Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Equilibrium Analysis of Thermochemical Cycles for Hydrogen Production

Simon L. Marshall[a]; James G. Blencoe[b]
[a] Electrochemical Systems, Inc., Oak Ridge, TN, USA [b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

To cite this Article Marshall, Simon L. and Blencoe, James G.(2005) 'Equilibrium Analysis of Thermochemical Cycles for Hydrogen Production', Separation Science and Technology, 40: 1, 483 — 505
To link to this Article: DOI: 10.1081/SS-200042508
URL: http://dx.doi.org/10.1081/SS-200042508

Separation Science and Technology, 40: 483–505, 2005
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200042508

Equilibrium Analysis of Thermochemical Cycles for Hydrogen Production

Simon L. Marshall
Electrochemical Systems, Inc., Oak Ridge, TN, USA

James G. Blencoe
Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Abstract: Thermochemical cycles for production of hydrogen from water can be constructed by appropriate combination of hydrogen- and oxygen-producing reactions carried out at different temperatures. While hundreds of specific reaction schemes are possible, the individual reactions can be regarded as belonging to relatively few general types. On the basis of published thermochemical data, we describe a procedure whereby an equilibrium analysis of these reaction types can be carried out systematically for a large number of specific sets of reactants. This provides quantitative criteria for assessing the inherent thermodynamic viability of possible reaction cycles, which may be of use when coupled with the more practical considerations that have traditionally formed the basis for the design of thermochemical hydrogen-production schemes. Results of applying this thermodynamic screening process systematically to hydrogen production reactions involving a large number of metal–metal oxide and metal–metal oxide-carbon systems show that polythermal reaction schemes involving the latter systems are highly efficient in generating hydrogen from coal, in comparison with usual coal gasification processes.

Funding for the research was provided by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR22725, Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

Address correspondence to Simon L. Marshall, Electrochemical Systems, Inc., 102 Midland Lane, Oak Ridge, TN 37830, USA.

INTRODUCTION

The replacement of conventional combustion of fossil fuels by the electrochemical combustion of hydrogen has long been regarded as highly desirable from energetic, economic, and environmental viewpoints. Although a hydrogen-based economy was envisioned many years ago, the recent successful development and use of fuel-cell powered vehicles has given unprecedented impetus to research on the more practical aspects of realizing this goal; in particular, on viable methods by which hydrogen can be safely produced, stored, and distributed. Separation processes already play a crucial role in the removal of carbon monoxide from the product streams of steam-reformation processes. Alternative methods for hydrogen production can be regarded as posing a separation problem of a different and more challenging kind: the separation of hydrogen from oxygen by breaking the chemical bonds of water. The fact that the energy output from combustion of hydrogen to liquid water at 298 K is so high (about 117.6 MJ/kg, compared to about 46.36 MJ/kg for *n*-octane) means that the direct thermal decomposition of water to oxygen and hydrogen requires a large energy input and proceeds to a negligible extent except under extreme conditions. This is also true for any isothermal combination of reactions that adds to give the same net result. The feasibility of such a process can be substantially enhanced by use of a nonisothermal combination of reactions (e.g., a low-temperature hydrogen-producing reaction with a high-temperature oxygen-producing reaction) occurring at temperatures at which each is thermodynamically favorable. The overall energy input required for such a process would then be largely consumed by the regeneration of the reactants rather than by the direct thermolysis of water. This fundamental concept of thermochemical water splitting is of considerable current interest not only as a specific means of generating hydrogen fuel but also as a method by which the thermal output of nuclear or conventional power plants could be stored over long periods of time. The authors of many of the thermochemical hydrogen-production schemes that have been proposed in the literature appear to have made little use of thermodynamic calculations. For example, in a collection of 125 water-splitting cycles (1) and in a more recent technical report (2) no mention is made of the equilibrium constants for any of the reactions involved. This is somewhat surprising, given that compilations of thermochemical data for most of the chemical substances involved are available [e.g., from databases prepared by the U.S. Geological Survey (3) and the NBS/NIST (4)]. Admitting that thermodynamic feasibility is necessary rather than sufficient for any such process to be useful in practice, we feel that the application of thermodynamic principles provides the most rigorous basis for determining the conditions, if any, under which these reaction schemes are feasible. Thermodynamic feasibility in this context is manifested not only by the values of the equilibrium constants of the constituent reactions but also by the equilibrium conversions achievable for specified feed compositions. In the present paper, we describe thermodynamic criteria by which equilibrium performance limits of thermochemical hydrogen-production schemes of various general types can be evaluated, and we present calculations for a number of specific processes. Our use of the word "equilibrium" in this context refers only to the *chemical* equilibrium of the constituent reactions, which limits the conversion achievable under specific conditions. Since these processes are supposed to occur at different temperatures, the overall system is clearly not at equilibrium. The departure from *thermal* equilibrium that inevitably results from the occurrence of the constituent reactions at different temperatures also contributes significantly to the overall energy balance of thermochemical cycles (e.g., the enthalpy changes associated with removal of hydrogen) and combination of the remaining products with reactants at lower temperatures. Analysis of these contributions requires consideration of the heat- and mass-transfer characteristics of a particular installation and is beyond the scope of this paper. In focusing on the chemical equilibrium of the reactions, our aim is to facilitate identification of reaction schemes for which more detailed experimental investigations of reaction kinetics, heat/mass transfer, and other important determinants of viability are justified.

DIRECT THERMOLYSIS OF HYDRIDES

As observed previously, thermal decomposition of water is energetically unfavorable. To provide a basis for comparing what can be achieved by means of water-splitting cycles, it is of interest first to examine the equilibrium for the dissociation of water as a function of temperature. It is also of interest to examine the thermal dissociation of other naturally occurring hydrides, in particular hydrogen sulfide and methane, because these reactions are far simpler than the processes involved in many thermochemical water-splitting cycles that have been proposed and may in some situations represent a more economical use of thermal energy.

Water

Values for the standard Gibbs energy change $\Delta_f G^\circ \equiv -RT \ln K_f$ for the formation of water (i.e, the reaction)

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad (1)$$

are tabulated [(3), page 194] and are represented accurately by the empirical equation

$$\Delta_f G^\circ \equiv -RT \ln 10 \log_{10} K_f = A + BT + \frac{C}{T^2} \tag{2}$$

where $A = -2.4896 \times 10^2$, $B = 5.632 \times 10^{-2}$, and $C = 3.354 \times 10^5$. Denoting the extent of the reaction

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \tag{3}$$

at specified temperature as ξ and the initial number of moles of water present in a specified volume V as n_0, the numbers of moles of water, hydrogen, and oxygen present are, respectively, $n_0 - 2\xi$, 2ξ, and ξ, so that the total number of moles present (which determines the pressure) is $n_T = n_0 + \xi$. The required equilibrium constant is the reciprocal square of the formation equilibrium constant. Equilibrium requires

$$K \equiv \exp\left[-\frac{\Delta G^\circ}{RT}\right] = \frac{(2\xi)^2 \xi}{(n_0 - 2\xi)^2 (n_0 + \xi)} \cdot \frac{p}{p^\circ} \tag{4}$$

where the reference pressure p° is 1 bar. Assuming that the ideal gas equation of state applies (which is reasonable at high temperatures and low pressures) and substituting $p = n_T RT/V$, we obtain

$$\xi^3 - \frac{Kp^\circ V}{4RT}(4\xi^2 - 4\xi n_0 + n_0^2) = 0 \tag{5}$$

which can be solved exactly with the cubic formula. At 1000 K, the formation equilibrium constant is $10^{10.06}$, and with $n_0 = 1\,\text{mol}$ and $V = 1\,\text{m}^3$, this equation gives $\xi = 2.8360 \times 10^{-7}\,\text{mol}$; at 2000 K, where $K_f = 10^{3.54}$, $\xi = 0.49675 \times 10^{-2}\,\text{mol}$, corresponding to about 1% dissociation.

