

## **STAR-H2: A Calcium-Bromine Hydrogen Cycle Using Nuclear Heat**

**Richard D. Doctor** ([rdoctor@anl.gov](mailto:rdoctor@anl.gov); 630-252-5913)

**David C. Wade** ([dcwade@anl.gov](mailto:dcwade@anl.gov) ; 630-252-4858)

**Marshall H. Mendelsohn** ([mendelsohn@anl.gov](mailto:mendelsohn@anl.gov); 630-252-4467)

**Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, Illinois 60439**

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## **STAR-H2: A Calcium-Bromine Hydrogen Cycle Using Nuclear Heat**

By

Richard D. Doctor, David C. Wade, and Marshall H. Mendelsohn  
Argonne National Laboratory

### **ABSTRACT**

The Secure Transportable Autonomous Reactor (STAR) project is part of the U.S. Department of Energy's (DOE's) Nuclear Energy Research Initiative (NERI) to develop Generation IV nuclear reactors that will supply high-temperature heat at over 800°C. The NERI project goal is to develop an economical, proliferation-resistant, sustainable, nuclear-based energy supply system based on a modular-sized fast reactor that is passively safe and cooled with heavy liquid metal.

Through this discussion, we consider the STAR's three-fold potential in:

- A combined thermochemical water-splitting cycle to generate hydrogen,
- A steam turbine cycle to generate electricity, and
- An optional capability to produce potable water from brackish or salt water.

However, there has been limited reporting on critical elements of the thermochemical cycle: (1) establishing chemical reaction kinetics and operating pressures and (2) addressing materials issues for hydrogen production. This paper reviews the thermodynamic basis for a three-stage Calcium-Bromine water-splitting cycle [University of Tokyo Cycle #3] and discusses the further work that is required to develop an economical process.

### Non-Carbonaceous Primary Energy and Secondary Energy – the Driver for a Reinvigorated Nuclear Industry

Water, hydrogen, and electricity co-produced from nuclear power can sustainably deliver “clean energy” in abundance. Today, the highest levels of government are seriously considering how best to introduce the sustainable hydrogen economy [Conte, et al., 2001]. Past economic and technical barriers to realizing this vision need to be reexamined in light of several emerging issues, which recognize that:

- Stabilizing greenhouse-gas emissions on a worldwide scale presents a credible and long-term challenge to our present low-cost carbon-based energy supply.
- Our current fossil-based utility, industrial, and transportation sectors can only partially address greenhouse-gas emissions controls by strategies based on conservation, fuel switching, and carbon sequestration. For the near-term and mid-term, however, the efficient and clean use of fossil fuels will continue to be a high priority.
- The massive biosphere impacts from current strategies under consideration to sequester carbon dioxide — including the disposal of carbon dioxide in the deep oceans; iron-fertilization of the oceans; the redistribution of arable lands for carbon-sequestration; and the costly, limited, and problematic storage of carbon dioxide on geological timescales in porous underground reservoirs — are unproven, costly, and inadequate.
- When these externalities for fossil-fuel cycles are taken into consideration, the long-term responsible management of nuclear wastes compares favorably with alternatives of the long-term responsible management of fossil-fuel wastes.
- A burgeoning world population — which today stands at six billion — will have the first demand on the produce of arable lands and fresh water resources.
- The development of a hydrogen economy using any of today’s technologies is linked to the reforming of a carbon feedstock with water and produces carbon dioxide. Hence, it is not a “clean” energy source.
- The sensible global consideration of these externalities will reinvigorate the U.S. industrial sector, since developing an infrastructure for carbon management offshore is even more costly and challenging than developing it domestically.
- Advancements in nuclear fuel cycles capable of operation at ever-higher temperatures open up the possibilities of economically producing hydrogen by employing even higher efficiency thermo-chemical water-splitting cycles.
- And finally, these nuclear cycles can be made proliferation-resistant.

