Thermochemical Cycles for the Production of Hydrogen:
The Adiabatic UT-3 and Sulfur-Iodine

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Abstract

Presently, there is no method of producing hydrogen which is cost-effective, environmentally-friendly, and suitable for large-scale production. Thermochemical water-splitting cycles promise to provide such a method, since they reduce the temperature required for thermolysis of water while increasing the product turnover rate. In particular, the Adiabatic UT-3 and Sulfur-Iodine cycles have proven to be the most advanced and have the greatest potential for meeting these criteria. The Adiabatic UT-3 cycle has been pursued almost exclusively by researchers in Japan, and consists of the following reactions:

\[
2\text{Br}_2(g) + 2\text{CaO}(s) \rightarrow 2\text{CaBr}_2(s) + \frac{1}{2} \text{O}_2(g)
\]
\[
3\text{FeBr}_2(s) + 4\text{H}_2\text{O}(g) \rightarrow \text{Fe}_3\text{O}_4(s) + 6\text{HBr}(g) + \text{H}_2(g)
\]
\[
\text{CaBr}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{CaO}(s) + 2\text{HBr}(g)
\]
\[
\text{Fe}_3\text{O}_4(s) + 8\text{HBr}(g) \rightarrow \text{Br}_2(g) + 3\text{FeBr}_2(s) + 4\text{H}_2\text{O}(g)
\]

This cycle has been tested at a pilot plant and is the closest to commercial production; however, the gas-solid nature of the reactants and products in this cycle limit the completion of reactions, and there seems to be little room for improvement of the cycle’s 36-40% efficiency.

The Sulfur-Iodine cycle is being researched primarily by the U.S. Department of Energy:

\[
x\text{I}_2(l) + \text{SO}_2(aq) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{HI}_x(l) + \text{H}_2\text{SO}_4(aq)
\]
\[
\text{H}_2\text{SO}_4(g) \rightarrow \text{SO}_2(g) + \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g)
\]
\[
2\text{HI}(l) \rightarrow \text{I}_2(l) + \text{H}_2(g)
\]

Its estimated efficiency, based on integrated flowsheet analysis, is 50%, but the thermodynamics of the sulfuric acid decomposition step are not well-established. Excesses of I\(_2\) and H\(_2\)O must also be managed, as well as extraction of HI from the “HI\(_x\)” mixture resulting from the cycle’s first reaction. A pilot plant test is currently in development.

Construction materials are key requirements for the success of both cycles, due to the highly corrosive nature of the heated Br\(_2\), HBr, H\(_2\)SO\(_4\), and HI reactants. High-temperature nuclear reactor designs are also examined, in particular the Generation IV High Temperature Gas-cooled Reactor (HTGR).
Introduction

Hydrogen presents a two-fold solution to the current energy crisis – it is currently used to process heavy hydrocarbon fuels, and may soon serve as an ecologically friendly alternative energy resource for transportation. In Alberta, Canada, a method called hydrodesulfurization (HDS) uses hydrogen gas to reduce the sulfur and nitrogen content of the fuel extracted from the oil sands present there\(^1\) by a hydrogenation reaction, allowing for the production of cleaner synthetic crude oil\(^2\). This process has contributed to the oil sands’ currently providing 62% of Alberta’s crude oil\(^3\), which substantially alleviates that province’s energy needs. Heavy oil, which consists of heavy hydrocarbons, may also be treated with gaseous hydrogen to reduce its viscosity in a process called hydro-cracking\(^3\).

The proposal to use fuel cells to power the vehicles of the near-future also requires the use of hydrogen. Because it is an energy carrier, and not an energy source, however, hydrogen must be manufactured, and this production must be in a manner which preferably 1) does not emit greenhouse gases, 2) is on a scale which would support the needs of a hydrogen-based economy, and 3) produces hydrogen that is pure enough that it will not contaminate fuel cells.