Hydrogen Sulfide

Significant quantities of hydrogen sulfide are produced from geothermal systems, sour gas wells, and as a byproduct of commercial petrochemical processes. The current method of disposal relies on combustion to sulfur dioxide; it is therefore of interest to examine the feasibility of thermolysis as an environmentally friendly method of disposal that does not contribute to the generation of acid rain. Thermolysis of hydrogen sulfide is also of interest since it occurs in several thermochemical cycles [(1), cycles 82, 83, 84, 90, 92, and 95]. Since the stoichiometry of the dissociation reaction is identical to that of Eq. (3), the calculated equilibrium extent of the reaction

$$2H_2S(g) \longrightarrow 2H_2(g) + S_2(g) \tag{6}$$

can be determined simply by substituting the appropriate values of the equilibrium constant. The formation equilibrium constant (adopting ideal diatomic sulfur gas at 1 bar as the reference state for S) is given by an equation of the same form as Eq. (2) but with $A = -9.0671$, $B = 4.942 \times 10^{-2}$, and $C = 2.4475$. At 1000 K, the formation equilibrium constant is $10^{2.15}$, corresponding to a dissociation equilibrium constant of $10^{-5.30}$. With $n_0 = 1$ mol and $V = 1\ \mathrm{m}^3$, this equation gives $\xi = 1.0568 \times 10^{-1}$ mol or about 10% dissociation. Calculation of the reaction equilibrium at lower temperatures is complicated by the need to consider the concurrent decomposition of hydrogen sulfide to (liquid) sulfur as well as diatomic sulfur gas, according to the reactions

$$2H_2S \longrightarrow 2H_2 + S_2 \tag{7}$$

$$H_2S \longrightarrow H_2 + S. \tag{8}$$

The occurrence of the second reaction depends on the initial concentration of hydrogen sulfide in the system; specifically, on whether the initial amount of H_2S is sufficient to allow the coexistence of liquid sulfur with diatomic sulfur vapor.

Methane

In addition to its importance as a fuel in its own right, current interest in hydrogen-powered fuel cells has focused much attention on the use of methane (from natural gas) as a source of hydrogen. The classical method for achieving this is steam reforming, but the fact that this generates a carbon monoxide/carbon dioxide waste stream has motivated the search for other viable hydrogen-producing processes, including dissociation. According to the tabulation of equilibrium constants [(3), page 119] for the formation reaction

$$C(\mathit{graphite}) + 2H_2(g) \longrightarrow CH_4(g) \tag{9}$$

the reverse of this process is considerably more favorable than the decomposition of water and hydrogen sulfide. For example, at 800 K, these authors give a formation equilibrium constant of $10^{0.13} = 1.35$, so that the equilibrium constant of the dissociation reaction is 0.741. Denoting the extent of dissociation as ξ and the initial amount of methane present in volume V as n_0, the amounts of methane and hydrogen present are, respectively, $n_0 - \xi$ and 2ξ, so that the total number of moles present is again $n_T = n_0 + \xi$. With the further assumption of the ideal gas equation of state, the equation for ξ is easily shown to be

$$K = \frac{RT}{p^\circ V} \frac{4\xi^2}{n_0 - \xi} \tag{10}$$

which has the solution

$$\xi = \frac{-k + \sqrt{k^2 + 16kn_0}}{8}, \quad k \equiv \frac{p^\circ V}{RT} K \qquad (11)$$

For this reaction, as with the others, ξ depends strongly on the assumed values of n_0 and V. For $n_0 = 1$ mol and $V = 1$ L, ξ is about 0.05; while if $V = 100$ L, it is about 0.40. Some of the newer methods of facilitating the dissociation of methane are discussed by Muradov (5) in a recent book on various aspects of hydrogen production and storage (6). These include catalysis by metals or metal oxides and photcatalytic activation, in which methane is adsorbed on silica-supported polyoxytungstates and dissociated into atoms and radicals by absorption of ultraviolet light. More exotic processes like plasma decomposition have been suggested (7), but Muradov (5) points out that because the electricity required comes largely from thermal power plants, the net effect is still production of carbon dioxide. As pointed out by Lackner (8), an even more fundamental objection to this process is that it allows use to be made only of the energy obtainable from the combustion of hydrogen and not of the carbon. The calculations presented in this section not only confirm the thermodynamic infeasibility of the direct thermolysis of water as a method of hydrogen production but also indicate that the thermolysis of hydrogen sulfide deserves more careful study. It is also worth pointing out that the decomposition of other hydrides—in particular, those of the halogens—figures prominently in many of the thermochemical water-splitting cycles that were identified recently (2) as leading candidates for commercialization. For example, the sulfur-iodine process produces hydrogen by dissociation of hydrogen iodide. The other hydrogen halides are, however, considerably less thermally labile than HI but may be dissociated electrochemically.

CYCLIC PROCESSES

Assessment of the overall efficiency of a thermochemical hydrogen-production cycle operating between a high and a low temperature involves complex calculations that take account of the heat transfers associated with addition of reactants, removal of products, raising reactants to the high temperature, and cooling products to the low temperature, in addition to the enthalpy changes of the various reactions (9). In some situations it might be necessary also to include the calorific yield of the hydrogen produced by the cycle. An overview of the technical and economic criteria that are applicable to thermochemical hydrogen production from water has been given by Beghi (10). In the present paper, we focus on the thermodynamic characteristics of the reactions, which we feel are crucial to the viability of such cycles.

