500	0.33093	0.18523	0.15992	0.08047	0.19334	0.05011
5000	0.14817	0.18329	0.29187	0.15015	0.18297	0.04356

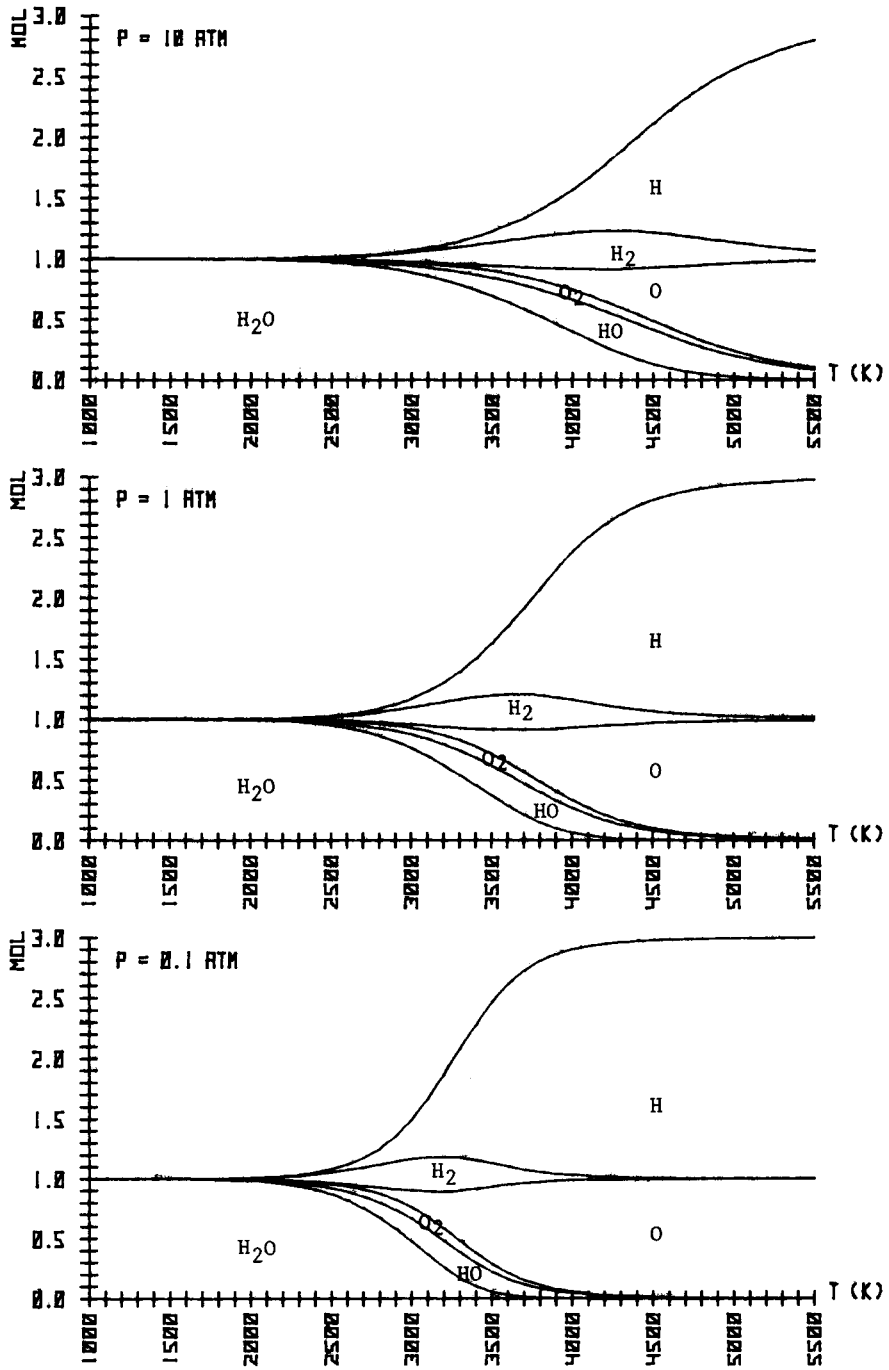


Fig. 4.1. Concentrations of the components in the dissociated water vapour.

The enthalpy and entropy of each component are calculated from Eqs. (4.12) and (4.13). In the same way, we can write the thermodynamic functions for the products separated from the reactant as

$$H_p = \sum_3^6 n_i H_i, \quad (4.26)$$

$$S_p = \sum_3^6 n_i S_i - S_m, \quad (4.27)$$

$$G_p = H_p - TS_p, \quad (4.28)$$

where the subscript p designates the product, and  $n_i$  is the concentration of the product of i species. The second term on the right side of Eq. (4.27) means the entropy of mixing, and is given by

$$S_m = -R \left( n_3 \ln \frac{n_3}{n_3 + n_5} + n_5 \ln \frac{n_5}{n_3 + n_5} + n_4 \ln \frac{n_4}{n_4 + n_6} + n_6 \ln \frac{n_6}{n_4 + n_6} \right).$$

Thus, it is necessary to calculate the concentrations of monatomic and diatomic hydrogen,  $n_3$  and  $n_5$ , and those of monatomic and diatomic oxygen,  $n_4$  and  $n_6$ . To determine those, we solve independently Eqs. (4.17) and (4.18) each with  $X_3 + X_5 = 1$ , and  $X_4 + X_6 = 1$ ; then using the expressions similar to Eqs. (4.21) and (4.22), we obtain  $n_3 = 2.016X_3/(1.008X_3 + 2.016X_5)$ ,  $n_5 = 2.016X_5/(1.008X_3 + 2.016X_5)$ ,  $n_4 = 32X_4/(16X_4 + 32X_6)$ , and  $n_6 = 32X_6/(16X_4 + 32X_6)$ . The thermodynamic quantities per fixed mass of product are needed for our purpose, so that the mass of a mol of undissociated hydrogen (2.016 g) and the mass of a half mol of undissociated oxygen (16 g) are used here as the constant reference quantities.

The calculated results for the enthalpy of reactant,  $H_r$ , and for the enthalpy of products,  $H_p$ , are plotted in Fig. 4.2 as functions of temperature for the total pressures of 0.1, 0.3, 1, 3, 10, and 30 atm. The standard state enthalpy of water at 298 K is 68.3 kcal/mol, and the vertical distances between this value and the lower solid curves, which show the enthalpy of reactant  $H_r$ , at any temperature on the abscissa indicate the required thermal energy for heating water to that temperature. The vertical distance between  $H_p$  and  $H_r$  of the same pressure is the enthalpy change in going from the initial state, the reactant, to the final state, the products.