Methods of Hydrogen Production

The current principal method by which hydrogen is produced today is through Steam Methane Reforming of natural gas (SMR). This method, which produces 95% of the hydrogen in the U.S.\(^4\), works by the following two reactions:
(1) \[ \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \] (700-1000°C) (3-25bar)

(2) \[ \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2 + \text{H}_2(\text{g}) \]

(Each of the reactions here mentioned will have their own designated numbers throughout this paper, in order to more easily reference them as needed).

Although the efficiency of this process is approximately 80%\(^5\), it is clear from the presence of CO\(_2\) as a byproduct, as well as the use of natural gas, that it is neither an environmentally friendly method nor a cost-effective one. By some estimations, the amount of natural gas required to produce enough hydrogen to support an economy based on fuel cells would be 8% greater than that currently required for all uses combined in the U.S\(^5\). In addition, the subsequent higher demand for, and depletion of natural gas resources would also rapidly increase the cost of hydrogen produced by this method.

These drawbacks then eliminate SMR technology as a viable means of production for a hydrogen economy. The remaining methods involve either the electrolysis of water or the use of thermochemical water-splitting cycles. Direct thermolysis of water is not considered on account of its requiring temperatures of 2500°C or more for only 10% water decomposition, as well as a method of separating the newly produced hydrogen and oxygen to prevent their recombination\(^6\).

For the electrolytic cycles, the method by which the electricity used is produced is integral to the calculation of the cycles’ overall efficiencies\(^4,7\). Given current and projected methods of electricity production, the overall efficiency of an electrolytic cycle is thus between 25% and 40%\(^5\). Electrochemical cycles also require thin membranes
located at each of the electrodes, in order to maintain only “minimal mixing of the anodic and cathodic products”\(^6\); this limits the reactors to a size which may be adequately covered by such membranes (in order to preserve economic efficiency), thereby reducing the thermodynamic efficiency\(^6\). The U.S. Department of Energy (DOE) continues to fund research towards improving this number, but for now, low efficiencies and the surface nature\(^7\) of the reaction are significant drawbacks. Electrochemical cells are also subject to significant degradation over time, further reducing their reliability for long term use; other options must therefore be explored. These other options include the thermochemical cycles, which have been estimated to cost approximately 60% of the amount of money required to produce hydrogen by electrolytic methods\(^8\).

**Thermochemical Cycles**

Thermochemical cycles accomplish the same net water-splitting as does direct water thermolysis, but at significantly lower temperatures and with higher conversion rates\(^6\). They consist of a series of reactions involving several different chemical compounds in addition to water. Typically, one or more of these reactions is highly endothermic, allowing energy (as heat) to be absorbed into the system\(^6\). Like a heat engine, the cycles then later go through an exothermic reaction to release some of the heat, and may require another final reaction to completely recycle all reactants except water\(^6\) (see Figure 1 below).
In July 2000, the Nuclear Energy Research Initiative (NERI) submitted its annual report on General Atomics Project 30047 to the DOE, entitled *High Efficiency Generation of Hydrogen Fuels Using Nuclear Power*. In it, authors Brown, Funk, and Showalter performed a survey of “over one hundred thermochemical water-splitting cycles” as the initial part of a 3-phase evaluation, designed with the intent to “define an economically feasible concept for production of hydrogen, by nuclear means, using an advanced high temperature nuclear reactor as the energy source”. Using the following series of criteria (see Tables 1 and 2), they conducted a literature survey in phase 1, and narrowed the list down to the highest rated cycles for further examination in the following 2 phases of the study.
<table>
<thead>
<tr>
<th>RATIONAL FOR DEVELOPMENT OF FIRST ROUND SCREENING CRITERIA</th>
</tr>
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<tbody>
<tr>
<td><strong>Desirable Characteristic</strong></td>
</tr>
<tr>
<td>1  Higher ranked cycles will have a minimum number of chemical reactions steps in the cycle.</td>
</tr>
<tr>
<td>2  Higher ranked cycles will have a minimum number of separation steps in the cycle.</td>
</tr>
<tr>
<td>3  Higher ranked cycles will have a minimum number of elements in the cycle.</td>
</tr>
<tr>
<td>4  Higher ranked cycles will employ elements which are abundant in the earth's crust, oceans and atmosphere.</td>
</tr>
<tr>
<td>5  Higher ranked cycles will minimize the use of expensive materials of construction by avoiding corrosive chemical systems, particularly in heat exchangers.</td>
</tr>
<tr>
<td>6  Higher ranked cycles will minimize the flow of solids.</td>
</tr>
<tr>
<td>7  Higher ranked cycles will have maximum heat input temperature compatible with high temperature heat transfer materials.</td>
</tr>
<tr>
<td>8  Higher ranked cycles will have been the subject of many papers from many authors and institutions.</td>
</tr>
<tr>
<td>9  Higher ranked cycles will have been tested at a moderate or large scale.</td>
</tr>
<tr>
<td>10 Higher ranked cycles will have good efficiency and cost data available.</td>
</tr>
</tbody>
</table>
Table 2: Screening criteria for phase 1, stage 2 evaluation of thermochemical water-splitting cycles. Reprinted from Brown, Funk, & Showalter (July 2000).