Stoichiometric Analysis

The systematic evaluation of reaction cycles is greatly facilitated by the application of the theory of stoichiometry [as outlined, for example, by Smith and Missen (11), chapter 2]. The fundamental concept involved here is that a multicomponent system can be characterized by a stoichiometric matrix, **A**, in which the *j*-th element of the *i*-th row is the subscript of the *i*-th chemical element symbol in the formula of the *j*-th component. This matrix plays a vital role in both "nonstoichiometric" and "stoichiometric" calculations of the equilibrium composition in chemically reacting systems. Thus, in the former, **A** is the coefficient matrix of the system of linear constraints that expresses the conservation of each element. In the latter, changes in the composition of the system are expressed in terms of the extents of a set of chemical reactions, which are in general quite distinct from the molecular processes that actually take place. The problem of finding the stoichiometric coefficients in these reactions (i.e., of balancing the equations) is reduced to straightforward operations of linear algebra on the columns of **A**. The stoichiometric formulation is of particular relevance to the study of thermochemical cycles, where the basic idea is to find combinations of reactions that are additively equivalent to the dissociation of water. It is accordingly appropriate to summarize very briefly the main steps involved; further details can be found in Smith and Missen [(11), chapter 2]. For a system consisting of C components and E elements, the number of reactions is in general $R = C - E$. The first step in finding these reactions is to arrange the columns of **A** in the form $[\mathbf{A}_E|\mathbf{A}_R]$, where $\mathbf{A}_E$ is an $E \times E$ square submatrix consisting of E linearly independent columns of **A**. Next, $\mathbf{A}_E$ is inverted, and the product $\mathbf{Z} = \mathbf{A}_E^{-1}\mathbf{A}_R$ is evaluated. Finally, the $N \times R$ matrix $\mathbf{N} = [-\mathbf{Z}, \mathbf{I}_R]^T$ is formed, where $\mathbf{I}_R$ is the R-dimensional identity matrix and T signifies the transpose of a matrix. This contains the required stoichiometric coefficients, using the convention that positive numbers refer to products, negative numbers to reactants, and zero to species that do not participate in the reaction. Balancing the equations is thus seen to be equivalent to expressing columns $E + 1$ to C of **A** as linear combinations of the basis columns 1 to E. Each of the R reactions obtained as just described can be characterized by a standard Gibbs energy change, which, for the i-th reaction, can be written in the general form

$$\Delta G_i^\circ = \sum_j \nu_{ij}\mu_j^\circ \tag{12}$$

where ν_{ij} is the ij-th element of $\mathbf{N}^T$ and μ_j° is the standard-state chemical potential. The latter quantity can be identified in a variety of ways [(11), section 3.12]. For present purposes, it is most convenient to equate it to the standard Gibbs energy of formation for component j, since Robie and

Hemingway (3) provide both tabulations and empirical functions expressing these quantities as a function of temperature. Thus,

$$\Delta G_i^\circ = \sum_j \nu_{ij} \Delta_f G_j^\circ \tag{13}$$

and the corresponding equilibrium constant is

$$K_i = \exp\left[-\frac{\Delta G_i^\circ}{RT} \right] \tag{14}$$

From a computational viewpoint, none of the operations discussed so far presents any particular difficulty. The potentially time-consuming input of the stoichiometric matrix elements can be avoided by use of a subprogram that accepts a vector of molecular formulae as character strings, dissects each formula into numbers and chemical symbols, and uses these to construct **A**.

Metal–Metal Oxide Cycles

A simple type of two-reaction thermochemical cycle is one in which water reacts with a metal (or some other reducing agent) M at the lower temperature to produce hydrogen and an oxidized product MO, while M is regenerated by thermal decomposition of MO at the higher temperature, i.e.,

$$x\mathrm{M}(s) + y\mathrm{H_2O}(g) \longrightarrow \mathrm{M}_x\mathrm{O}_y(s) + y\mathrm{H_2}(g) \tag{15}$$

$$\mathrm{M}_x\mathrm{O}_y(s) \longrightarrow x\mathrm{M}(s) + \frac{y}{2}\mathrm{O_2}(g) \tag{16}$$

These two equations clearly add to give

$$y\mathrm{H_2O}(g) \longrightarrow y\mathrm{H_2}(g) + \frac{y}{2}\mathrm{O_2}(g) \tag{17}$$

but the most important point is that H_2O and H_2 are at the lower temperature, T_1, and O_2 is at the higher temperature, T_2. It is possible to derive a quantitative criterion that can be used to examine the suitability of reactions for inclusion in this type of process. The standard Gibbs energy change for reaction 15 is

$$\Delta G_1^\circ = \Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s), T_1] - y\Delta_f G^\circ[\mathrm{H_2O}(g), T_1] \tag{18}$$

while that for Eq. (16) is

$$\Delta G_1^\circ = -\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}y(s), T_2] \tag{19}$$

The equilibrium constants for each reaction will be greater than 1 if these standard Gibbs energy changes are less than zero. Thus, we can expect this cycle to be thermodynamically feasible if

$$\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s), T_1] < y\Delta_f G^\circ[\mathrm{H_2O}(g), T_1] \tag{20}$$

and

$$\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s), T_2] > 0 \tag{21}$$

The operation of the stoichiometric analysis described in the preceding two paragraphs can be illustrated by noting that $C = 5$, $E = 3$, $R = 2$, identifying $\mathrm{M}(s)$, $\mathrm{M}_x\mathrm{O}_y(s)$, $\mathrm{H_2O}(g)$, $\mathrm{H_2}(g)$ and $\mathrm{O_2}(g)$ as species 1, 2, 3, 4, and 5, respectively, and selecting the first three species as the algebraic basis. Then, if M, O, and H are denoted as elements (rows) 1, 2, and 3, respectively, the stoichiometric matrix and its submatrices are

$$\mathbf{A} = \begin{bmatrix} 1 & x & 0 & 0 & 0 \\ 0 & y & 1 & 0 & 2 \\ 0 & 0 & 2 & 2 & 0 \end{bmatrix}, \quad \mathbf{A}_E = \begin{bmatrix} 1 & x & 0 \\ 0 & y & 1 \\ 0 & 0 & 2 \end{bmatrix}, \quad \text{and} \quad \mathbf{A}_R = \begin{bmatrix} 0 & 0 \\ 0 & 2 \\ 2 & 0 \end{bmatrix} \tag{22}$$

Next, by simple algebra it is easily shown that

$$\mathbf{A}_E^{-1} = \begin{bmatrix} 1 & -\frac{x}{y} & \frac{x}{2y} \\ 0 & \frac{1}{y} & -\frac{1}{2y} \\ 0 & 0 & \frac{1}{2} \end{bmatrix}, \quad \text{and} \quad \mathbf{Z} \equiv \mathbf{A}_E^{-1}\mathbf{A}_R = \begin{bmatrix} \frac{x}{y} & -\frac{2x}{y} \\ -\frac{1}{y} & \frac{2}{y} \\ 1 & 0 \end{bmatrix} \tag{23}$$

from which the required stoichiometric coefficients are obtained as

$$\mathbf{N} \equiv [-\mathbf{Z}, \mathbf{I}_R]^T = \begin{bmatrix} -\frac{x}{y} & \frac{2x}{y} \\ \frac{1}{y} & -\frac{2}{y} \\ -1 & 0 \\ 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{24}$$