Non-carbonaceous primary energy and secondary energy supplies are needed to sustain economic growth, and these needs can only be met by the expansion of a reinvented and reinvigorated nuclear industry.

### Steam Methane Reforming – Cost Constraints on Nuclear Hydrogen

The general pathways to hydrogen production are shown in Fig. 1. The leading system for hydrogen production employs steam-methane reforming (SMR) of natural gas feeds. It is important to recognize that there are significant domestic resources of natural gas available at selling prices near \$2.70/MM Btu. If natural gas at this price is the feedstock to a 50-MM scf/day hydrogen production facility costing \$82 MM, hydrogen could be delivered at the fence for \$5.51/MM Btu (\$5.22/GJ).

Here, no argument is made about the cost advantages of SMR, even if natural gas were to experience a sustained rise in price. However, two recent developments have warranted a renewed interest in water-splitting cycles. The first is the emergence of designs for a new competitive class of Gen IV nuclear power plants that could economically supply the

high temperatures at over 800°C. This new generation of reactors could directly reach the temperatures required for water-splitting cycles.

The second is the recognition that the carbon dioxide release from a hydrogen economy based on SMR will contribute to the world's greenhouse gas inventory as a consequence of:



In a carbon-constrained world where the CO<sub>2</sub> produced during reforming is recovered and sequestered, costs for hydrogen rise to \$8.05/MM Btu (\$7.63/GJ). Compared against other energy cycles, there is an inherent advantage in SMR that must be recognized. For SMR, because the hydrogen and CO<sub>2</sub> must be separated during the reforming process, there is no additional cost for CO<sub>2</sub> capture. At present, this CO<sub>2</sub> generally is released to the atmosphere. Approximately 31% of the cost increase for the CO<sub>2</sub> sequestration scenario is attributable to CO<sub>2</sub> compression and transport through a 500-km pipeline in a fully commercial CO<sub>2</sub> transport infrastructure. The remainder is the estimated cost for reservoir disposal.

Natural gas prices might be expected to rise, but even here, there are limits. By using tanker ships, expansive resources of natural gas are available for delivery as liquefied natural gas (LNG). To be competitive, the market must be willing to pay \$10.00/ MM Btu for the LNG. By estimating costs based on the LNG price for natural gas, hydrogen costs rise to \$12.24/GJ without CO<sub>2</sub> controls, or \$14.65/GJ with CO<sub>2</sub> sequestration. This is approximately a 46% increase over the base case. Considering these prices as the lower and upper boundaries, we have established some constraints for the competitive price range for nuclear hydrogen from any process.

### Calcium-Bromine Cycle for Thermochemical Water Splitting

Beginning in the 1960s, interest in thermochemical water-splitting cycles for the large-scale production of hydrogen began to grow [Funk, 2000]. Although many cycles have been published, few have been the subject of rigorous studies based on detailed thermodynamic calculations; fewer yet have undergone laboratory testing to establish kinetics and yields or to develop the chemical and physical properties needed to complete detailed mass and energy balances. The identification of conceptual cycles must then consider secondary environmental releases and special challenges to implementing some cycles (for example, those that employ large volumes of mercury).

Among the cycles that have the highest commercial potential, a recent screening study identified the two leading candidate cycles as Sulfur-Iodine and Calcium-Bromine [Besenbruch, et al., 2001]. The Sulfur-Iodine cycle is being actively investigated by General Atomics and JAERI [Shimizu, et al., 2001]. One of the leading Japanese cycles is a Calcium-Bromine cycle being investigated by JAERI. It is called the UT-3 cycle to honor the University of Tokyo. The work on this cycle has been regularly reported on since the early 1990s [Yoshida, et al., 1990]. The UT-3 cycle is well enough advanced to

be considered in detailed technical reviews [Tadokoro, et al., 1997; Takodoro and Sato, 1998]. At Argonne National Laboratory, we are investigating a variant of this cycle [Wade, et al., 2001] that we call the “Calcium-Bromine cycle, or Ca-Br cycle,” to avoid confusing it with the excellent efforts on the UT-3 cycle.