<table>
<thead>
<tr>
<th>Cycles down-rated for the following reasons:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. If any reaction has a large positive Gibbs free energy [change], that cannot be shifted by pressure, concentration or any other modification of the conditions of the reaction.</td>
</tr>
<tr>
<td>2. If it requires the flow of solids.</td>
</tr>
<tr>
<td>3. If it is excessively complex.</td>
</tr>
<tr>
<td>4. If it can not be well matched to the characteristics of a high temperature reactor.</td>
</tr>
<tr>
<td>5. If it requires an electrochemical step.</td>
</tr>
</tbody>
</table>

As seen in Tables 1 and 2 (above), all aspects of hydrogen production are taken into account in the study, including concerns specific to chemical, physical, engineering, economical, and safety perspectives. Of the 115 cycles reviewed in the first stage (see Table 1), the top twenty-five were selected to proceed on to the second stage’s review, where they were down-rated if they possessed any of the characteristics given in Table 2. The two highest rated cycles after this final literature review were the adiabatic UT-3 and the Sulfur-Iodine.

The Adiabatic UT-3

Developed by the University of Tokyo (UT), the adiabatic UT-3 cycle is currently being pursued extensively by the Japan Atomic Energy Research Initiative (JAERI). It consists of the following four reactions:
Table 3: Adiabatic UT-3 reactions and thermodynamic data. Gibbs free energies were not available for this cycle.

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>Reaction</th>
<th>Temp (°C)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2Br₂(g) + 2CaO(s) → 2CaBr₂(s) + ½ O₂(g)</td>
<td>672</td>
<td>-73</td>
</tr>
<tr>
<td>4</td>
<td>3FeBr₃(s) + 4H₂O(g) → Fe₃O₄(s) + 6HBr(g) + H₂(g)</td>
<td>560</td>
<td>384</td>
</tr>
<tr>
<td>5</td>
<td>CaBr₂(s) + H₂O(g) → CaO(s) + 2HBr(g)</td>
<td>760*</td>
<td>212</td>
</tr>
<tr>
<td>6</td>
<td>Fe₃O₄(s) + 8HBr(g) → Br₂(g) + 3FeBr₂(s) + 4H₂O(g)</td>
<td>210</td>
<td>-274</td>
</tr>
</tbody>
</table>

*Note: all literature available to the author denotes this as the temperature at which this reaction (5) occurs, yet, this is above CaBr₂’s documented melting point of 730°C, a discrepancy which strongly affects the structure of any hydrogen production plant using this cycle. It is unclear why this is the case, particularly with the reports produced by JAERI, which has done much of the research and development in this area. This has also been noted by Funk, Brown, & Showalter (July 2000).

Figure 2: Flow diagram of the adiabatic UT-3 cycle. Reprinted from Brown, Funk, & Showalter (July 2000).