The columns of **N** correspond to the chemical reactions

$$\frac{x}{y}\mathrm{M}(s) + \mathrm{H_2O}(g) \longrightarrow \frac{1}{y}\mathrm{M}_x\mathrm{O}_y(s) + \mathrm{H_2}(g) \tag{25}$$

and

$$\frac{2}{y}\mathrm{M}_x\mathrm{O}_y(s) \longrightarrow \frac{2x}{y}\mathrm{M}(s) + \mathrm{O_2}(g) \tag{26}$$

which are clearly equivalent to Eq. (15) multiplied throughout by $1/y$, and Eq. (16) multiplied throughout by $2/y$, respectively. In chemical terms, Eq. (20) means that water needs to be a stronger oxidizing agent than $\mathrm{M}_x\mathrm{O}_y$ at temperature T_1, and Eq. (21) means that the oxide needs to be thermodynamically unstable with respect to the metal at temperature T_2. Among the substances for which $\Delta_f G^\circ(T)$ is tabulated by Robie and Hemingway (3), there are many for which the first condition is satisfied at ambient temperatures but none for which the second condition is satisfied except under extreme values of T_2. There are some oxides that decompose to lower oxides at high temperatures (such as $\mathrm{PbO_2/Pb_3O_4}$), but none of these satisfy the first condition at lower temperatures. However, Bamberger [(1), cycle 28] lists the set of reactions

$$\mathrm{Cd} + 2\mathrm{H_2O} \longrightarrow \mathrm{Cd(OH)_2} + \mathrm{H_2} \tag{27}$$

$$\mathrm{Cd(OH)_2} \longrightarrow \mathrm{CdO} + \mathrm{H_2O} \tag{28}$$

and

$$\mathrm{CdO} \longrightarrow \mathrm{Cd} + \frac{1}{2}\mathrm{O_2} \tag{29}$$

which is of the same general form, with a maximum temperature of 1500 K. Assessment of the thermodynamic feasibility of this process (in particular, of reaction 28) requires thermodynamic data that are not available either in (3) or in the JANAF Tables (4). By making the alternative identification of the standard-state chemical potential as

$$\mu^\circ \equiv \Delta_f H^\circ(298.15) + T\left[\frac{G^\circ(T) - H^\circ(298.15)}{T}\right] \tag{30}$$

[(11), page 67], it is possible to calculate the standard Gibbs energy of formation of CdO from the estimate $\Delta_f H^\circ(298.15) = -255.7\,\mathrm{kJ\cdot mol^{-1}}$ (12) and tabulated values of $-[G^\circ(T) - H^\circ(298.15)]/T$ for CdO(s) (13), for Cd(l) [(14), page 64], and for $\mathrm{O_2}$ [(4), page 1667]. In this way, it is found that the formation equilibrium constant for CdO(s) is $10^{8.082}$ at 1000 K and $10^{7.466}$ at 1100 K. Since the requisite data for calculations at higher temperature do not exist, the best one can do is to make a log-linear extrapolation as a function of $1/T$ from these two points to 1500 K. The estimate of K_f thus obtained is $10^{5.823}$, which is still too large to give reasonable conversions in reaction 28. This cycle therefore does not seem to be thermodynamically feasible. The fact that several transition metals form oxides corresponding to different valences suggests the possibility of identifying M in Eqs. (15) and (16) as a low-valent oxide. The general pattern that emerges for these systems is that it is the low-temperature reaction that is unfavorable. One example is the magnetite-hematite system, for which the reaction

$$3Fe_2O_3 \longrightarrow 2Fe_3O_4 + \frac{1}{2}O_2 \tag{31}$$

has a standard Gibbs energy change of $-6.8\,\mathrm{kJ \cdot mol^{-1}}$ at 1800 K [(3), pages 192–193]. However, as we will show later, the corresponding hydrogen-evolution reaction

$$2Fe_3O_4 + H_2O \longrightarrow 3Fe_2O_3 + H_2 \tag{32}$$

has a low equilibrium constant at low temperatures. In any event, the energy costs of maintaining temperatures as high as 1800K would probably be prohibitive.

Metal–Metal Oxide-Carbon Cycles

The unsuitability of the reaction scheme represented by Eqs. (15) and (16) as a practical method for generating hydrogen could have been anticipated; the impossibility of preparing most metals by thermolysis of their oxides is, after all, well known. However, it has also been known—since antiquity—that many metals can be prepared by reducing their oxides with carbon. The reaction of steam with iron coupled with reduction of iron oxide by carbon has, in fact, already been proposed as the basis for supplying hydrogen to automotive fuel cells (15). This suggests that it might be worth examining other reaction schemes consisting of the hydrothermal oxidation of a metal with a carbothermic reduction of its oxide. The production of a carbon oxide ($CO-CO_2$) waste stream may be identified as an obvious disadvantage of such processes. The adverse effects of carbon oxide production could, however, be mitigated on the one hand by the application of promising new technologies for carbon sequestration [reviewed recently by Lackner (8)], and on the other hand by possible enhancements in the efficiency of coal utilization. Systematic analysis of the feasibility of generating hydrogen by reacting steam with a metal, followed by use of carbon to reduce the metal oxide, each according to the reaction scheme

$$x\mathrm{M}(s) + y\mathrm{H_2O}(g) \longrightarrow \mathrm{M}_x\mathrm{O}_y(s) + y\mathrm{H_2}(g) \tag{33}$$

$$\mathrm{M}_x\mathrm{O}_y(s) + y\mathrm{C}(s) \longrightarrow x\mathrm{M}(s) + y\mathrm{CO}(g) \tag{34}$$

is facilitated by formulating an analytical condition analogous to that expressed by Eqs. (19) and (20) for metal-oxide cycles. Writing the hydrogen-evolution reaction as the resultant of the two processes

$$x\mathrm{M}(s) + \frac{y}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{M}_x\mathrm{O}_y(s) \tag{35}$$

and

$$y\mathrm{H}_2\mathrm{O}(g) \longrightarrow y\mathrm{H}_2(g) + \frac{y}{2}\mathrm{O}_2(g) \tag{36}$$

for which the standard Gibbs energy changes are $\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s)]$ and $-y\Delta_f G^\circ[\mathrm{H}_2\mathrm{O}(g)]$, respectively, the equilibrium constant for the combined process will be greater than 1 if

$$\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s)] < y\Delta_f G^\circ[\mathrm{H}_2\mathrm{O}(g)] \tag{37}$$

Similarly, writing the second reaction as the sum of the reactions

$$\mathrm{M}_x\mathrm{O}_y(s) \longrightarrow x\mathrm{M}(s) + \frac{y}{2}\mathrm{O}_2(g) \tag{38}$$

and

$$y\mathrm{C}(s) + \frac{y}{2}\mathrm{O}_2 \longrightarrow y\mathrm{CO}(g) \tag{39}$$

for which the standard Gibbs energy changes are $-\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s)]$ and $y\Delta_f G^\circ[\mathrm{CO}(g)]$, respectively, the equilibrium constant for the combined process will be greater than 1 if

$$\Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s)] > y\Delta_f G^\circ[\mathrm{CO}(g)] \tag{40}$$

Combining these two conditions, the use of the combined process will therefore be thermodynamically favorable if the inequality

$$y\Delta_f G^\circ[\mathrm{CO}(g)] < \Delta_f G^\circ[\mathrm{M}_x\mathrm{O}_y(s)] < y\Delta_f G^\circ[\mathrm{H}_2\mathrm{O}(g)] \tag{41}$$

is satisfied over some temperature range. This condition is illustrated geometrically in Figure 1, in which the standard Gibbs energies of formation for water and carbon monoxide are shown as a function of temperature. The inequality expressed by Eq. (40) is satisfied within the triangular region to the right of the point of intersection between the two graphs. The point of intersection of the graphs is the temperature at which the standard Gibbs energy change for the reaction

$$\mathrm{C}(s) + \mathrm{H}_2\mathrm{O}(g) \longrightarrow \mathrm{CO}(g) + \mathrm{H}_2(g) \tag{42}$$

is zero, or equivalently, that its equilibrium constant is exactly equal to 1. This is of great significance in coal gasification processes, as we discuss later.