#### Indirect Heat Exchange with the STAR Gen-IV or Current Na-Cooled Nuclear Reactor

Currently available Na-cooled reactors could also be employed if a strategy of “bootstrapping,” which involves employing product recycle to raise the steam temperature from 550°C to the 750°C required for water-splitting reactions in the Ca-Br cycle, is used. If we assume a 33% efficiency H<sub>2</sub> yield for the Phase-1 cycle, then:

- 750°C steam requires 11.6% of H<sub>2</sub>/O<sub>2</sub> product
- 800°C steam requires 14.8% of H<sub>2</sub>/O<sub>2</sub> product

This assumed efficiency is half of theoretical efficiency, as will be shown later in Eqn. 8, and is higher than electrolysis efficiencies. Hence, while there is a significant efficiency loss, a sodium-cooled system is workable with the Ca-Br water-splitting cycle, and this approach to carbon-free hydrogen does not need to wait for the development and deployment of Gen-IV nuclear reactors. What is critical is that we will need to see whether this efficiency loss puts this variant on the Ca-Br cycle at a disadvantage vis-à-vis electrolysis.

The design for the Gen-IV reactor STAR reactor emerged from considerations of passive safety in nuclear cycles [Wade, et al., 1997; Hill, et al., 1998; Spencer, et al., 2000; Feiverson, 2001]. The highest heats from STAR will drive the thermochemical cycle, the mid-level heat will be used for electric power generation, and the low-level heat will be used for desalinization (see Fig. 2). The STAR reactor is envisioned as a modular cassette that can be transported and left in operation for 15–20 years with no maintenance of fuel elements (see Fig. 3). For the nuclear-thermochemical interface, indirect heat exchange will be employed. Although indirect heat exchange reduces efficiency, it is necessary to facilitate maintenance for both systems in the event of leakage across the heat exchangers. There is a practical complication of heat exchanger designs operating at an industrial scale with *two* novel heat-exchange media: (1) the liquid metal coolant from STAR and (2) the high-temperature, high-pressure steam and HBr from the Ca-Br cycle. Hence, the design conditions are:

- First generation should use He at >20 bar and
- Second generation should consider CO<sub>2</sub> [Beech and May, 2000].

Throughout this project, consideration is always given to making the proposed cycle sustainable and capable of export. From this perspective, the use of helium as a heat-exchange fluid becomes less attractive than carbon dioxide.

## Nuclear Heat-Driven “Energy Park” for Recycle Paper Mills

At some point, the opportunities for a nuclear-heat-driven “energy park” should be considered. As an example, the paper industry is a major consumer of low-pressure steam. Because of climbing natural gas prices, the cost for recycle paper that is linked to natural gas also rises. A paper-line needs to run at the same high availability as a nuclear plant, and this may represent a good early opportunity for a nuclear-based “energy park.”

### Thermochemical Considerations for the UT-3 Cycle

Establishing chemical reaction kinetics and operating pressures for the Calcium-Bromine thermochemical cycle is one critical program element that requires further experimental investigation since, thus far, the full kinetics have not yet appeared in the open literature. Nevertheless, the significant aspects of the thermodynamic operation of the UT-3 cycle can be discussed with reasonable assurance and to illuminate the overall development of the process. To begin:

- The thermodynamic feasibility of the proposed Calcium-Bromine cycle is favorable.
- It is attractive because the two most critical stages employ gas-solid reactions, thereby simplifying reagent-product separations.
- We recognize that practical thermochemical cycles will need to employ elements that are inexpensive and abundant, such as calcium and bromine. No precious metals are anticipated in this cycle.