As can be seen in Figure 2 (above), the production facility consists of a nuclear reactor, a secondary heat exchanger, four chemical reactors, three process heat exchangers, two membrane separators, and a recycle compressor. The reactions themselves take place in two pairs of stationary chemical reactors which contain all of the solid compounds.
(including the reactants and subsequently the products) – one containing the calcium compounds, and another the iron compounds. The solids may be in the form of packed beds of pellets, or honeycombed. Only the gases move through the system, warmed by the heat flowing from the nuclear reactor through the secondary heat exchanger. The gaseous reactants flow through the beds of solid products until they reach the solid reactant front; the reaction then takes place, and the gaseous product is whipped away to be heated or cooled before entering the next chamber. Rapidly removing the gaseous products from the chamber shifts the reaction equilibrium towards completion, a necessary step since reactions 3-5 have positive Gibbs free energies (note: the exact Gibbs free energies are not available). The reaction front within each reactor progresses from one end of the chamber to the other; just before it reaches the very end, the direction of flow is reversed, and the reactors exchange roles. Thus, the reaction front again moves back towards the (original) front of the chamber.

The minimum steam pressure is 18.5 atm in the total gas stream’s pressure of 20 atm, a majority of which is necessary for the gaseous mixture to carry adequate heat for the reaction to proceed; the gaseous reactant or product is not by itself sufficient for this, and an inert material (excess water vapor) is needed. In order to ensure the separation of hydrogen and oxygen products from each other (partial pressures are 0.2 atm and 0.1 atm, respectively) and the rest of the gaseous mixture, semipermeable membranes are used in a countercurrent exchange, with steam flowing along the reverse side of the membrane. The membranes used are composite – the one used to separate hydrogen, for example, is made of zirconium-silica.
Efficiency

The UT-3 cycle has been briefly run at the pilot plant MASCOT (Model Apparatus for the Study of Cyclic Operation in Tokyo) \(^9\), and at the time of this writing, the results of this test run are unavailable to the author of this paper. The method for determining the theoretical thermal efficiency (\(\eta\)) is based upon “the first and second laws of thermodynamics, for an open and steady flow system”\(^10\), as applied using the ASPEN-PLUS® modeling software\(^10\):

\[
\eta = \frac{Q_{H2} + Q_c}{\sum E_i}
\]

Where \(Q_{H2}\) is the high heating value of hydrogen, \(Q_c\) is the excess heat in the process, and \(\sum E_i\) is the total thermal input supplied to the process\(^10\). According to such a model, the projected efficiency of a hydrogen plant running on the adiabatic UT-3 cycle is approximately 36%-40\(^\%\)\(^6\), depending on the membrane recovery rate\(^6,10\). It is also speculated that if the plant were to “co-generate both hydrogen and electricity”\(^6\), the efficiency may increase to 49\(^\%\)\(^6,10\).

Advantages & Disadvantages

In summary, the UT-3 cycle is the most advanced of the thermodynamic cycles, and due to the test run of MASCOT, is considered to be “the closest to commercial development”\(^6\). There are, however, several drawbacks to the system:

1) It involves the use of solids, which precludes it from operating at a steady state\(^6\); this will affect the efficiency and heat requirements of the system, although it is not at this time clear to what extent\(^6\).
2) The gas-solid nature of the compounds limits the completion of the reaction, as it is difficult to allow for adequate diffusion of the gas into the solid without risking solid particles becoming swept up into the gas stream\textsuperscript{11}.

3) CaO and CaBr\textsubscript{2} have different lattice properties – “calcium oxide has a cubic structure with a lattice parameter of 4.81Å, while calcium bromide is orthorhombic with larger lattice parameters”\textsuperscript{11}, resulting in a “76% volume increase”\textsuperscript{11} in converting from CaO to CaBr\textsubscript{2}. The repeated subsequent reduction in size which occurs when the cycle is reversed will probably result in the cracking and breakup of the solid compounds\textsuperscript{11}.

4) There seems to be little space for improvement of the cycle – reaction 5’s maximum operating temperature of 760\degree C is actually above CaBr\textsubscript{2}’s melting point of 730\degree C (see note for Table 3), and so care must be taken to prevent the compound from moving through the system\textsuperscript{6}.