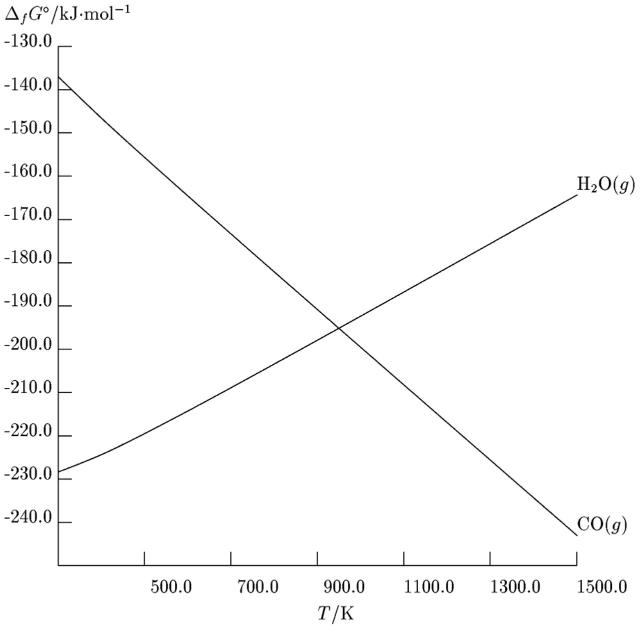

Figure 1. Standard Gibbs energies of formation for CO(g) and H_2O(g) as a function of temperature, calculated from empirical functions given by Robie and Hemingway [1995, pages 180, 194].

Application of the stoichiometric procedure can be achieved by observing that $C = 6$, $E = 4$, $R = 2$, identifying C, M, H_2O, M_xO_y, CO, and H_2 as species 1, 2, 3, 4, 5, and 6, and C, M, H, and O as elements 1, 2, 3, and 4, respectively. Then, with

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & x & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 2 \\ 0 & 0 & 1 & y & 1 & 0 \end{bmatrix}, \quad \mathbf{A}_E = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & x \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 1 & y \end{bmatrix},$$

$$\mathbf{A}_R = \begin{bmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 2 \\ 1 & 0 \end{bmatrix} \tag{43}$$

we obtain

$$\mathbf{A}_E^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & \dfrac{x}{2y} & -\dfrac{x}{y} \\ 0 & 0 & \dfrac{1}{2} & 0 \\ 0 & 0 & -\dfrac{1}{2y} & \dfrac{1}{y} \end{bmatrix} \quad \text{and} \quad \mathbf{Z} = \mathbf{A}_E^{-1}\mathbf{A}_R = \begin{bmatrix} 1 & 0 \\ -\dfrac{x}{y} & \dfrac{x}{y} \\ 0 & 1 \\ -\dfrac{1}{y} & \dfrac{1}{y} \end{bmatrix} \tag{44}$$

from which it follows that

$$\mathbf{N} = \begin{bmatrix} -1 & 0 \\ \dfrac{x}{y} & -\dfrac{x}{y} \\ 0 & -1 \\ -\dfrac{1}{y} & \dfrac{1}{y} \\ 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{45}$$

The first and second columns of **N** contain the stoichiometric coefficients of Eqs. (33) and (34), respectively, divided throughout by y.

In the following paragraphs we identify some of the systems that seem to have potential merit for use in hydrogen production. The calculations of the equilibrium constants are based on a generalization of Eq. (2), viz.,

$$\Delta_f G_j^\circ(T) = a_{0j} + a_{1j}T + a_{2j}T^2 + a_{3j}T^3 + \frac{b_j}{T^2} \tag{46}$$

in terms of which the standard Gibbs energy change for the i-th reaction is

$$\Delta G_i^\circ(T) = \sum_j \nu_{ij}\Delta_f G_j^\circ(T) = \Delta a_0(i) + T\Delta a_1(i) + T^2\Delta a_2(i) + T^3\Delta a_3(i) + \frac{1}{T^2}\Delta b(i) \tag{47}$$

where

$$\Delta a_0(i) = \sum_j \nu_{ij}a_{0j}$$

The equilibrium constants were calculated as function of temperature between 300 K and 1500 K, which includes the operating range of most published thermochemical cycles. Of particular interest are the temperatures at which the equilibrium constants are greater than 1, since this indicates that the reaction is thermodynamically favorable. The value of the hydrogen-producing reaction at ambient temperatures (300 K) is also given. For ease of future reference the values of $\Delta a_0(i)$, $\Delta a_1(i)$, $\Delta a_2(i)$, $\Delta a_3(i)$, and $\Delta b(i)$ are given for each reaction i.

Iron Oxides

In addition to the iron-magnetite system already proposed by Otsuka et al. (15), similar schemes involving conversion of wustite (FeO) to magnetite and magnetite to hematite (Fe_2O_3) are in principle possible.

System: Fe-FeO
Reactions:

1. $C + FeO \rightarrow Fe + CO$
2. $Fe + H_2O \rightarrow FeO + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta a_3(r)$	$\Delta b(r)$
1	0.1588E + 03	−0.1530E + 00	0.0000E + 00	0.0000E + 00	−0.7580E + 05
2	−0.2290E + 02	0.1002E − 01	0.0000E + 00	0.0000E + 00	−0.2594E + 06

$K_1 > 1$ between 1000 and 1050 K; $K_2 < 1$ above 1550 K; $K_2(300) = 10^{3.97}$.

System: Fe-Fe_3O_4
Reactions:

1. $C + \frac{1}{4}Fe_3O_4 \rightarrow \frac{3}{4}Fe + CO$
2. $\frac{3}{4}Fe + H_2O \rightarrow \frac{1}{4}Fe_3O_4 + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta\ a_3(r)$	$\Delta b(r)$
1	0.1584E + 03	−0.1609E + 00	0.0000E + 00	0.0000E + 00	0.3594E + 06
2	−0.2250E + 02	0.1790E − 01	0.0000E + 00	0.0000E + 00	−0.6946E + 06

$K_1 > 1$ between 950 and 1000 K; $K_2 < 1$ between 1250 and 1300 K; K_2 (300) $= 10^{4.32}$.