It is seen that both  $H_r$  and  $H_p$  increase as the temperature is raised, and the increase corresponds to the increase in the total number of molecules and atoms in the dissociated water shown in Fig. 4.1. Conversely, the enthalpy change decreases with the increase in temperature until it reaches zero at the temperature where all of the components in the process are monatomic hydrogen and oxygen. This enthalpy change upon conversion of reactant into products can be expressed in terms of the change in entropy and free energy as

$$\Delta H = H_p - H_r = (G_p - G_r) + T(S_p - S_r) = \Delta G + T\Delta S. \quad (4.30)$$

Therefore, we can see the proportions of useful work,  $\Delta G$ , and heat,  $T\Delta S$ , to the net energy,  $\Delta H$ , required for producing stoichiometric products of hydrogen and oxygen from the dissociated water vapour. The relation between the required energy and temperature for the pressure of 1 atm is illustrated in Fig. 4.3 showing the proportions of useful work and heat by the broken line. For example, water heating from the room temperature to 2000 K entails an enthalpy change ( $\Delta H_r$ ) of 28.20 kcal per 18.016 g, and the production of hydrogen of 2.016 g and oxygen of 16 g from the heated water at this temperature involves an enthalpy change ( $\Delta H$ ) of 60.02 kcal of which 32.46 kcal has to be supplied as useful work ( $\Delta G$ ).



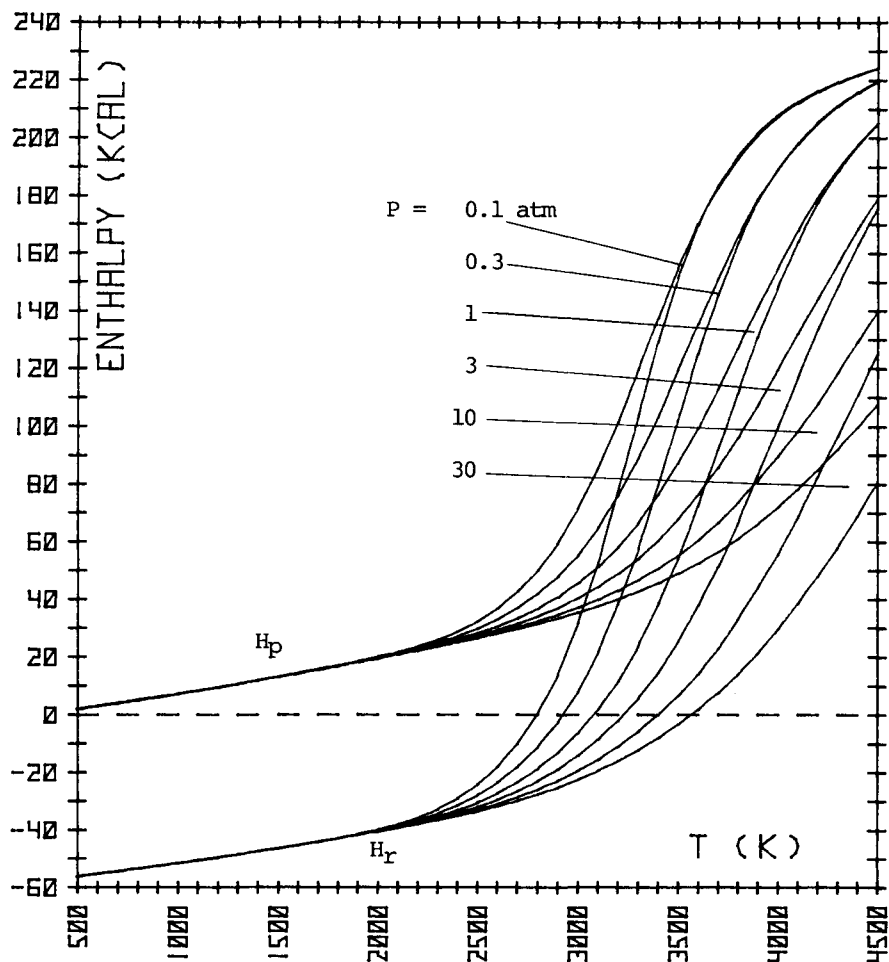


Fig. 4.2. Enthalpy-temperature diagram for the dissociated water of 18.016 g,  $H_R$ , and the dissociated hydrogen of 2.016 g plus dissociated oxygen of 16 g,  $H_P$ .

The useful work is the sum of the work of decomposition and the work of separation. The work of separation,  $W_S$ , may be expressed separately by calculating the difference of the entropy of mixing between the state of stoichiometric mixture of products and that of separated products as

$$W_S = T \left\{ S_m - R \sum_3^6 n_i \ln \left( \frac{n_i}{\sum_3^6 n_i} \right) \right\}. \quad (4.31)$$

It can be shown that  $W_S$  takes the value of about 1 to 15 kcal for the range of temperatures and pressures shown in Fig. 4.2, and the proportion of  $W_S$  in the useful work increases as the degree of dissociation of water becomes larger. At temperature above the temperature of complete dissociation, the work of decomposition equals zero and  $\Delta G$  equals  $W_S$ . In general, however, the work of decomposition and the work of separation would not necessarily be supplied independently. For example, it may be possible to obtain separated products by supplying electric

power as useful work in an electrolysis cell which contains high temperature water vapour.

Another example of useful work is selective pumping of hydrogen and oxygen from the reactant. An ideal isothermal work per reference quantities of products,  $W_i$ , is given by

$$W_i = \sum_3^6 n_i RT \ln(X_{pi}/X_i) = TS_m - RT \sum_3^6 n_i \ln X_i, \quad (4.32)$$

where  $X_{pi}$  is the mol fraction of  $i$  species in the product. It should be noted that the ideal work of pumping,  $W_i$ , is identical with the change in free energy,  $\Delta G$ , within the accuracy of calculation of mol fractions,  $X_{pi}$  and  $X_i$ .

