

DIRECT THERMOMAGNETIC SPLITTING OF WATER

R. L. CURL

Department of Chemical Engineering, The University of Michigan, Ann Arbor, MI 48109, U.S.A.

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Abstract—The application of a magnetic field to water tends to cause its decomposition into hydrogen and oxygen. Based upon the thermomagnetochemistry of the phenomenon, a process is suggested for carrying out the reaction and separating the product hydrogen and oxygen. The process would have nearly Carnot efficiency, although the requisite magnetic field ($\sim 10^4$ tesla) is not at present attainable.

NOMENCLATURE

A_i	Chemical species designation
B	Magnetic field strength (tesla)
g	Molar Gibbs free energy of species (J/gmole)
Δg_r	Free energy of reaction (J/gmole)
h	Molar enthalpy (J/gmole)
Δh_r	Enthalpy of reaction
K_r	Equilibrium constant for water decomposition
m_i	Molar magnetization of species i (J/T gmole)
m_o	Molar magnetization of oxygen (J/T gmole)
\hat{m}_o	Molar magnetization of reaction mixture per gmole water (J/T gmole)
N	Avagadro Number, 6.024×10^{23} gmole $^{-1}$
P	Pressure (N/m 3 or atm)
P_1	Pressure in reactor (N/m 3 or atm)
P_2	Pressure in condenser (N/m 3 or atm)
Q	Heat supplied to process units (Table 3) (kJ/gmole)
R	Ideal gas constant
s	Molar entropy (J/gmole K)
S	Spin quantum number
T	Temperature (K)
u	Molar internal energy (J/gmole)
v	Molar volume (m 3 /gmole)
\hat{v}	Molar volume per gmole water (m 3 /gmole)
X	Conversion of water

Greek symbols

α	Fraction hydrogen removed in reactor
β	Bohr magneton (9.272×10^{24} A m 2)
ν	Stoichiometric coefficient (in reaction)

Superscript

$^\circ$	Standard state
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Subscript

i	Species i
o	With $B = 0$ (except in m_o)
1	P In reactor
2	P In condenser.

INTRODUCTION

WATER is too stable to be easily thermally decomposed at moderate temperatures [1]. It is, however, well known that molecular oxygen is a paramagnetic substance and is therefore attracted into a magnetic field. Since water and hydrogen are not paramagnetic, the application of a magnetic field to water should tend to "extract" the oxygen and enhance the reaction



Previous studies by Delhez [2, 3] and Chen *et al.* [4] have shown that the shift in the equilibrium of a chemical reaction involving paramagnetic substances is quite small with "ordinary" magnetic

fields of the order of 1 tesla ($1T = 10^4$ G). It is the purpose here to explore the magnetic fields required for a practical shift in the equilibrium of reaction (1) and to suggest a system by which water might be thermomagnetically decomposed into hydrogen and oxygen.

THERMOMAGNETOCHEMISTRY

The following is a simplified and idealized thermodynamic analysis of chemical systems with a magnetic field.

It is known (e.g. Guggenheim [5]; Hsieh [6]) that the first-law expression including magnetization is, on a molar basis,

$$du = Tds + Bdm - Pd v, \quad (2)$$

where u = molar internal energy (J/gmole),

T = Temperature (K),

s = molar entropy (J/K kgmole),

B = magnetic field strength ($T(= \text{Wb}/\text{m}^2 = \text{J}/\text{A m}^2)$),

m = molar magnetization ($\text{Am}^2/\text{gmole} (= \text{J}/\text{T gmole})$),

P = pressure (N/m^2) and

v = molar volume (m^3).

The magnetic Gibbs free energy is defined as [5, 6]

$$g = u + Pv - Bm - Ts, \quad (3)$$

from which it follows that

$$dg = -sdT - mdB + vdP. \quad (4)$$

For an ideal gas mixture at constant temperature, the molar free energy of species "i" may be obtained by integrating (4), with $v_i = RT/P_i$, to give

$$g_i(B, T) = g_{i0} - \int_0^B m_i dB + RT \ln P_i, \quad (5)$$

where g_{i0} is the standard state free energy of "i" at T and $B = 0$. For the chemical reaction $\sum v_i A_i = 0$ where the v_i are the stoichiometric coefficients of the reaction, it follows that, at equilibrium,

$$\Delta g_r = \sum v_i g_{i0} - \int_0^B \sum v_i m_i dB + RT \sum v_i \ln P_i = 0. \quad (6)$$