System: FeO-Fe_3O_4
Reactions:

1. $C + Fe_3O_4 \rightarrow 3FeO + CO$
2. $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta a_3(r)$	$\Delta b(r)$
1	$0.1572E+03$	$-0.1846E+00$	$0.0000E+00$	$0.0000E+00$	$0.1665E+07$
2	$-0.2130E+02$	$0.4156E-01$	$0.0000E+00$	$0.0000E+00$	$-0.2000E+07$

$K_1 > 1$ between 850 and 900 K; $K_2 < 1$ between 600 and 650 K; K_2 (300) $= 10^{5.40}$. Comparison of the results for these systems shows that above about 650 K, wustite is thermodynamically stable with respect to magnetite in the presence of steam. The temperature at which iron, magnetite, and wustite are in equilibrium is an invariant point, defined by the reaction

$$\mathrm{Fe} + \mathrm{Fe_3\,O_4} = 4\mathrm{FeO}.$$

System: $Fe_3O_4 - Fe_2O_3$
Reactions:

1. $3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO$
2. $2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta a_3(r)$	$\Delta b(r)$
1	$0.1416E+03$	$-0.2327E+00$	$0.0000E+00$	$0.0000E+00$	$-0.3469E+06$
2	$-0.5700E+01$	$0.8968E-01$	$0.0000E+00$	$0.0000E+00$	$0.1170E+05$

$K_1 > 1$ between 600 and 650 K; $K_2 < 1$ above 300 K; K_2 (300) $= 10^{-3.71}$. This shows that it is not possible to oxidize magnetite to hematite with steam. The Gibbs energies of formation of wustite, and magnetite are shown in Fig. 2.

Tin Oxide

System: $Sn\text{-}SnO_2$
Reactions:

1. $C + \frac{1}{2}SnO_2 \rightarrow \frac{1}{2}Sn + CO$
2. $\frac{1}{2}Sn + H_2O \rightarrow \frac{1}{2}SnO_2 + H_2$

r	Δa_0 (r)	Δa_1 (r)	Δa_2 (r)	Δa_3 (r)	Δb (r)
1	$0.1750E+03$	$-0.1909E+00$	$0.0000E+00$	$0.0000E+00$	$0.8794E+05$
2	$-0.3915E+02$	$0.4788E-01$	$0.0000E+00$	$0.0000E+00$	$-0.4232E+06$

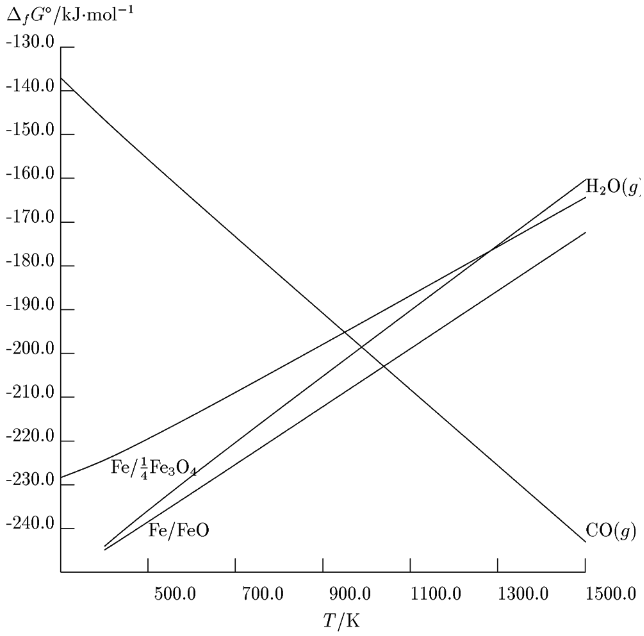

Figure 2. Standard Gibbs energy of formation for iron oxides, calculated from the functions given by Robie and Hemingway [1995, pages 191–193].

$K_1 > 1$ between 900 and 950 K; $K_2 < 1$ between 800 and 850 K; $K_2(300) = 10^{5.13}$.

Tungsten Oxide

System W-WO_2:
Reactions:

1. $C + \frac{1}{2}WO_2 \rightarrow \frac{1}{2}W + CO$
2. $\frac{1}{2}W + H_2O \rightarrow \frac{1}{2}WO_2 + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta a_3(r)$	$\Delta b(r)$
1	0.1757E + 03	−0.1718E + 00	0.0000E + 00	0.0000E + 00	0.3365E + 06
2	−0.3980E + 02	0.2878E − 01	0.0000E + 00	0.0000E + 00	−0.6717E + 06

$K_1 > 1$ between 1000 and 1050 K; $K_2 < 1$ between 1350 and 1400 K; K_2 (300) $= 10^{6.73}$.

Other Possibilities

System: Co-CoO
Reactions:

1. $C + CoO \rightarrow Co + CO$
2. $Co + H_2O \rightarrow CoO + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta a_3(r)$	$\Delta b(r)$
1	0.1205E + 03	−0.1582E + 00	0.0000E + 00	0.0000E + 00	0.1632E + 06
2	0.1540E + 02	0.1520E − 01	0.0000E + 00	0.0000E + 00	−0.4984E + 06

$K_1 > 1$ between 800 and 850 K; K_2 increases from $10^{-2.5}$ at 300 K to $10^{-1.3}$ at 1500 K.

System: Mo-MoO$_3$:
Reactions:

1. $C + \frac{1}{3}MoO_3 \rightarrow \frac{1}{3}Mo + CO$
2. $\frac{1}{3}Mo + H_2O \rightarrow \frac{1}{3}MoO_3 + H_2$

r	$\Delta a_0(r)$	$\Delta a_1(r)$	$\Delta a_2(r)$	$\Delta a_3(r)$	$\Delta b(r)$
1	0.1302E + 03	−0.1653E + 00	0.0000E + 00	0.0000E + 00	0.2675E + 06
2	0.5700E + 01	0.2228E − 01	0.0000E + 00	0.0000E + 00	−0.6027E + 06

$K_1 > 1$ between 750 and 800 K. K_2 decreases slowly from about 10^{-1} to $10^{-1.3}$. These schemes can be regarded as marginally feasible; K_2 for each is sufficiently close to 1 that the reaction could be driven in the desired direction by high pressure or removal of H_2.

DISCUSSION

In the same way as the simple metal–metal oxide reaction schemes considered earlier are equivalent to the dissociation of water, the metal–metal oxide-carbon systems considered in the preceding section are clearly equivalent to

$$C(T_2) + H_2O(T_1) \longrightarrow CO(T_2) + H_2(T_1) \qquad (48)$$

The isothermal counterpart of reaction 48 represents a very significant use of coal; it also provides a natural basis for comparing the performance of the non-isothermal processes. This comparison is facilitated by applying the stoichiometric analysis of the preceding section with M identified as CO, which results in this pair of reactions:

$$2CO \longrightarrow C + CO_2 \tag{49}$$

$$C + H_2O \longrightarrow CO + H_2. \tag{50}$$

We refer to these reactions as 1 and 2, respectively. The constants required for calculation of standard Gibbs energy changes from Eq. (47), together with numerical values of the corresponding equilibrium constants, are given in Table 1. At about 1000 K, both reactions have equilibrium constants of about 1, which means that each can be expected to occur to a significant extent; the immediate practical consequence of this is that equilibrium results in a mixture of all four gaseous components. At 1500 K, where K_1 is more than 5 orders of magnitude less than K_2, the product will be a mixture of CO and H_2. This can be burned as a fuel or used as a feedstock for a variety of chemical processes (such as hydroformylation of alkenes or Fischer-Tropsch synthesis of higher hydrocarbons), but would not be useful as a source of hydrogen for fuel cells in which the electrodes are "poisoned" by adsorption of carbon monoxide. To explore this point further, let us calculate the equilibrium composition of the mixture resulting from reaction of n_c moles of carbon and n_w moles of steam in a volume of 1 m^3. Denoting C, CO, H_2O, CO_2, and H_2 as species 1, 2, 3, 4, and 5, respectively, the vector of mole numbers are related to the extents ξ_1 and ξ_2 of the two