*Thermodynamic efficiency.* Figure 4.4 shows an assumed diagram for the direct thermal decomposition process. The dissociator and separator accepts heat,  $Q$ , and work,  $W$ , at a high temperature,  $T$ , in an isothermal and isobaric condition. Produced hydrogen and oxygen are cooled through the heat exchanger which restores a part of heat,  $q_u$ , to the dissociator and rejects the rest of heat,  $q_r$ , at room temperature,  $T_0$ . Then the product gases are compressed consuming work,  $W_c$ , from the process pressure to some high pressure to be stored in a high pressure reser-

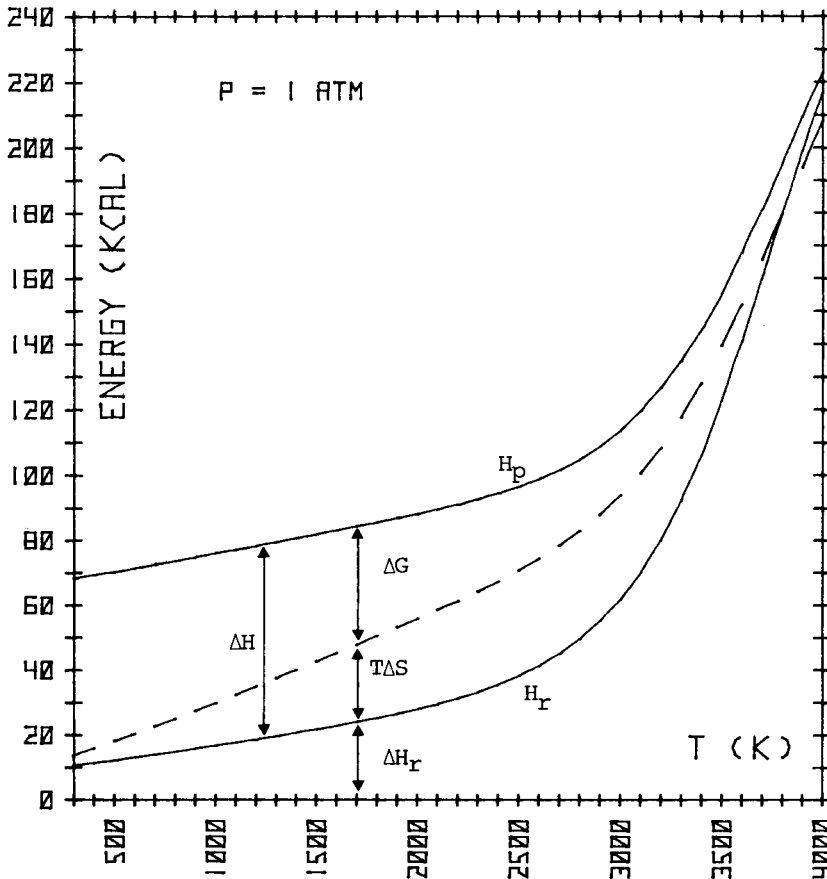


Fig. 4.3. Energy-temperature diagram for the production of hydrogen and oxygen from water.

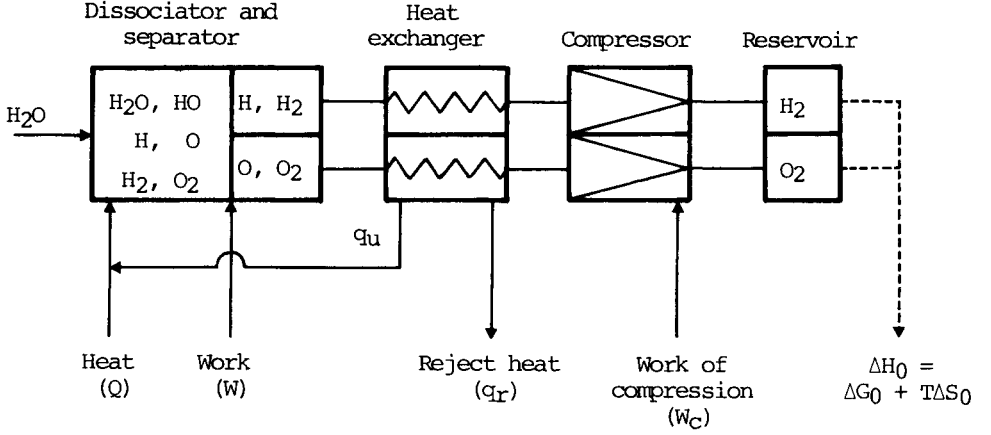


Fig. 4.4. Direct thermal splitting process diagram.

voir. The stored energy is the heat of formation of water,  $\Delta H_0$ , of 68.3 kcal/g mol  $H_2$  at 298 K and 1 atm, which is released upon combustion of the products. The thermodynamic efficiency of the process may be defined as

$$\eta_p = \frac{\Delta H_0}{Q + \frac{W}{\epsilon_1 \epsilon_2} + \frac{W_c}{\epsilon_1}}, \quad (4.33)$$

where  $Q$  is the thermal energy input,  $W$  the direct useful work input,  $W_c$  the work of compression of products,  $\epsilon_1$  the efficiency of converting thermal energy to work, and  $\epsilon_2$  the efficiency of work input. As discussed in the preceding section, it can be shown

$$W = \Delta G, \quad (4.34)$$

$$Q + q_u = Q + \Delta H_p - q_r = \Delta H_r + T\Delta S, \quad (4.35)$$

where  $\Delta H_p$  is the enthalpy change in cooling the products from the temperature of  $T$  to room temperature. From the first law of thermodynamics we may write

$$Q + W = \Delta H_0 + q_r = \Delta G_0 + T_0\Delta S_0 + q_r, \quad (4.36)$$

where  $\Delta G_0$  and  $\Delta S_0$  are 56.7 kcal/g mol and 0.039 kcal/g mol K, respectively, at 298 K and 1 atm. The lowest limit of the reject heat,  $q_r$ , is estimated from the second law of thermodynamics which may be written by

$$\frac{q_r + T_0\Delta S_0}{T_0} \geq \frac{Q}{T}. \quad (4.37)$$

Combining Eqs. (4.33) to (4.37) we obtain

$$\eta_p = \frac{\Delta H_0}{\Delta H_0 + q_r + \Delta G\left(\frac{1}{\epsilon_1 \epsilon_2} - 1\right) + \frac{W_c}{\epsilon_1}}, \quad (4.38)$$