Since $\sum v_i g_{i0} = \Delta g_{r0}$, the standard state free energy of reaction, and $\sum v_i \ln P_i = \ln K_p$ (K_p = pressure equilibrium constant),

$$-RT \ln K_p = \Delta g_{r0} - \int_0^B \sum v_i m_i dB. \quad (7)$$

For the water splitting reaction (1), only oxygen is significantly paramagnetic while the diamagnetism of hydrogen or water is weak in comparison. Neglecting these, and writing hereafter $m_{\text{O}_2} = m_0$, and with $v_{\text{O}_2} = \frac{1}{2}$, we obtain

$$\Delta g_r^\circ = -RT \ln K_p = \Delta g_{r0}^\circ - \frac{1}{2} \int_0^B m_0 dB. \quad (8)$$

Magnetization, therefore, reduces the apparent standard state free energy of reaction, increases K_p , and promotes the decomposition of water.

MOLAR MAGNETIZATION OF MOLECULAR OXYGEN

Oxygen is a substance with a net electron spin quantum number of $S = 1$, narrow multiplet interval and little spin-orbital coupling. Its magnetization is known to be given by the Brillouin function (Van Vleck [7]; Guggenheim [5])

$$m_0 = (2S + 1)N\beta \text{ctnh}((2S + 1)N\beta B/RT) - N\beta \text{ctnh}(N\beta B/RT), \quad (9)$$

where $N =$ Avagadro number (6.024×10^{23} gmole $^{-1}$),

$\beta =$ Bohr magneton (9.272×10^{24} A m 2),

($N\beta = 5.586$ Am 2 /gmole) and

$R = 8.314$ J/K gmole.

With the substitution of eq. (9), and integration, eq. (8) becomes, with $S = 1$,

$$\Delta g_r^\circ = \Delta g_{r0}^\circ - \frac{1}{2} RT \ln \left(\frac{\sinh(3N\beta B/RT)}{3 \sinh(N\beta B/RT)} \right). \quad (10)$$

It follows, by application of the Van't Hoff thermodynamic identity,

$$\frac{\partial(\Delta g/T)}{\partial(1/T)} = \Delta h,$$

that the standard-state enthalpy of reaction is given by

$$\Delta h_r^\circ = \Delta h_{r0}^\circ - \frac{1}{2} m_o B = \Delta h_{r0}^\circ - \frac{1}{2} N\beta B \left(3 \operatorname{ctnh} \frac{3N\beta B}{RT} - \operatorname{ctnh} \frac{N\beta B}{RT} \right). \quad (11)$$

When $B = 0$,

$$\Delta g_{r0}^\circ = -RT \ln K_{p0}. \quad (12)$$

and eq. (8) may be expressed as

$$\ln \frac{K_p}{K_{p0}} = \frac{1}{2} \ln \left(\frac{\sinh(3N\beta B/RT)}{3 \sinh(N\beta B/RT)} \right). \quad (13)$$

For small magnetic fields ($B \rightarrow 0$), this reduces to

$$\ln \frac{K_p}{K_{p0}} = \frac{2(N\beta B)^2}{3(RT)^2}. \quad (14)$$

in agreement with the result obtained by Chen *et al.* [4]. This result also follows from assuming that the molecular magnetic susceptibility is given by Curie's Law. The Brillouin function was used here because, as will be seen, the magnetic fields required for a significant shift of the equilibrium of reaction (1) lead to paramagnetic (electron spin) saturation.

From eqs (11) and (13) we may calculate Δh_{r0}° and $-\log_{10} K_p$ as a function of B and T . Some results are shown in Table 1.

TABLE 1. Heat of reaction and equilibrium constant, for water decomposition, as a function of magnetic field strength

B (Tesla)	$T = 300$ K		$T = 600$ K		$T = 900$ K		$T = 1200$ K	
	Δh_r° (kJ/gmole)	$-\log_{10} K_p$	Δh_r° (kJ/gmole)	$-\log_{10} K_p$	Δh_r° (kJ/gmole)	$-\log_{10} K_p$	Δh_r° (kJ/gmole)	$-\log_{10} K_p$
0	242	39.8198	245	18.6620	247	11.5135	249	7.9003
10^3	236	39.0834	239	18.3901	243	11.3751	246	7.8176
10^4	186	30.3336	189	14.0382	191	8.5105	193	5.7076
10^5	-317	-57.1888	-314	-29.7230	-311	-20.6637	-310	-16.1730
4.119×10^4	11.7	0						
4.329×10^4	0	-2.0399						
3.887×10^4			27.7	0				
4.382×10^4			0	-2.4063				
3.625×10^4					44.7	0		
4.425×10^4					0	-2.5919		
3.347×10^4							62.1	0
4.458×10^4							0	-2.699

ΔH_{r0}° and $-\log_{10} K_{p0}$ from Ref. [8].