Table 1. Equilibrium constants for reactions 49 and 50 calculated from Eqs. (47) and (46)[a]

T/K	$\log K_1$	$\log K_2$	T/K	$\log K_1$	$\log K_2$
300	20.2973	−15.5444	350	16.1134	−12.4042
400	12.9755	−10.0038	450	10.5349	−8.1135
500	8.5825	−6.5881	550	6.9851	−5.3323
600	5.6539	−4.2809	650	4.5275	−3.3882
700	3.5620	−2.6208	750	2.7253	−1.9543
800	1.9932	−1.3701	850	1.3471	−0.8538
900	0.7729	−0.3944	950	0.2591	0.0172
1000	−0.2033	0.3878	1050	−0.6216	0.7235
1100	−1.0020	1.0288	1150	−1.3492	1.3077
1200	−1.6676	1.5636	1250	−1.9604	1.7990
1300	−2.2307	2.0164	1350	−2.4810	2.2178
1400	−2.7135	2.4049	1450	−2.9299	2.5791
1500	−3.1318	2.7417	1550	−3.3208	2.8939

[a] Constants required are as follows. For $r = 1$: Δa_0 (r), −0.1682E + 03; Δa_1 (r), 0.1721E + 00; Δa_2 (r), 0.0000E + 00; Δa_3 (r), 0.0000E + 00; Δb (r), −0.3715E + 03. For $r = 2$: For Δa_0 (r), 0.1359E + 03; Δa_1 (r), −0.1430E + 00; Δa_2 (r), 0.0000E + 00; Δa_3 (r), 0.0000E + 00; Δb (r), −0.3352E + 06.

reactions by

$$\begin{bmatrix} n_1 \\ n_2 \\ n_3 \\ n_4 \\ n_5 \end{bmatrix} = \begin{bmatrix} n_c \\ 0 \\ n_w \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 1 & -1 \\ -2 & 1 \\ 0 & -1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \xi_1 \\ \xi_2 \end{bmatrix} = \begin{bmatrix} n_c + \xi_1 - \xi_2 \\ -2\xi_1 + \xi_2 \\ n_w - \xi_2 \\ \xi_1 \\ \xi_2 \end{bmatrix} \tag{51}$$

Treating the mixture as ideal, the equilibrium conditions are

$$K_1 = \frac{p_4/p^\circ}{(p_2/p^\circ)^2} \quad \text{and} \quad K_2 = \frac{(p_2/p^\circ)(p_5/p^\circ)}{p_3/p^\circ} \tag{52}$$

where $p^\circ = 1$ bar and the partial pressures $p_1 - p_5$ are

$$p_2 = \frac{(-2\xi_1 + \xi_2)RT}{V}, \quad p_3 = \frac{(n_w - \xi_2)RT}{V}, \quad p_4 = \frac{\xi_1 RT}{V}, \quad \text{and}$$
$$p_5 = \frac{\xi_2 RT}{V} \tag{53}$$

Defining $k_1 = K_1 \; (RT/p^\circ V)$ and $k_2 = K_2 \; (RT/p^\circ V)^{-1}$, the equilibrium equations simplify to

$$k_1 = \frac{\xi_1}{(\xi_2 - 2\xi_1)^2} \quad \text{and} \quad k_2 = \frac{\xi_2(\xi_2 - 2\xi_1)}{n_w - \xi_2} \tag{54}$$

From the requirement that the mole numbers be positive, it is immediately apparent that $\xi_2 < n_w$ and that $\xi_1 < \xi_2/2$, or that the quantity $u = \xi_2 - 2\xi_1 > 0$. The second equilibrium equation can be solved to express ξ_2 in terms of u:

$$\xi_2 = n_w \frac{k_2}{k_2 + u} \tag{55}$$

Combining the first of Eq. (54) with this result and $\xi_1 = (\xi_2 - u)/2$ leads to a cubic equation for u:

$$\frac{1}{2}\left(n_w \frac{k_2}{k_2 + u} - u\right) = k_1 u^2$$
$$\Rightarrow u^3 + \left(k_2 + \frac{1}{2k_1}\right)u^2 + \frac{k_2}{2k_1}u - \frac{k_2}{2k_1}n_w = 0 \tag{56}$$

which can be solved exactly. For example, assuming that $T = 1000$ K, we have $k_1 = 0.052017$ and $k_2 = 29.412270$. With $n_c = 1000$ mol and $n_w = 100$ mol, Eq. (56) gives $u = 19.670423$ mol, in terms of which $\xi_1 = 20.126744$ mol and $\xi_2 = 59.923912$ mol. From Eq. (51), the respective mole numbers of species 1 to 5 are therefore 960.202832, 19.670423, 40.076088, 20.126744, and 59.923912. Finally the mole fractions of the gaseous species are $y_2 = 0.140707$, $y_3 = 0.286673$, $y_4 = 0.143971$, and $y_5 = 0.428649$, and the equilibrium pressure is 11.623449 bar. The results of repeating this calculation for temperatures up to 1500 K are shown in Table 2; the best that can be expected is evidently an equimolar mixture of CO and H_2.

If, on the other hand, the same quantity of water were to be reacted with Sn (for example) at 400 K, at which the equilibrium constant of the reaction $Sn + 2H_2O \rightarrow SnO_2 + 2H_2$ is 10^{296}, the equilibrium ratio of the fugacities of hydrogen and steam would be $\sqrt{10^{2.96}} = 10^{1.48} = 30.20$, corresponding to hydrogen of roughly 97% purity. Further purification by condensing the steam to liquid would be straightforward. The reduction of the tin dioxide formed in this process would in general give rise to a mixture of carbon monoxide and carbon dioxide, formed by the parallel reactions

$$SnO_2 + 2C \longrightarrow Sn + 2CO \tag{57}$$

$$SnO_2 + C \longrightarrow Sn + 2CO_2 \tag{58}$$

which are, in fact, the basis for the extractive pyrometallurgy of tin. Since each of these reactions involves only one gaseous species, the equilibrium partial pressures of CO and CO_2 (divided by $p^\circ = 1$ bar) are equal to the respective

Table 2. Equilibrium composition resulting from reaction of 100 moles of water with 1000 moles of carbon in a volume of 1 m^3