The cycle as proposed here is a three-stage modification of the original four-stage UT-3:

[1] Water splitting with HBr formation (730°C; solid-gas;  $\Delta G_T = +50.34$  kcal/gm-mole):



Near ambient conditions, calcium bromide ( $\text{CaBr}_2$ ) is deliquescent and capable of absorbing up to six molecules of water. It is widely used in drilling mud. The reaction in which water is split to form HBr requires the highest temperatures, is endothermic, and takes place slightly below the  $\text{CaBr}_2$  melting point. The developers of the UT-3 process have observed that in this series of reactions, the “...hydrolysis of  $\text{CaBr}_2$  is the slowest reaction” [Sakuri, et al., 1995; 1996a,b]. Hence, there is the greatest technical uncertainty about the practicality of this cycle because of this reaction.

[2] Oxygen formation occurs in an exothermic reaction (550°C; solid-gas;  $\Delta G_T = -18.56$  kcal/gm-mole):



In reviewing this system of reactions, there is a difficulty inherent in the first and second stages [Eqns. 2 and 3]. This difficulty is linked to the significant physical change in dimensions as the calcium cycles between bromide and oxide.

The CaO has a cubic structure ( $a = 4.81 \text{ \AA}$ ) that must undergo a dimensional change to accommodate the CaBr<sub>2</sub> orthorhombic structure ( $a = 6.58 \text{ \AA}$ ;  $b = 6.87 \text{ \AA}$ ;  $c = 4.34 \text{ \AA}$ ). Here, lattice parameters at ambient conditions are used; the actual dimensions at the operating conditions of 550–750°C will differ from these. This process must then be reversed. As the calcium reactant undergoes this change in dimensions, sintering will occur unless the calcium is carefully dispersed on a suitable support. Recent efforts by Sakurai et al. have considered pellets with the CaO supported on CaTiO<sub>3</sub> at CaO:CaTiO<sub>3</sub> ratios between 0.5 and 2 [Sakurai, et al., 1995]. Sakurai reported plugging of pore volumes as the cycle is reversed and the CaBr<sub>2</sub> is regenerated. We intend to investigate suitable support structures for the calcium that will tolerate this cycling.

After recovering the HBr, the UT-3 process proposes bromine regeneration at 220°C in a solid-gas reaction followed by heating to regenerate the hydrogen at 650°C at a temperature close to the FeBr<sub>2</sub> melting point of 684°C:

[3] Bromine regeneration (220°C; solid-gas;  $\Delta G_T = 29.470 \text{ kcal/gm-mole}$ ;  $\Delta H_T = 65.012 \text{ kcal/gm-mole}$ ):



[4] Hydrogen formation from FeBr<sub>2</sub> (650°C; solid-gas;  $\Delta G_T = 32.178 \text{ kcal/gm-mole}$ ;  $\Delta H_T = 91.913 \text{ kcal/gm-mole}$ ):



The thermodynamics for this reaction system are favorable, and a diagram of the Gibbs free energies for a simplified reaction network appears in Fig. 4. In this diagram, the last two stages are reduced to the basic process of HBr splitting.

#### The Ca-Br Cycle – a Modified UT-3 Cycle

We propose to employ a *modified* UT-3 cycle – with a single-stage, rather than a two-stage, HBr-cracking step. Here, the hydrogen formation will employ either commercial HBr electrolysis or the use of a plasma chemistry technique operating near ambient conditions [Nestor, et al., 1988]. Process conditions for the plasma-chemical approach are ~100°C; gas phase;  $\Delta G_T = +27.32 \text{ kcal/gm-mole}$ :



The reasons for adopting this strategy can be seen from consideration of the Gibbs free energies for this cycle (see Fig. 4). This stage takes advantage of power requirements

that now are lowered to 48% of those necessary for water electrolysis (where  $\Delta G_{T[\text{H}_2\text{O}]} = +56.70$  kcal/gm-mole). Power draws of  $\sim 1\text{eV}$  are more realistic for a commercial facility:



Losing the electron to the bromine is economically unacceptable; hence, efforts that began at the Kurchatov Institute (Moscow, Russia) during the 1980s work with plasma-chemical systems so that the products of the dissociation do not recombine. Advances in this technique employing “reverse-vortex flow” have recently been reported [Gutsol and Baleken, 1998; Gutsol and Kalinnikov, 1999]. Applying this technique will result in a small draw on the electric power from the system to produce a cold plasma-chemical reaction.