$$q_r \geq \frac{T_0}{T - T_0}(\Delta H_r + T\Delta S - \Delta H_p) - \frac{T_0}{T - T_0}\Delta S_0, \quad (4.39)$$

in which  $\Delta H_p$  equals the value calculated for  $H_p$  since the enthalpy of the products at room temperature equals zero. If reciprocating machines are used to compress hydrogen and oxygen from the system pressure,  $P$ , to some high pressure,  $P_h$ , at room temperature, the work of compression,  $W_c$ , can be estimated from the theoretical work for an isentropic compression written by

$$w = kRT_0 \left\{ \left( \frac{P_h}{P} \right)^{1/k} - 1 \right\}, \quad k = \frac{\gamma}{\gamma - 1} \quad (4.40)$$

where  $\gamma$  is the polytropic index of expansion and compression, and takes the value of 1.405 for hydrogen and 1.395 for oxygen at room temperature. It is assumed in the later calculation that  $P_h$  is 30 atm, and that both hydrogen and oxygen are compressed. The efficiency of converting thermal energy to work,  $\epsilon_1$ , is usually estimated from the Carnot efficiency multiplied by a coefficient proper to a particular engine, and  $\epsilon_1 = 0.7(T - T_0)/T$  is assumed here. The efficiency of work input for pumping  $N_i$  moles of the  $i$  species from the partial pressure in the reactant of  $PX_i$  to the partial pressure in the product of  $PX_{pi}$  is defined as

$$\epsilon_i = \frac{N_i RT \ln \left( \frac{X_{pi}}{X_i} \right)}{N_i RT \ln \left( \frac{X_{pi}}{X_i} \right) + W_i}, \quad (4.41)$$

where  $W_i$  is the loss associated with frictional work independent of partial pressures. Other loss terms such as pressure drop and volumetric efficiency must be taken into account in a practical process design, and they may be related to the first term in the denominator of Eq. (4.41). If we neglect other losses except frictional loss, the work required for pumping the product of  $n_i$  moles can be written by  $(1/\epsilon_i)n_i RT \ln(X_{pi}/X_i)$ , so that the efficiency of work input,  $\epsilon_2$ , is given by

$$\epsilon_2 = \frac{\Delta G}{\sum_3 \left\{ n_i RT \ln \left( \frac{X_{pi}}{X_i} \right) + \frac{n_i}{N_i} W_i \right\}}. \quad (4.42)$$

Since the method for extracting products is not specified at present, the loss,  $W_i$ , can only be treated as a parameter. As an indication of the order of its magnitude, let us assume  $W_i = fRT = fPV$  where  $f$  is the nondimensional parameter, and  $V$  is the volumetric flow of gas of one mol.

The theoretical attainable efficiencies of the process which have been calculated from Eqs (4.38) and (4.39) are illustrated in Fig. 4.5 for the system pressure of 0.1, 1, and 10 atm and the delivery pressure of 30 atm. The solid curves in this figure show the calculated results for  $W_i = 0.01 RT$  ( $f = 0.01$ ), and the broken lines show the results for  $W_i = 0$  ( $f = 0$ ). The possibility of high efficiency of the process is seen at high temperatures, but the efficiency is influenced significantly by the loss due to frictional work especially at the temperatures lower than 2000 K. If the molar density of a gas to be pumped out from the reactant is very low, a great number of cycles of pumping operation must be repeated to obtain a unit mass of product. Thus, the frictional work has significant influence on the process efficiency.

Figure 4.6 is a plot of the process efficiency for the system pressure of 1 atm showing the influence of frictional loss of  $f = 0, 0.01, 0.1$ , and 1. It should be noted in Figs. 4.5 and 4.6 that even at temperatures between 1500 and 2000 K, in which only a small fraction of water dissociates as shown in Fig. 4.1, the thermodynamic efficiency of the process is considerably high. Probably, the actual efficiency in such temperature range would be much lowered if the volumetric efficiencies of conventional pumps are assumed, and if a large pressure drop through a certain device for selective extraction of products is considered. The effect of

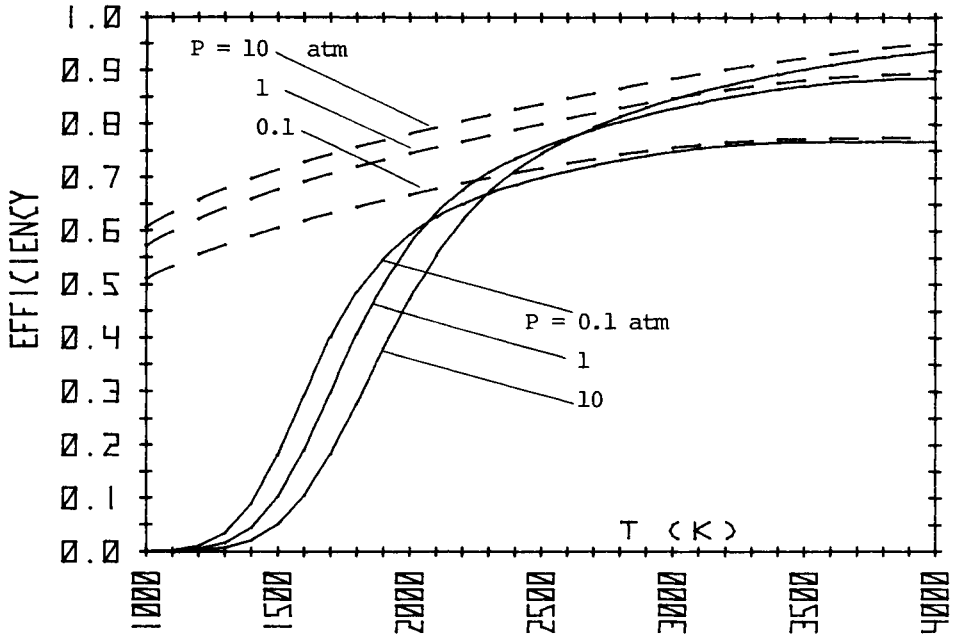


Fig. 4.5. Efficiency of the process,  $\eta_p$ , for the system pressure of  $0.1$ ,  $1$ , and  $10$  atm and the delivery pressure of  $30$  atm.