It is immediately apparent that very intense magnetic fields, of the order of 10^4 T, are required to increase significantly the equilibrium constant for water decomposition. High fields are still required at moderately elevated temperatures, even though Δg_r° decreases, because the molar magnetization decreases with increasing temperature. The fields required for either $\Delta h_r^\circ = 0$ or $\Delta g_r^\circ = 0$ ($K_p = 1$) are also shown at each temperature. It is interesting that the heat of reaction can be driven to zero but this is not unexpected as the effect of the magnetic field is essentially to reduce the entropy of reaction.

INTENSE MAGNETIC FIELDS

Paramagnetic saturation occurs for magnetic fields in excess of 10^4 T. For these large field strengths relations (10) and (11) simplify to

$$\ln \frac{K_p}{K_{p0}} = \frac{2N\beta B}{RT} \quad (15)$$

and

$$\Delta h_r^\circ = \Delta h_{r0}^\circ - N\beta B. \quad (16)$$

The practical attainment of steady, non-dissipative, magnetic fields of 10^4 T is not possible from current superconducting magnet technology [10, 11] because of inherent physical limitations on the superconductivity phenomenon as well as mechanical strength limitations. In addition, an appalling amount of energy is stored in such a field [4×10^7 J/cm³!]. The highest continuous field available today is of the order of 30 T [9] and this is by means of a hybrid superconducting-conventional coil arrangement that consumes considerable power. Fields up to 8.5 T have been generated by non-dissipative superconducting magnets [9, 10]. Up to 10^3 T has been generated momentarily (approx. 2 μ sec) in the laboratory [11]. Fields of 10^4 T are found, however, in certain stellar bodies [12].

In comparison with a direct high temperature (~ 2400 K) water-splitting technology [1], a direct thermomagnetic technology appears to be of similar if not greater difficulty. Nevertheless, the nature of the difficulty is very different and, while keeping the above considerations in mind, it appears worthwhile to visualize a water-splitting system based on thermomagnetochemistry. The ultimate benefits to be gained have been amply recorded in the pages of the *International Journal of Hydrogen Energy*.

As we have seen, both Δg_r° and Δh_r° go to zero in sufficiently intense fields. Nevertheless, in decomposing water into hydrogen and oxygen, Δh_{r0}° and Δg_{r0}° , must be supplied at some point. The question of where this occurs is one reason for pursuing the matter further.

It should be added that at field strength of 10^4 T other magnetochemical effects may appear. The Brillouin function for molar magnetization may not be sufficient due to the appearance of spin-orbital coupling and nuclear spin interaction. In addition, demagnetization from these fields may lead to microwave radiation. None of these effects have been evaluated.

FIELD MAINTENANCE

Energy is extracted from a magnetic field when oxygen is produced by thermomagnetic water decomposition. When oxygen is withdrawn from the field, magnetic energy is returned. These must be balanced to prevent either demagnetization of the magnet or the use of excessive external magnetic work. The electrical work of magnetization is given by (from eq. (2))

$$\int B dm_o \quad (17)$$

In Fig. 1 is shown a sketch of m_o vs B at various temperatures (the actual temperature effect has been exaggerated to better illustrate the point). If the reaction occurs isothermally (which would occur adiabatically when $\Delta h_r^\circ = 0$), path A will be followed during the decomposition. If the oxygen is then removed adiabatically, it will undergo adiabatic demagnetization and follow path B. The area within the paths represents a net energy removed from the magnetic field. Conversely, if the reaction mixture is heated to a higher temperature during removal from the field, path C might be followed

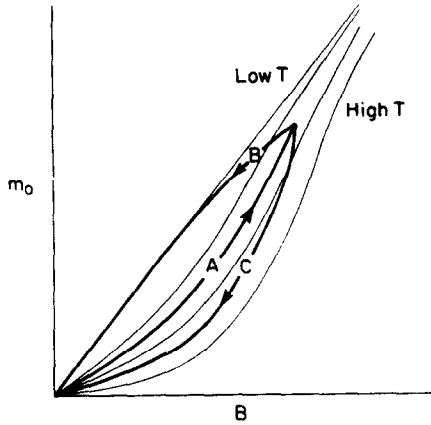


FIG. 1. Molar magnetization isotherms and alternate demagnetization paths.

and net magnetic energy will be given to the field (this could contribute to field maintenance in the face of coil losses). The temperature path during reaction and demagnetization must be carefully controlled. Isothermal reaction and demagnetization will be assumed for the purposes of further evaluation, and there will be no net energy exchange with the magnetic field.