With minor energy recovery in the oxygen-formation stage [Eqn. 2], the calcium-bromine cycle has a 66% ideal efficiency, defined as [Funk and Reinstrom, 1966; Veziroglu, 1975]:

$$\text{Efficiency} - \text{ideal} = \Delta H_{\text{Cycle}} / \Delta G_{\text{Cycle}}^* (T_{\text{reactor}} - T_{\text{ambient}}) / T_{\text{reactor}} \quad [\text{Eqn. 8}]$$

Practical considerations for the UT-3 cycle suggest an efficiency of 45–49% [Besenbruch, et al., 2000].

### Materials Considerations

From a practical point of view, an additional problem appears to be the choice of materials suited to these operations. Vessels need to be resistant to corrosion from hydrobromic acid at high temperatures of  $750^\circ\text{C}$ . Onay and Saito [1993] report on the metallurgy for this reaction series and finds the greatest success with Fe-20Cr alloys. Smudde et al. [1995] report favorably on Hastelloy C-22 in HBr service. The development of materials for the aggressive conditions of water splitting will be a mandatory program element.

### Summary

Nuclear power can play a significant role in mitigating climate change and seems the only viable carbon-free route to supplying massive quantities of hydrogen that are needed for the transportation sector. The thermochemical water-splitting cycles are currently under investigation so that cost issues can be better defined. Capital cost reductions for the nuclear heat source should come from advanced designs and production methods anticipated for the Generation-IV systems. There are no insurmountable technical barriers to nuclear expansion, but the expansion must be performed under very high safety and accountability standards. The thermochemical water-splitting route, in theory, is more efficient than current electrolysis pathways to hydrogen. Considerable effort is needed to see whether this promise can be translated into practical operating systems.