In addition, materials development is also a crucial aspect of the research needed for this cycle, due to the extremely corrosive nature of the heated Br\textsubscript{2} and HBr gases flowing through the reactor beds.

The Sulfur-Iodine Cycle

The Sulfur-Iodine (S-I) cycle has been actively pursued by the US DOE at several of its national laboratories, and in conjunction with General Atomics. The following reactions occur:
Table 4: Sulfur Iodine Cycle reactions and thermodynamic data\textsuperscript{6,12}.

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>Reaction</th>
<th>Temp (°C)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>(xI_2(l_2) + SO_2(aq) + 2H_2O(l_2) \rightarrow 2HI_x(l) + H_2SO_4(aq))</td>
<td>120</td>
<td>-41</td>
<td>-216</td>
</tr>
<tr>
<td>8</td>
<td>(H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g))</td>
<td>850</td>
<td>-137</td>
<td>371</td>
</tr>
<tr>
<td>9</td>
<td>(2HI(l) \rightarrow I_2(l) + H_2(g))</td>
<td>450</td>
<td>24</td>
<td>12</td>
</tr>
</tbody>
</table>

In summary, the above steps are illustrated in Figure 5 below:

Figure 3: the Sulfur-Iodine Cycle. Reprinted from Elder, et al.

Reaction 7: the Bunsen Reaction

The cycle begins with what is typically called the Bunsen reaction\textsuperscript{7}, i.e., the formation of sulfuric and hydriodic acids (see reaction 7 in Table 4). Research by General Atomics\textsuperscript{7} revealed that excess iodine and water in the Bunsen reaction lead to a spontaneous two-
phase liquid system, allowing for easy separation of the sulfuric acid (light phase) from the hydrogen iodide and iodine mixture (heavy phase); the latter is hereafter referred to as HIx:\(^6,^7\):

\[
9 \text{I}_2 + \text{SO}_2 + 16 \text{H}_2\text{O} \rightarrow (2\text{HI} + 10 \text{H}_2\text{O} + 8 \text{I}_2) + (\text{H}_2\text{SO}_4 + 4 \text{H}_2\text{O})
\]

The thermodynamics of this reaction (including the heat of reaction and phase compositions) are not well known\(^7\). Excess water and iodine are required for the following reasons\(^7\):

1) Side reactions, including

\[
\text{H}_2\text{SO}_4 + 6 \text{HI} \rightarrow \text{S} + 3\text{I}_2 + 4\text{H}_2\text{O}
\]

\[
\text{H}_2\text{SO}_4 + 8\text{HI} \rightarrow \text{H}_2\text{S} + 4 \text{I}_2 + 4\text{H}_2\text{O}
\]

are kept to a minimum when in the presence of large iodine and water excesses.

2) Phase purity must also be adequately provided for – this is accomplished by excess iodine.

Although these excesses serve to aid the reaction and provide favorable kinetics, they must be kept at a minimum in order to diminish wasted heat and reduce costs. This is a key goal of current research associated with the Sulfur-Iodine cycle, driven by the expectation that “it could lead to significant dehydration of the iodine rich phase [HIx]… [which] would be a major breakthrough for the cycle”\(^7\).

**Reaction 8: Sulfuric Acid Dehydration**

Reaction 8 in Table 4 describes the dehydration of the sulfuric acid into SO\(_3\), which subsequently decomposes into SO\(_2\) (later reused in the Bunsen reaction) and oxygen\(^7\).
minimize the energy required to heat the diluted sulfuric acid solution, the amount of
water used is also minimized by first concentrating the H₂SO₄⁷:

\[(H₂SO₄ + 4H₂O)(l) \rightarrow (H₂SO₄ + H₂O)(l) + 3H₂O \ (g)\]

“To optimize energy consumption,” the concentration is performed “in several flashes
with increasing temperature and pressure”⁷. Once complete, the following reactions
occur⁷:

- **Vaporization:** \( H₂SO₄(l) \rightarrow H₂SO₄(g) \) (350°C)
- **Dehydration:** \( H₂SO₄ \rightarrow H₂O + SO₃ \) (500°C)
- **Decomposition of SO₃:** \( SO₃ \rightarrow SO₂ + \frac{1}{2} O₂ \) (870°C)

By performing these reactions in three steps instead of one (necessarily at a high
temperature), the minimization of the heat is achieved⁷. Unlike the Bunsen reaction, the
thermodynamics of the sulfuric acid dehydration are well-established, but the following
challenges do exist concerning the SO₃ decomposition, including⁷:

1) Identifying specific catalysts,

2) Research & development of membranes for oxygen separation, since effective use
of such membranes could further reduce the temperature for this step.

**Reaction 9: Decomposition of HI**

The final step (Table 4, reaction 9) is the decomposition of HI into hydrogen and iodine –
this section is vital to the cycle’s overall efficiency. The mixture entering this section,
however, as seen in the above discussion of reaction 7, is HIₓ, consisting of the following
mixture of hydrogen iodide, iodine, and water:

\[ HIₓ = 2HI + 10H₂O + 8I₂ \]
The hydrogen iodide must be removed from the mixture in order to proceed with the decomposition, but this poses the following challenges:

1) The large amount of water increases the heat requirement for the separation,

2) The actual HI decomposition is slow and incomplete.

Simple distillation is not a viable option for the extraction of HI because of the azeotropic nature of the HI and H₂O mixture at 57 wt% HI. There are, therefore three other possibilities which may accomplish this – electrodialysis, extractive distillation, and reactive distillation:

![Figure 4: Options for extraction and subsequent decomposition of HI from the HIₓ mixture. Reprinted from Carles, Vitart, & Anzieu.](image)

As with the electrolytic water-splitting cycles, electrodialysis lowers the efficiency of the cycle, and thus is eliminated. In addition, the need for a third compound (phosphoric acid) in extractive distillation unfavorably complicates the cycle. Subsequently, the use of reactive distillation within the Sulfur-Iodine cycle appears to be the best option, especially since it is capable of extracting and decomposing HI within the same reactor.
**Reactive Distillation of HIₙ**

Although it has yet to be used experimentally\(^7,13\), reactive distillation provides a much simpler solution to the problem of HI extraction. This process does not break the HIₙ azeotrope; instead, the “HIₙ is distilled inside a pressurized reactive column, and the HI gas within the HIₙ vapor stream is decomposed catalytically, resulting in a gas mixture of HI, I₂, H₂, and H₂O”, report authors Russell, Jones, & Thomas in their book *Materials for the Hydrogen Economy*\(^13\). This is achieved by heating the HIₙ feed from reaction 7 (see Table 4) to 262°C before it flows into the reactive column\(^13\) (refer to Figure 6 below for an illustration of the entire process).

![Flowsheet of the reactive distillation method. Reprinted from Russell, Jones, & Thomas.](image)

**Figure 5:** Flowsheet of the reactive distillation method. Reprinted from Russell, Jones, & Thomas.

Once in the column, the HIₙ begins to boil at its base (at approximately 310°C\(^13\)), creating an “equilibrium vapor pressure of 750psi [51.0 atm] inside the distillation
The vaporized HIx then flows through a catalyst bed at the height of the column, where the decomposition of the HI within the gaseous mixture is accomplished at 310°C. The resulting compressed H₂ gas is removed from the top of the column, and the unreacted I₂, HI, and H₂O are condensed and refluxed to the bottom. The resulting HIx is rich in iodine content, and is now used to supply the I₂ necessary for reaction.