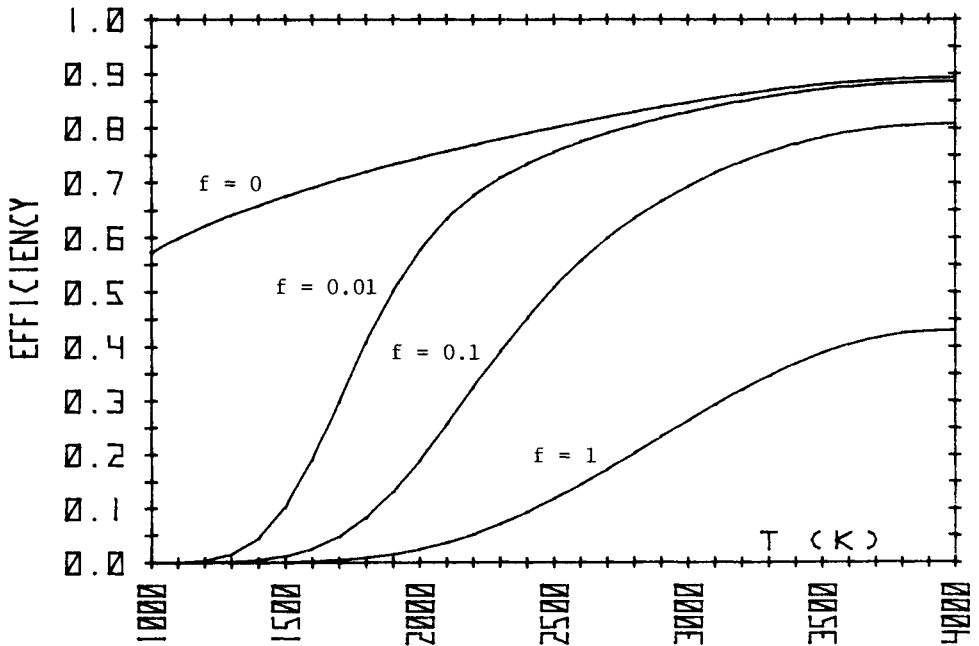


Fig. 4.6. Efficiency of the process,  $\eta_p$ , for the system pressure of  $1$  atm and delivery pressure of  $30$  atm. The  $f$  values on the curves are the loss factors of  $W_1 = fRT$  in Eq. (4.42).

these factors differ widely depending upon the scheme of products extraction, and they should be treated separately taking account of future possibilities.

#### 4-3 SOLAR THERMAL ENERGY

*Available heat flux.* As seen in the preceding section, operating temperatures of higher than 1500 K is desirable for the direct thermal decomposition process. In order to obtain such high temperature thermal energy, an optical system which concentrates solar radiation onto a small target can be utilized. In this section the required properties prevailing in the optical system producible of high power thermal energy at high temperatures will be evaluated.

The available energy,  $Q$ , from a solar concentrator is equated to the collected solar energy minus the radiation loss from the target [12],

$$Q = \alpha \eta_c E_0 A_1 - \epsilon \sigma T^4 A_r . \quad (4.43)$$

The first term on the right side of this equation means the solar energy collected by the concentrator of which overall area is  $A_1$  m<sup>2</sup>. The concentrator may be mirrors or lenses.  $\alpha$  is the black body absorption coefficient of the heat flux receiver constituting a water vapour heating surface, e.g. the target,  $\eta_c$  is the efficiency of mirrors or lenses, and  $E_0$  is the incident solar energy. The second term means the radiation loss from the target of which area is  $A_r$  m<sup>2</sup>.  $\epsilon$  is the emissivity, and  $\sigma$  is the Stefan-Boltzmann constant of  $5.67 \times 10^{-8}$  W/m<sup>2</sup>K<sup>4</sup>. The size of the target  $A_r$  is usually determined by the solar image size at the focal plane. The efficiency of the solar concentrator,  $\eta_s$ , can be determined from Eq. (4.43) as

$$\eta_s = \frac{Q}{E_0 A_1} = \alpha \eta_c \left( 1 - \frac{\epsilon \sigma T^4 A_r}{\alpha \eta_c E_0 A_1} \right) = \alpha \eta_c \left( 1 - \frac{\sigma T^4}{\eta_c E_0 C} \right), \quad (4.44)$$

where  $C$  is the concentration ratio defined as  $C = (\alpha/\epsilon)(A_1/A_r)$ , and it is the key factor for determining attainable temperature of the concentrator. The overall efficiency of the direct thermal decomposition process utilizing solar energy is then a product of the process efficiency,  $\eta_p$ , and  $\eta_s$ ,

$$\eta = \eta_p \times \eta_s . \quad (4.45)$$

The incident solar energy,  $E_0$ , can take the value of 400 to 1000 W/m<sup>2</sup> on the earth depending upon the climate, seasons, and location. When mirrors are used as the concentrator, the efficiency of concentration,  $\eta_c$ , is the reflection coefficient. It takes 0.8 to 0.9 for a single reflection system made of heliostats, and 0.65 to 0.8 for a double reflection system having heliostats and concentrating mirror. The efficiency of Fresnel lense depends upon the size, focal length, and material, and it may take the value of 0.7 to 0.9.

If there is an optical transmission loss in the system, it should be included in the efficiency of concentration,  $\eta_c$ .

Figure 4.7 exemplifies the solar energy utilization efficiency of the direct thermal decomposition process calculated from Eq. (4.45) taking the concentration ratio as parameter. Assumed constants for the process are the system pressure of 1 atm, the loss factor of 0.01, and the delivery pressure of 30 atm. The process efficiency for this case is shown in Fig. 4.6. The constants assumed for the solar concentrator are the incident solar energy of 600 W/m<sup>2</sup>, the efficiency of concentration of 0.75, and  $\alpha = \epsilon = 0.9$ . The efficiency of the process itself increases by a temperature increase as shown in Fig. 4.5 and 4.6, whereas according to Eq. (4.44) the radiation loss deteriorates the solar concentrator efficiency at very high temperatures. Thus, it is seen in Fig. 4.7 that there is an optimum operating