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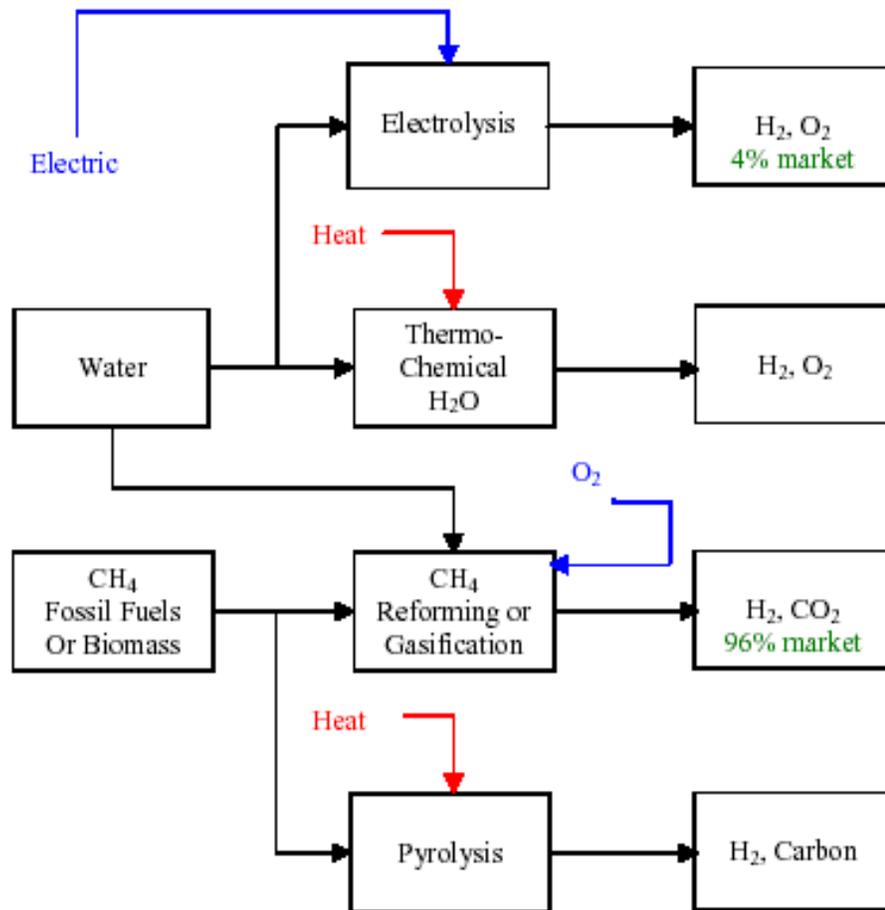
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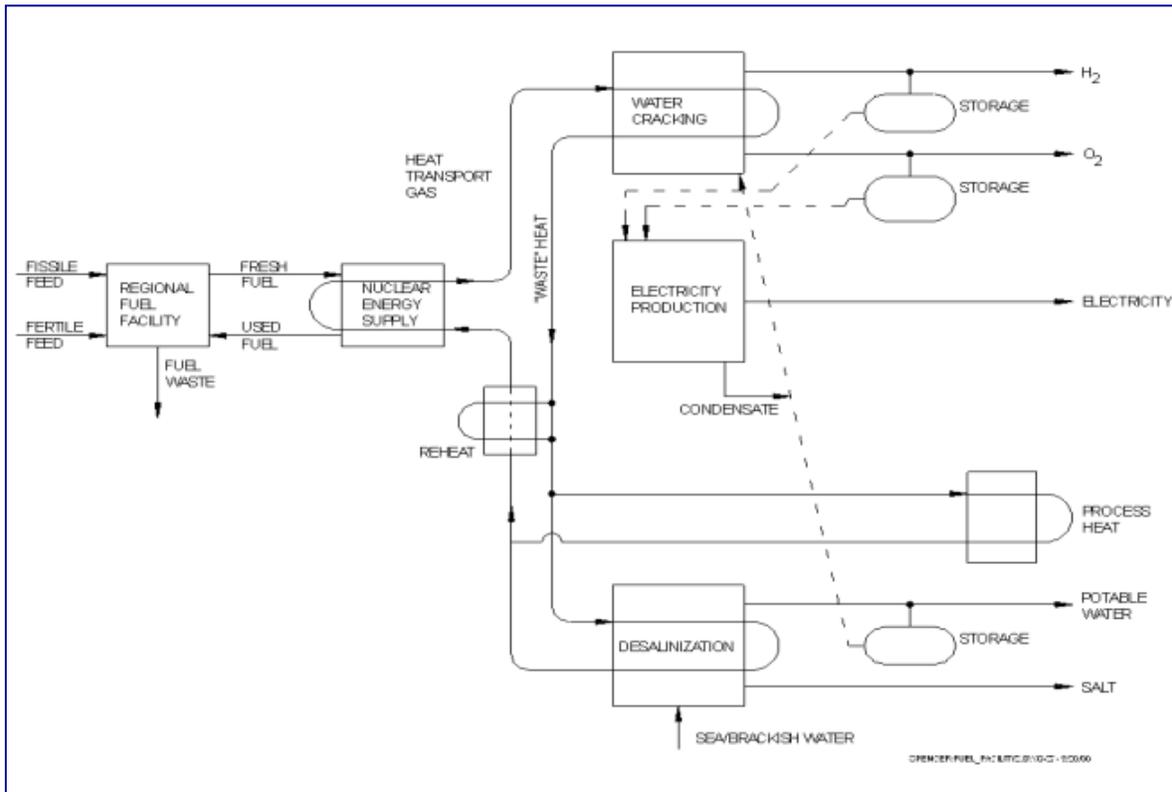
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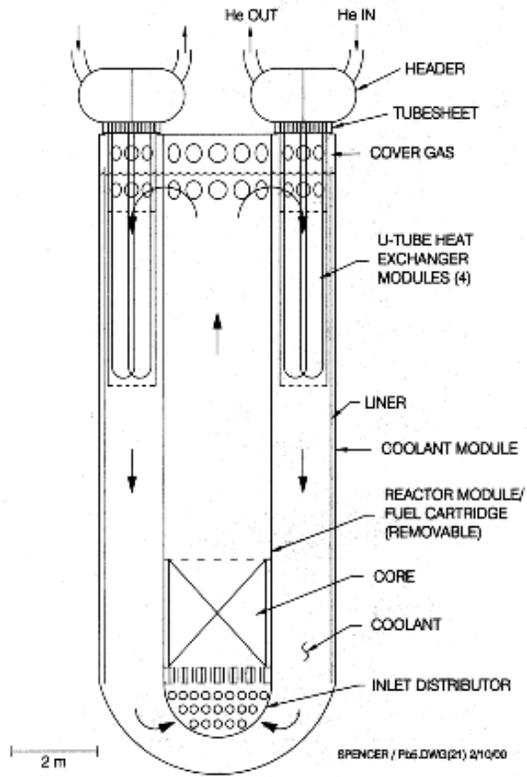
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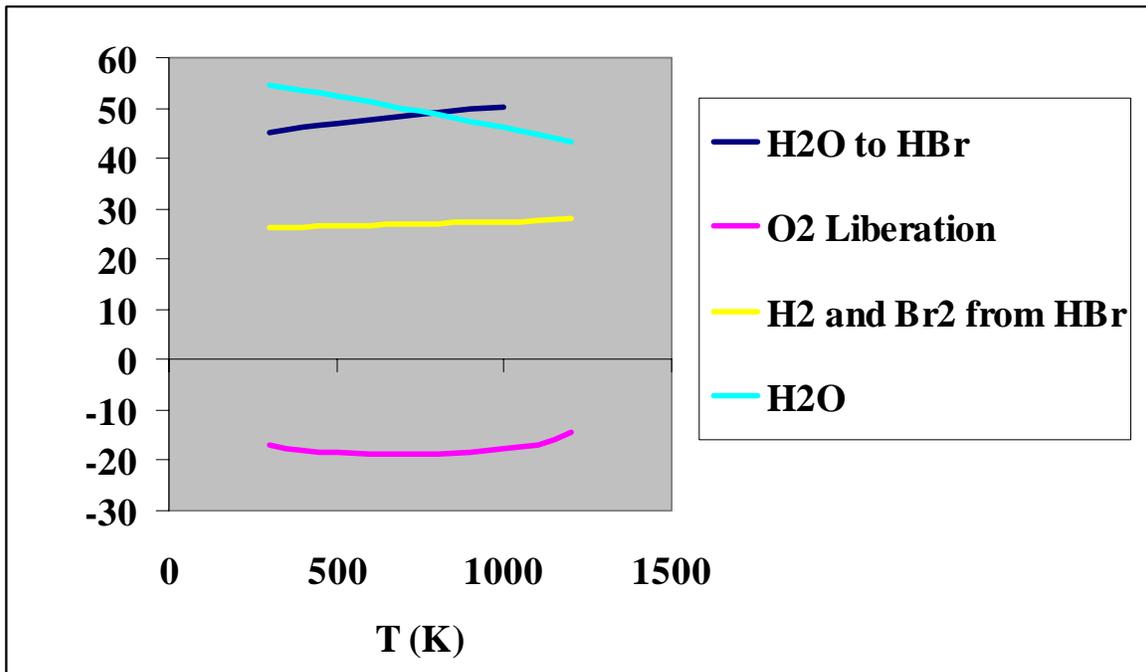
**Fig. 1 General Pathways to Hydrogen Production**



**Fig. 2 STAR-H<sub>2</sub> System Overview Showing the Integration of Elements of the Nuclear- and Hydrogen-Based Energy**



**Fig. 3 A Modularized STAR Generation-IV Nuclear Reactor**



**Fig. 4 Gibbs Free Energies for the Calcium-Bromine Cycle**