**Efficiency**

Because the thermodynamics of the Bunsen reaction are not currently well-established, and the effect of the reactive distillation of HIx has yet to be experimentally determined, the efficiency of the Sulfur-Iodine cycle can only be approximated at 50%. Theoretically, however, according to Drs. Paul Pickard and Lloyd Brown (of Sandia National Laboratory and General Atomics, respectively), the efficiency of the Sulfur-Iodine is based on the Carnot cycle, using flowsheets. The Carnot cycle “consists of four reversible stages:

1. Reversible isothermal expansion from A to B at T_h; the entropy change is q_h/T_h, where q_h is the energy supplied to the system as heat from the hot source.
2. Reversible adiabatic expansion from B to C. No energy leaves the system as heat, so the change in entropy is zero. In the course of the expansion, the temperature falls from T_h to T_c, the temperature of the cold sink.
3. Reversible isothermal compression from C to D at T_c. Energy is released as heat to the cold sink; the change in entropy of the system is q_c/T_c; in this expression q_c is negative.
4. Reversible adiabatic compression from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from T_c to T_h.”
A comparison of Figures 1 and 6b illustrates (at least on a cursory level) the connection between the heat engine and thermochemical cycles in general. In the words of Atkins’ *Physical Chemistry*, “any reversible cycle can be estimated as a collection of Carnot cycles[,] and the cyclic integral around an arbitrary path is the sum of the integrals around each of the Carnot cycles”\(^{16}\). In this way, the theoretical efficiency \(\varepsilon\) may be calculated using the following equation for a heat engine\(^{16}\):

\[
\varepsilon = \frac{|w|}{q_h}
\]

where \(|w|\) is the work performed. Following the logic of Atkins’ textbook, flowsheet analyses are made using “a complete thermodynamic description of the process”\(^{15}\) and modeled using ASPEN-PLUS\(^{\circledR}\)\(^{14,12}\) [a process simulator], which allows for the necessary
“input flexibility and thermophysical data to account for the energy required”\textsuperscript{14}, write Brown and Pickard. In this way, it is possible to “model the complete chemical plant, including all heat inputs, waste heat outputs and internal heat recovery, as well as all the process chemistry (chemical reactions, chemical separations, etc.)”\textsuperscript{15}

In addition, there is the potential for significant efficiency improvement (up to approximately 60\%\textsuperscript{6}) if the following occur\textsuperscript{6,7}:

1) Water and iodine excesses are reduced,

2) The cycle is coupled with a nuclear reactor which co-produces electricity, and

3) Constant extraction of hydrogen is performed by employing selective membranes\textsuperscript{7}.

In the event that the H\textsubscript{2}O and I\textsubscript{2} excesses may not be reduced in the Bunsen reaction, pervaporation membranes may be used to remove water from HI\textsubscript{x} in reaction 9\textsuperscript{7}. In view of this, it is also reported that “an experimental program on membranes has been undertaken at CEA [Commissariat à l’Energie Atomique] in collaboration with French and European universities”\textsuperscript{7}.

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\textit{Advantages & Disadvantages}

Due to the high temperatures and pressure required, the reactive distillation of HI\textsubscript{x} is considered to be “one of the most corrosive environments within the S-I cycle”\textsuperscript{13}. It will require construction materials which are able to withstand these circumstances for a significant amount of time (in order to keep the process cost-efficient), making the development of such materials key for the success of this
cycle, as well as for the UT-3. Several criteria must be met, including “good thermal conductivity”, “suitable mechanical and creep properties”, and “availability, to make a hydrogen production plant practical”\textsuperscript{13}. In addition, the thermodynamics of the S-I cycle (particularly the sections concerning HI\textsubscript{x}) must be determined; initial analysis has indicated, for example, that the HI vapor content of the liquid-vapor HI\textsubscript{x} mixtures may actually be higher than existing flowsheet models have allowed – if this is proven to be true, it may reduce the heat requirements for this section\textsuperscript{7}. A significant advantage of the Sulfur-Iodine over the UT-3 is that the S-I cycle produces pressurized hydrogen (approximately 50 atm), thereby avoiding the expensive task of compressing the H\textsubscript{2} gas for distribution\textsuperscript{6} required by the latter cycle.