T/K	y_2	y_3	y_4	y_5	p/bar
600.0	0.000125	0.891243	0.036169	0.072463	5.176585
650.0	0.000536	0.832923	0.055335	0.111206	5.724251
700.0	0.001837	0.762957	0.077790	0.157416	6.323692
750.0	0.005236	0.684818	0.101570	0.208376	6.981552
800.0	0.012794	0.602302	0.124037	0.260867	7.706027
850.0	0.027416	0.518770	0.142132	0.311681	8.510234
900.0	0.052350	0.436899	0.152800	0.357950	9.414431
950.0	0.090054	0.358872	0.153674	0.397401	10.444359
1000.0	0.140707	0.286673	0.143971	0.428649	11.623449
1050.0	0.201142	0.222188	0.125176	0.451494	12.958987
1100.0	0.265173	0.166979	0.100891	0.466956	14.427284
1150.0	0.325556	0.121908	0.075660	0.476876	15.968503
1200.0	0.376586	0.086894	0.053311	0.483209	17.501078
1250.0	0.415754	0.060940	0.035851	0.487455	18.951909
1300.0	0.443618	0.042443	0.023440	0.490499	20.281518
1350.0	0.462444	0.029618	0.015165	0.492773	21.486938
1400.0	0.474813	0.020853	0.009841	0.494494	22.587344
1450.0	0.482866	0.014880	0.006463	0.495791	23.608209
1500.0	0.488130	0.010787	0.004318	0.496765	24.572358

equilibrium constants, *viz.*, $K_1 = K_f\,(\mathrm{CO})^2/K_f\,(\mathrm{SnO_2})$ and $K_2 = K_f\,(\mathrm{CO_2})/K_f\,(\mathrm{SnO_2})$. From Robie and Hemingway [(3), pages 180, 181, 219], $K_f\,(\mathrm{CO}) = 10^{10.44}$, $K_f\,(\mathrm{CO_2}) = 10^{20.68}$, and $K_f\,(\mathrm{SnO_2}) = 10^{19.18}$; therefore $K_1 = 10^{1.50}$ and $K_2 = 10^{1.70}$. The mole fraction of CO in the product stream would accordingly be about 0.39. In general, the ratio of the partial pressures of the two carbon oxides is equal to K_1/K_2, which is easily shown to be the reciprocal of the equilibrium constant for reaction 49. This reaction is known to be catalyzed by WO_3 and has been suggested as a means by which waste carbon dioxide could be transformed into a solid product (16).

CONCLUSIONS

The purpose of this paper was to describe a procedure by which the thermodynamic feasibility of reaction cycles for hydrogen production from water could be related to the thermodynamic characteristics of the individual oxygen- and hydrogen-producing reactions. This procedure was illustrated for processes involving a low-temperature reaction of a metal (or other reducing agent) with steam, followed either by (a) simple thermolysis of the oxidized species at some higher temperature, or (b) reduction with carbon. Examination of about 45 metal–metal-oxide systems leads to the conclusion that the first choice for the high-temperature process is not feasible, as a result of the high stability of the oxides. Reduction by carbon is thermodynamically favorable for many metal oxides. For several specific systems (Fe–FeO, Sn–SnO_2, and W–WO_2) the low-temperature reaction with steam and high-temperature reduction of the oxide are thermodynamically favorable at temperatures between 300 and 1000 K. Use of these reaction schemes to generate hydrogen has two great advantages for coal utilization (*viz.*, that hydrogen production is accomplished with a lower energy input and that separate streams of hydrogen and carbon oxides are created, thereby avoiding the need for subsequent separation).

REFERENCES

1. Bamberger, C.E. (1978) Hydrogen Production from Water by Thermochemical Cycles: A 1977 Update. *Cryogenics*, 18: 170–182.
2. Brown, L.C., Funk, J.F., and Showalter, S.K. (2000) *Initial Screening of Thermochemical Water-Splitting Cycles for High-Efficiency Generation of Hydrogen Fuels Using Nuclear Power.* Technical Report GA-A23373, General Atomics Corporation.
3. Robie, R.A. and Hemingway, B.S. (1995) *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures*, United States Government Printing Office: Washington,

DC, Volume 2131 of U.S. Geological Survey Bulletin. A summary of the thermodynamic data for minerals at 298.15 K together with calculated values for the functions $C^0_{p,T}$, $\Delta_f H^0_T$, $\Delta_f G^0_T$, S^0_T, $(H^0_T - H^0_{298})/T$, and $(G^0_T - H^0_{298})/T$ at temperatures up to 1800 K.

4. Chase, M.W., Jr., Davies, C.A., Downey, J.R., Jr., Frurip, D.J., McDonald, R.A., and Syverud, A.N. (1985) *JANAF Thermochemical Tables*, 3rd edition; National Bureau of Standards: Washington, DC.
5. Muradov, Nazim. Hydrogen from Fossil Fuels without CO_2 Emissions. In *Advances in Hydrogen Energy*; Grégoire Padró, C.E. Lau, F., Eds.; Kluwer Academic/Plenum Publishers: New York, 2000; 1–16. Proceedings of an American Chemical Society Symposium on Hydrogen Production, Storage and Utilization, New Orleans, LA, August 22–26, 1999.
6. Grégoire Padró, C.E. and Lau, F. *Advances in Hydrogen Energy*. Kluwer Academic/Plenum Publishers: New York, 2000. Proceedings of an American Chemical Society Symposium on Hydrogen Production, Storage and Utilization, New Orleans, LA, August 22–26, 1999.
7. Gordon, C.L., Lobban, L.L., and Mallinson, R.G. The Production of Hydrogen from Methane Using Tubular Plasma Reactors. In *Advances in Hydrogen Energy*. Grégoire Padró, C.E. and Lau, F., Eds.; Kluwer Academic/Plenum Publishers: New York, 2000, 57–67. Proceedings of an American Chemical Society Symposium on Hydrogen Production, Storage and Utilization, New Orleans, LA, August 22–26, 1999.
8. Lackner, K.S. (2002) Carbonate Chemistry for Sequestering Fossil Carbon. *Ann. Rev. Energy Environ.*, 27: 193–232.
9. Broggi, A., Joels, R., Morbello, M., and Spelta, B. (1977) OPTIMO — Method for Process Evaluation Applied to Thermochemical Decomposition of Water. *Int. J. Hydrogen Energy*, 2 (1): 23–30.
10. Beghi, G.E. (1986) A Decade of Research on Thermochemical Hydrogen at the Joint Research Centre, Ispra. *Int. J. Hydrogen Energy*, 11 (12): 761–771.
11. Smith, W.R. and Missen, R.W. (1982) *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*; Wiley: New York.
12. Schuffenecker, L., Balesdent, D., and Houriez, J. (1981) Calorimetry and Equilibrium Measurements for the Reaction of Cadmium on Divalent Lead Oxide Between 740 and 1050 K. Standard Molar Enthalpy of Formation of Cadmium Oxide. *J. Chem. Thermodyn.*, 13: 849–856.
13. Mills, K.C. (1972) The Heat Capacities of Ga_2 O_3 (c), Tl_2 O_3 (c), ZnO(c), and CdO(c). *High Temp. — High Press.*, 4: 371–377.
14. Hultgren, R., Orr, R.L., Anderson, P.D., and Kelley, K.K. (1963) *Selected Values of Thermodynamic Properties of Metals and Alloys*; Wiley: New York.
15. Otsuka, K., Yamada, C., Kaburagi, T., and Takenaka, S. (1972) Hydrogen Storage and Production by Redox of Iron Oxide for Polymer Electrolyte Fuel Cell Vehicles. *Int. J. Hydrogen Energy*, 28 (3): 335–342.
16. Isihara, T., Fujita, T., Mizuhara, Y., and Takita, Y. (1991) Fixation of Carbon Dioxide to Carbon by Catalytic Reduction Over Metal Oxides. *Chem. Lett.*, 12: 2237–2240.