To attain isothermal oxygen removal and demagnetization, thermal energy must be provided. This may be shown to be equal to $m_0 B$ per mole oxygen for isothermal removal from a field of strength B . From eq. (11) we see that

$$\Delta h_r^\circ + \frac{1}{2}m_0 B = \Delta h_{r,0}^\circ, \tag{18}$$

and therefore the total thermal energy that must be provided consists of the Δh_r° during the reaction and $\frac{1}{2}m_0 B$ during isothermal demagnetization, for the total of $\Delta h_{r,0}^\circ$, the original ($B = 0$) heat of reaction.

THERMOMAGNETIC WATER-SPLITTING SYSTEM

The system shown in Fig. 2 embodies the components of a direct thermomagnetic water-splitting scheme. Water vapor at relatively elevated temperature and pressure is provided by a boiler and fed

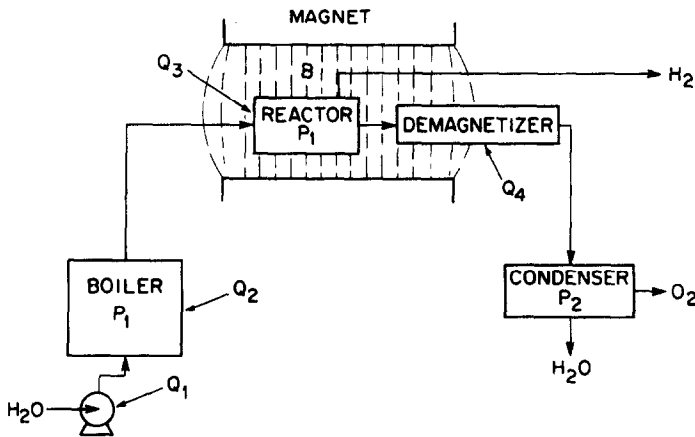


FIG. 2. Thermomagnetic water-splitting process.

to a reactor contained between the poles of a magnet. The reactor is visualized as a tube-in-shell diffuser using palladium tubes through which H_2 , but not O_2 or H_2O , may diffuse [13]. Hydrogen is removed from (say) the shell side of the reactor, while undecomposed water, oxygen and some residual H_2 are removed at the end of the tubes. If a catalyst is required to enhance water decomposition it may be packed into the tubes.

It will be assumed for the purposes of a simple analysis that reaction occurs only within a region of uniform magnetic field and that none occurs in either the feed or product removal lines. Therefore the pressure in the reactor is that in the boiler, but this is significantly higher than in the condenser and H_2O/O_2 separator because of the work required to remove a paramagnetic substance from a magnetic field. The hydrogen, being non-paramagnetic, is recovered at approximately the equilibrium pressure in the reactor (minus pressure drop necessary for diffusion through the palladium tubes which will be neglected here).

Assuming reversible isothermal expansion (for field maintenance) as the oxygen-rich stream leaves the field, the pressure change will be given by eq. (4). On the basis of one mole of water fed to the system, this may be expressed as

$$\int_{P_1}^{P_2} \hat{v} dP = \int_B^0 \hat{m} dB, \quad (19)$$

where \hat{v} and \hat{m} are the specific volume and specific magnetization on a common basis of one mole of water. If X is the fractional conversion of the water fed and α is the fraction of H_2 produced that is recovered in the H_2 product stream ($\alpha < 1.0$), stoichiometry yields the following relations applicable to the oxygen-rich product stream (assuming ideal gas conditions)

$$\hat{v} = [1 + (0.5 - \alpha)X] \frac{RT}{P} \quad (20)$$

and

$$\hat{m} = \frac{1}{2} X m_G \quad (21)$$

An assumption of no reaction between residual H_2 and O_2 in the oxygen product stream eliminates a rather complicated calculation for the expansion of this stream. Combining eqs (8) and (19), we obtain

$$- \frac{1}{X} \int_{P_1}^{P_2} \hat{v} dP + \Delta g_r^\circ = \Delta g_{r0}^\circ \quad (22)$$

Since the first term is the flow-expansion work available per mole water reacted and Δg_r° is the (isothermal) work necessary to return the products to standard conditions (small for K_p of the order of one), we see that the standard state ($B = 0$) work of water decomposition is being provided primarily by the pressure drop during demagnetization. The remainder (Δg_{r0}°) is provided magnetically, but returned to the field during isothermal demagnetization.