In 2007, the Japan Atomic Energy Agency (JAEA) announced plans to construct a bench-scale hydrogen production plant in order to test the Sulfur-Iodine cycle\textsuperscript{18}. The pilot test will be coupled to a High Temperature Gas-Cooled Reactor (HTGR) (high pressure helium gas will be used as the coolant), which will supply the heat the test will take place over a 6 year period, although it is unknown when the project will commence\textsuperscript{18}. 
Each of the three options previously discussed for the extraction and decomposition of HI from HIₓ (extractive distillation, electrodialysis, and reactive distillation) will be examined (Figure 7 shows electrodialysis), and thermodynamic data will be collected\textsuperscript{18}. Corrosion tests on selected materials will also be performed. The overall length of the test is expected to be six years – three for the construction of the plant itself, and an additional three for hydrogen production tests to take place\textsuperscript{18}. The data collected from the pilot test may then be compared with that extracted from MASCOT (the pilot plant for the UT-3 cycle), in order to more adequately evaluate the two cycles and their viability for adoption as the primary method of future hydrogen production.
Nuclear Reactors

The intense heat required for hydrogen production by thermochemical cycles gives rise to questions concerning the source of such high temperatures. Generation IV nuclear reactors are considered the best option, since they offer the ability to match the thermal energy requirements for hydrogen production facilities at a large scale.\(^8\) To avoid the synergistic effects of an accident at either of the two facilities, the plant and the reactor must be kept at considerable distances from one another,\(^8\) while still supplying large quantities of heat. This is “best met by using an intermediate molten-salt or other high-heat-capacity (low heat losses and small piping), low viscosity (low pumping cost) liquid for the heat transfer loop between the reactor and the chemical plants.”\(^8\)

A modular high-pressure-helium cooled Very High Temperature Reactor (VHTR), similar to the one which will be used in the pilot test of the Sulfur-Iodine cycle, is considered to be the best-suited for these needs.\(^8,20\) Such a reactor has an exit temperature of 950°C, suitable for either of the thermochemical cycles which have been discussed here. In addition, “the high pressure helium can be directly coupled to a direct-cycle gas turbine to produce electricity.”\(^8\)
Currently, such reactors do not exist; they are not slated for construction until the year 2050. One of the few exceptions, however, is the Next Generation Nuclear Plant (NGNP), a VHTR prototype which is expected to be built by 2015 for the purpose of demonstrating electricity and hydrogen production with the S-I cycle\textsuperscript{21}. Other than the NGNP, the lack of Generation IV reactors poses the greatest obstacle to mass hydrogen production by thermochemical methods – without them, it is impossible to efficiently achieve hydrogen production on a large-scale in the near future.

\textbf{Figure 8:} Illustration of a hydrogen production plant coupled to a Modular Helium Reactor (MHR). Reprinted from Schultz\textsuperscript{20}.
Conclusion

Much research and development remains to be done on the UT-3 and Sulfur-Iodine cycles before it becomes possible to employ either of them in steady hydrogen production. As discussed above, the S-I cycle must be tested on a pilot scale, and its thermodynamic properties and HI decomposition must be further explored. For the UT-3, the membranes used require additional development, while the structure of the solid compounds (either honeycombed or beds of pellets) must be perfected so as to provide maximum surface area for reaction with the gas flow without the risk of small particles breaking off. Contingent on the results of JAEA’s pilot test, it appears that the Sulfur-Iodine cycle will emerge as the principal cycle, for the following reasons:

1) It has the highest predicted efficiency,

2) It has a temperature range large enough to be well-suited to a nuclear reactor,

3) It produces pressurized hydrogen gas without any additional steps.

The implementation of thermochemical cycles will not occur for the next several decades, as research is continued, construction materials are developed, and the Generation IV reactors are built and tested. Subsequently, large-scale greenhouse emission-free manufacturing of hydrogen must also be postponed until the production methods are fully developed. Such methods do, however, promise to adequately serve the needs of a hydrogen-based economy, and are steadily advancing towards full maturity.
References


19. Gonzaga University, Dept of Chemistry webpage.  
http://guweb2.gonzaga.edu/faculty/cronk/chemistry/resources.cfm?resource=topics&topic=entropy (accessed Jan 9, 2009).