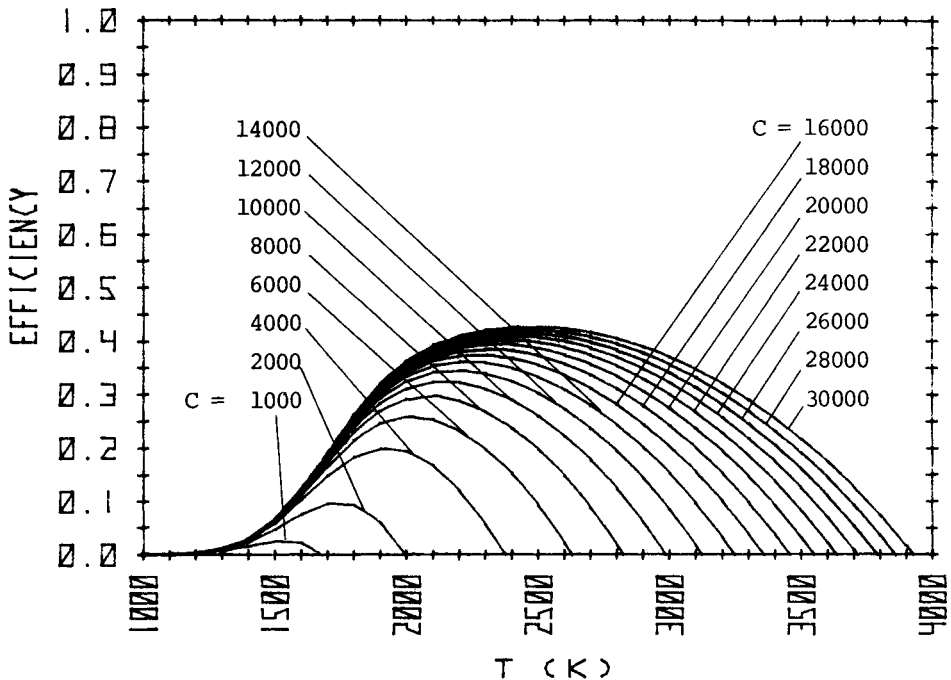


Fig. 4.7. Solar energy utilization efficiency of the direct thermal splitting process,  $\eta = \eta_p \cdot \eta_s$ , for the various concentration ratio  $C$ . Process efficiency  $\eta_p$  is shown in Fig. 4.6 marked as  $f = 0.01$ . The incident solar radiation of  $600 \text{ W/m}^2$  and the collector efficiency of 0.75 has been assumed.

temperature at which the overall efficiency reaches maximum. Another important observation made from this figure is that the concentration ratio,  $C$ , of higher than 4000 is desirable for obtaining the solar utilization efficiency of higher than 20 %, although the figures are somewhat variable according to the assumed constants. Higher concentration ratio is better for the solar energy utilization efficiency, but it requires very high accuracy both in production and control of the optical system. Moreover, as can be seen in Fig. 4.7, the gain in efficiency by making the concentration ratio very high becomes gradually small. Therefore, the analysis on the benefit in efficiency against the cost must be made for determining an optimum concentration ratio.

As an indication of required land area for the solar concentrator, let us consider the hydrogen production system of  $15,000 \text{ m}^3/\text{hr}$  or about 50 MW of hydrogen product. If the concentration ratio of 8000 is assumed, the maximum efficiency of solar energy utilization is 30 % at the operating temperature of 2100 K as shown in Fig. 4.7. Hence, the solar energy to be collected is 167 MW, for which the total solar collector area is about  $278,000 \text{ m}^2$  since the incident solar energy has been assumed as  $600 \text{ W/m}^2$ . If the ground coverage factor of collector is assumed to be 0.5, the total land area is about  $556,000 \text{ m}^2$ . The radius of the collector field is 420 metre if a circular land is considered. The surface area of the heat flux receiver is  $35 \text{ m}^2$ .

*Solar collectors.* To obtain high power solar energy at high concentration ratio,

a combination of an array of tracking mirrors and a large concentrating mirror can be used. The best example of such double reflection system is the one at Odeillo-Font Romeu, France [13], of which attainable temperature exceeds 4000 K.

It may be also possible to use a single reflection system. The concept of tower top focus energy collector [12], which uses an array of tracking flat heliostats to reflect the solar energy to a central receiver located on top of a tower, is widely known. In a similar system, concentration ratio of order 1000 to 2000 will be attained by the superposition of images of the sun from the heliostats. As described, the required concentration ratio is 2 to 10 times higher than that. If a heliostat array made of concentrating mirrors is used instead of the flat ones, an additional concentration ratio of 2 to 10 will be easily attained by each heliostat. Thus, the total concentration ratio of 10,000 to 20,000 would be possible. An obvious advantage of the single reflection system is that the efficiency of solar collection can be made at least 10 % higher than that of the double reflection system. Also, the cost would be reduced because it is not necessary to use a large concentrating mirror.

If the required concentration ratio is not too high, Fresnel lenses would be available as the solar energy collector. In this case, the solar energy is focused at each small focal point of the lens. Therefore, optical guides should be used to collect the focused but distributed energy to utilize it at a large reactor for hydrogen production. Properties, except the price, of recent optical fiber-tube are attractive for this purpose. It has been estimated by calculation that fused-silica-core optical fibers transmit solar radiation over distances of about 40 m with the efficiency higher than 80 % [14]. The power carrying capability of the present high quality optical fiber is said to be 10 kW/cm<sup>2</sup>, though the price is very much expensive. The terminal devices for receiving and releasing high density radiation, as well as the cost reduction, would be the major subject of further development.

#### 4-4 SEPARATION METHODS

*Possibilities.* A number of useful techniques have been developed for the separation of gaseous mixtures since separation is one of the fundamental procedures in science and technology. Various methods could be suggested for the separation of hydrogen or oxygen from water vapour on the basis of those techniques. However, most of them are eliminated for further consideration by evaluating their commercial feasibility according to the following criteria:

1. The separation must be carried out at high efficiency and low cost.
2. The gases should be separated continuously from the reaction site, and the temperature of gases are very high.
3. The limit of flammability of hydrogen in oxygen is 4 - 95 %, and the purity of separated hydrogen must not be fallen into this range.

One of the possibilities of satisfying these criteria would be the use of selective membrane made of refractory materials.

There are, broadly speaking, two types of selective membrane: The one is a porous screen made of finely woven refractory metal cloth, or made of porous refractory oxides. The other is a solid membrane, which has no pores in a macroscopic sense, made of specific metal or oxide that can transport hydrogen atoms or oxygen ions by a lattice diffusion.