Integrating eq. (22) using eqs (20) and (15) (for $B > 10^4$ T) yields

$$\frac{(1 + (0.5 - \alpha)X)}{X} \ln \frac{P_1}{P_2} = \frac{2N\beta B}{RT} \quad (23)$$

In addition, it follows from the definition of K_p that

$$K_p = \frac{P_{H_2} P_{O_2}^2}{P_{H_2O}} = \frac{(1 - \alpha)P_1^2 X^3}{(1 - X)(2 + X - 2\alpha X)^{1/2}} = K_{p0} \exp\left(\frac{2N\beta B}{RT}\right) \quad (24)$$

Equations (23) and (24) involve P_1 , P_2 , B , α , X and T , giving four degrees of freedom to the design decisions. We also perceive that P_1 and T should be as high as possible, B as low as possible, and P_2 not too small, compatible with a large X and a large α .

For the purposes of illustrating a design, I will choose the boiler to operate at 600 K, without superheat, giving $P_1 = 121.6$ atm (slightly below the critical point of water). In addition, assuming $\alpha = 0.95$ (a "good" hydrogen recovery), we may obtain X and K_p (and B , and P_{H_2}) in terms of P_2 . The results are shown in Table 2.

We see that the lower the exhaust pressure (P_2), the better the conversion and the higher the hydrogen pressure. This is because more flow work is available at the higher ratio of P_1/P_2 . The field

TABLE 2. Alternative operating conditions for a thermomagnetic water-splitting system using $T = 600$ K, $P_1 = 121.6$ atm and $\alpha = 0.95$

P_2 (atm)	X	P_{H_2} (atm)	K_p	B (Tesla)
0.01	0.213	1.43	0.0511	1.786×10^4
0.10	0.166	1.09	0.0329	1.766×10^4
1.0	0.117	0.749	0.0181	1.740×10^4
10	0.0639	0.400	0.00682	1.696×10^4
100	0.00569	0.0347	0.000169	1.531×10^4

intensity required is not strongly dependent upon P_2 , but it should be observed that in this range K_p is strongly dependent upon B .

Although water vapor at 600 K and 121.6 atm departs from the ideal gas law, the treatment here (using eq. (20)) is considered adequate for the present purposes.

It would be desirable to make the reactor and demagnetizer as small as possible in order to minimize the volume of high-intensity magnetic field. This will depend upon the area requirements for hydrogen diffusion and heat transfer.

THERMAL EFFICIENCY

It is apparent that with only minor irreversibilities present in the idealized thermomagnetic water splitting system, the thermal efficiency should approach the Carnot efficiency. Assuming that liquid water is provided at 25°C and that both hydrogen and oxygen are produced at 1 atm and 25°C, we may calculate the heat requirements at each unit of the process. These are shown in Table 3 on the basis of 1 gmole water passing through the process with an exhaust pressure of 1 atm and a conversion of $X = 0.117$. A 30% efficiency has been adopted for the conversion of heat to compression work.

The significant heat terms, that for the heating and vaporization of the water feed, and that for reaction and isothermal demagnetization, are comparable in magnitude. As has been seen, the former is providing the work required for water decomposition; the latter, the heat required.

TABLE 3. Heat requirements for the thermomagnetic water-splitting process, per gmole water throughput (kJ)

Q_1	Liquid water compression (25°C)	0.74
Q_2	Vaporization	33.7
Q_3	Heat of reaction ($B = 1.74 \times 10^4$ T; $X = 0.117$)	17.3
Q_4	Isothermal demagnetization	11.4
Q_5	Hydrogen compression (to 1 atm, 25°C)	0.27
	Total	63.41

The free energy of water decomposition at 25°C and $B = 0$ is 228.5 kJ/gmole and therefore the efficiency at $X = 0.117$ and $\alpha = 0.95$ is 0.40. The comparative Carnot efficiency between 600 and 298 K is 0.50. The departure from Carnot efficiency is due primarily to not recovering, in this simplified process description, the heat available in the 600 K oxygen rich product stream. Actual efficiencies will, of course, be somewhat lower, after fully accounting for heat exchange and other losses.

The greatest practical difficulty (apart from producing $B = 1.74 \times 10^4$ T) lies in the heat exchanger required for isothermal demagnetization.

SUMMARY

It has been shown that water may be decomposed into hydrogen and oxygen by the use of a sufficiently strong magnetic field. Although the field required for a moderate conversion of water is far greater than any presently available, the problem reminds one somewhat of hydrogen-fusion power generation, where large volume intense magnetic fields up to 16.5 T are proposed [10, 14] and the working gases are heated to temperatures in the keV range. If the necessary intense fields could be obtained, a thermomagnetic water splitting process would be a "clean" system for providing future hydrogen without requiring a complex series of chemical reactions (in thermochemical methods) or temperatures in excess of about 600 K.

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