*Porous membranes.* Two separation processes that use porous membrane can be mentioned. The one is *mass diffusion process*, and the other is *gaseous diffusion process*. It has been reported that laboratory-scale separations of gas mixtures



containing hydrogen were demonstrated for both of these processes [15].

In the mass diffusion process, separation is obtained by the difference in the diffusion coefficients of components of the gas mixture with respect to an auxiliary gas. The auxiliary gas would be water vapour, in our case. The gas mixture and water vapour are bounded by a porous screen. One of the gases, which has larger diffusion coefficient with respect to water vapour, then flows through the pores of screen, and the same number of molecules of water vapour flows into the region of gas mixture by its partial pressure gradient. The pore size is determined so as to avoid, as possible, the gas flow caused by the pressure difference across the screen. If the total pressure is about 1 atm, hydrogen separation may be obtained with the pore diameter of smaller than  $10^{-4}$  cm.

The gaseous diffusion process utilizes the phenomenon of molecular effusion, that is the flow of gas through small orifices. When a gas mixture is confined in a vessel of which wall is porous, and if the pore diameters are the order of mean-free-path dimensions of the gas components, the lighter gas molecules in the mixture can escape more easily than the heavier ones. Since the mean-free-path is in inverse proportion to the square root of the molecular weight, the relative easiness of light versus heavy molecules in escaping through the pore is equal to the square root of the inverse ratio of the two molecular weights. If we treat the pores as a collection of straight circular capillaries, the rate of effusion through the membrane will be governed by Knudsen's law [15]:

$$N = \frac{4}{3} \frac{1}{\sqrt{2\pi MRT}} \frac{fd}{L} (P_h - P_l), \quad (4.46)$$

where  $N$  is the molar flow rate of gas per unit area through the membrane,  $M$  is the molecular weight,  $f$  is the open area fraction,  $L$  is the pore length or the thickness of the membrane, and  $P_h$  and  $P_l$  are the high- and low-side pressure of the membrane, respectively. Fletcher and Moen [8] have made a conceptual study on the process of an effusional separation of hydrogen from water, using solar energy, and their conclusion was that such process is "a tantalizing possibility".

*Non-porous membranes.* Palladium or palladium-silver alloys have been suggested for the hydrogen separation membrane of this type. In fact, these are occasionally used in laboratory experiments to obtain hydrogen of extremely high purity. The melting point of palladium is about 1800 K, and it may be possible to locate it near to the site of water dissociation. Ford and Kane [1] have estimated the required quantity of palladium at 1/500 ounce per square meter of collection area. So that a reasonable cost will be expected for the membrane though palladium itself is expensive.

The passage of hydrogen through a palladium membrane is not a unique phenomenon. Hydrogen permeates a large number of metals especially at high temperatures. The situation has been described approximately by the following equation:

$$N = \frac{K}{L} (\sqrt{P_h} - \sqrt{P_l}) \exp\left(\frac{-E}{RT}\right), \quad (4.47)$$

where  $N$  is the diffusion flow per unit area,  $K$  is a constant,  $L$  is the diffusion length or the thickness of the membrane,  $P_h$  and  $P_l$  are the high- and low-side pressure of the membrane, and  $E$  is the sum of the energy of solution and the activation energy of diffusion. Equation (4.47) was developed by O. Richardson at the turn of the century, and it seems still adequate for dealing with permeation phenomena in a simplified manner. It is seen by this equation that diffusion flow increases as the temperature is elevated and the pressure difference is increased.

In such conditions, oxygen also permeates metals. But we can expect selective separation of hydrogen because of the difference in activation energies of diffusion. In titanium at about 1000 K, for example, the activation energy of hydrogen diffusion is 6.64 kcal/mol and that of oxygen diffusion is 48.2 kcal/mol [16]. As the diffusion flow of gas in metal is inversely proportional to an exponential function of the activation energy, oxygen diffusion will be negligibly small compared with hydrogen diffusion.

Equation (4.47) shows that the small value of  $E$  and the high melting temperature are the major criteria for finding the materials of the membrane of this type. Simple elements that belong to 5b and 6b groups in the periodic table have such properties. However, some special method will be needed in using these metals for hydrogen separation at high temperatures, because they are very much unstable in the water vapour of above 1000 K.

Several ceramic oxides are known to have the oxygen ion transport property at high temperatures, and some of them have been developed as solid electrolytes. Typical materials are zirconia and ceria each stabilized in its cubic form by doping with  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ , or  $\text{Yb}_2\text{O}_3$ . The melting temperatures of zirconia and ceria are about 2900 K, and they are stable in the environment of high temperature water vapour. The amount of oxygen transferred through the membrane of this type may be written such that [5]

$$N = \frac{K}{L} \left\{ RT \ln \left( \frac{P_h}{P_l} \right) \right\} \exp \left( \frac{-E}{RT} \right), \quad (4.48)$$

where the notations used are common to those in Eq. (4.47).

Experimental measurements have been made to determine the value of  $E$ , the sum of the activation energy of diffusion and the energy of oxygen surface exchange, and some results on calcia-stabilized zirconia [17] shows that the activation energy of diffusion is about 31 kcal/mol and the energy of oxygen surface exchange is about 23 kcal/mol for the temperatures around 1200 K. A rough estimate using these values and Eq. (4.48) shows that the thickness of the membrane,  $L$ , should be thinner than 100  $\mu\text{m}$ . Such thin membranes can be fabricated by a chemical vapour deposition technique, or more efficiently by the use of a plasma flame spray gun. It has been demonstrated by the latter method that yttria-stabilized zirconia solid electrolyte can be made as thin as 50  $\mu\text{m}$  without having effective pores [18].

The method of oxygen separation using solid electrolyte membrane is essentially compatible with the electrolysis of high temperature water vapour. The water is heated on the surface of the membrane by the concentrated solar energy to a very high temperature at which dissociation is taken place. The evolved oxygen is ionized at the surface of the membrane by an external electric power supply. Then, the oxygen ions transport through the membrane and evolve on the other side giving back electrons to the external circuit. The resulted mixture of hydrogen and water vapour is separated by condensation. If the temperature is raised sufficiently high, it is not always necessary to heat water up to a highly dissociated state. An efficient electrolysis of water vapour would be achieved with this scheme since the required electropotential is substantially reduced at high temperatures [19].

#### 4-5 THE STATE OF EXPERIMENTAL WORKS

Only a few preliminary experiments have been reported so far concerning to the direct thermal decomposition of water.

Bilgen and his co-workers [6] have used the solar furnace to decompose water. The

solar radiation was first reflected on a flat heliostat and then concentrated by a parabolic mirror. The characteristics of the mirror were: diameter 200 cm; focal length 85 cm; energy density  $1.6 \text{ kW/cm}^2$ ; theoretical diameter of the focus image 0.8 cm; aperture  $120^\circ$ ; power 2 kW. Water vapour was injected into a zirconia self crucible which was heated at the focus of the parabolic mirror up to about 2500 K. In order to reduce the partial pressure of water vapour, argon gas was injected also into the crucible. The heated gas mixture was sampled from the bottom of the crucible and analysed with a quadrupole mass spectrometer. The amount of hydrogen they observed was in the order of 2-3 % in the product gas mixture. They have estimated that, because of an inefficient heat transfer, this amount was about a half of the theoretically possible production.

Experimental studies on the high temperature separation membranes are being made by us. The simplified drawing of the experimental arrangement is illustrated in Fig. 4.8 showing an arc imaging furnace and a test vessel. The beam sources are two xenon short arc lamps, the electrical input for each of which is 6.5 kW. The concentrating mirrors are the ellipsoidal ones each has the diameter of 40 cm and has the reflective surface coating formed by aluminum. Each mirror has two focal points: electric arc is placed at the first focal point,  $f_1$ , and the beam is focused at the second one,  $f_2$ . The distances of  $f_1$  and  $f_2$  are 9.5 cm and 70 cm, respectively from the bottom of the mirror. The second focal point,  $f_2$ , is a

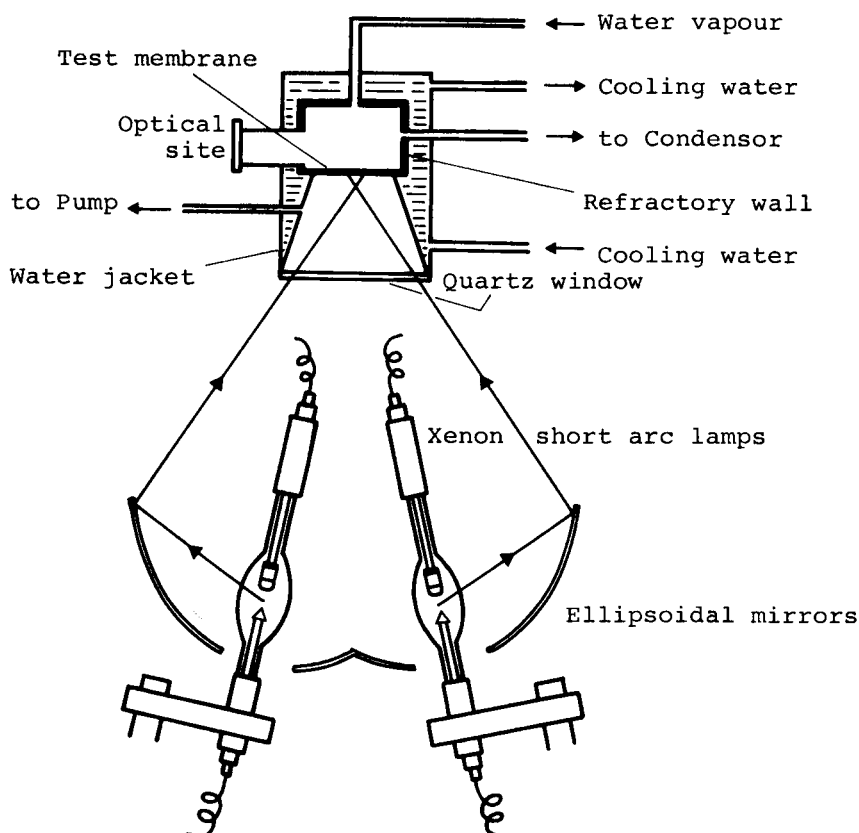


Fig. 4.8. Schematic drawing of an experimental arrangement for the separation membrane testing.

common one, so that the beam from two mirrors are focused and superimposed at this point. Measurements by a calorimeter have shown that the power of the beam at the common focal plane was 2 kW, and the power density was 1.47 kW/cm<sup>2</sup>. The theoretical maximum attainable temperature will exceed 4000 K. Inside of the test vessel is compartmented into upper and lower rooms by the test membrane. Water vapour is injected into the upper room and heated on the surface of the membrane to a very high temperature. The lower room is connected to a pump to collect the transported product gas through the membrane. The remaining products in the upper room go through a water vapour condensor, and are separated. The electrodes required for testing solid electrolyte membranes and other test leads are not shown in the figure. The materials presently being tested are, for example, palladium, titanium, niobium, and tantalum for hydrogen separation, and yttria-stabilized zirconia for oxygen separation. Also, the effusional hydrogen separation membranes made of porous ceramic oxides are being studied. We have seen, by gas chromatography, a small amount of hydrogen production from high temperature water vapour heated on these membranes. As one might expect, however, all of the metals tested were unstable in the water vapour of above 1000 K, and some of the ceramic oxides were incapable of resisting thermal shock. Therefore, studies on the processes that may offer an acceptable way to evade metal corrosion are necessary. It is also desired to work out high mechanical performances of ceramic oxides.

#### 4-6 CLOSING REMARKS

Since we have a great lack of knowledge about the method for hydrogen and oxygen separation at high temperatures, we cannot make at present an all-inclusive system analysis on the hydrogen production process of direct thermal decomposition of water utilizing solar energy. The overall efficiencies of the process have been estimated from a simplified thermodynamic analysis treating the irreversible losses associated with separation as a parameter. It may be concluded in this regard that the process can be made thermodynamically sound, and is worthy of further research and development. Extensive studies are needed to acquire a method that effects separation of hydrogen and oxygen from dissociated water at temperatures in the range from about 1700 to 3000 K. We suffer a considerable loss out of this range through irreversible works at lower temperatures, and reradiation losses at higher temperatures. Among the present possible ideas for separation, the author has an impression that a membrane separation method deserves serious consideration because of simplicity. If its irreversible losses can be made tolerably small, then the simplicity would largely profit capital cost of the plant.

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