

HYDROGEN CYCLE EMPLOYING CALCIUM-BROMINE AND ELECTROLYSIS

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Introduction

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. STAR consists of:

- 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 based on the University of Tokyo Cycle #3 [UT-3] and discusses the further chemistry work that is required to develop an economical process including modifying UT-3 to incorporate HBr dissociation.

Calcium-Bromine Cycle for Thermochemical Water Splitting

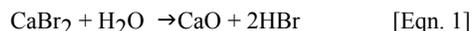
Beginning in the 1960s, interest in thermochemical water-splitting cycles for the large-scale production of hydrogen began to grow. Although many cycles have been published, few have been the subject of rigorous studies based on detailed thermodynamic calculations; fewer yet have undergone laboratory 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.¹ The Calcium-Bromine cycle is being investigated by JAERI and has been considered in detailed technical reviews.² At Argonne National Laboratory, we are investigating a variant of this cycle that offers some advantages over the original cycle.³ It is called the "Calcium-Bromine cycle, or Ca-Br cycle," to avoid confusing it with the excellent efforts on the UT-3 cycle.

Thermochemical Considerations for the UT-3 Cycle

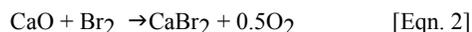
The significant aspects of the thermodynamic operation of the UT-3 cycle can be discussed with reasonable assurance. The developers of the UT-3 process have observed that in this series of reactions, the "...hydrolysis of CaBr₂ is the slowest reaction."⁴

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



Hence, there is the greatest 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):

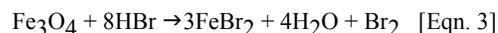


In reviewing this system of reactions, there is a difficulty inherent in the first and second stages [Eqns. 1 and 2]. This difficulty is linked to the significant physical change in dimensions as the calcium cycles between bromide and oxide. The CaO has a cubic structure ($a = 4.81$ Å) that must undergo a dimensional change to accommodate the CaBr₂ orthorhombic structure ($a = 6.58$ Å; $b = 6.87$ Å; $c = 4.34$ Å). 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 CaTiO₃ at CaO:CaTiO₃ ratios between 0.5 and 2.⁵ Sakurai reported plugging of pore volumes as the cycle is reversed and the CaBr₂ 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 FeBr₂ melting point of 684°C.

A steam turbine will be used to harvest reject heat (at ~550°C) and will supply the electrical demands for pumping reagents in the water cracking plant, for circulating brine and water in the desalinization plant, and for pressurizing the H₂ and O₂ products for distribution. A desalinization system will be the final heat rejection path from the cascaded thermodynamic cycles.

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



[4] Hydrogen formation from FeBr₂ (650°C; solid-gas; $\Delta G_T = 32.178$ kcal/gm-mole; $\Delta H_T = 91.913$ 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 **Figure 1**. In this diagram, the last two stages are reduced to the basic process of HBr dissociation.

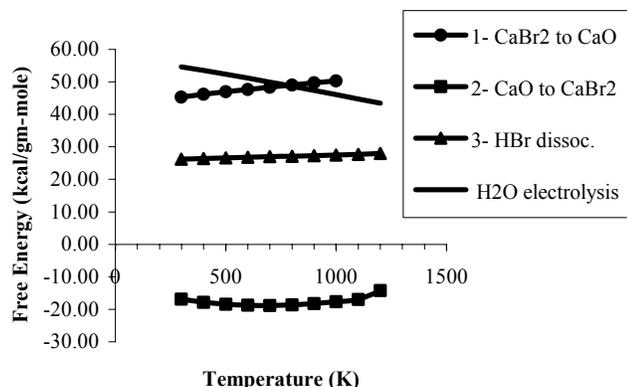
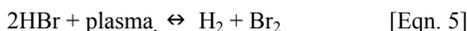


Figure 1. ΔG vs. Temperature ($^{\circ}\text{K}$) for the Calcium-Bromine 3-stage cycle contrasted with water electrolysis shows that the 3rd stage of HBr dissociation has a 48% lower electricity requirement.

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-dissociation step. Here, the hydrogen formation will employ either commercial HBr electrolysis or the use of a plasma chemistry technique operating near ambient conditions. Process conditions for the plasma-chemical approach are $\sim 100^{\circ}\text{C}$; gas phase; $\Delta G_T = +27.32$ kcal/gm-mole:



The reasons for adopting this strategy can be seen from consideration of the Gibbs free energies for this cycle. 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.^{6,7} 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:⁸

$$\text{Efficiency} - \text{ideal} = \Delta H_{\text{Cycle}} / \Delta G_{\text{Cycle}} * (T_{\text{reactor}} - T_{\text{ambient}}) / T_{\text{reactor}}$$

Practical considerations for the UT-3 cycle suggest an efficiency in the range of 45–49%.⁹

Summary

A Calcium-Bromine thermochemical water-splitting cycle is currently under investigation so that basic process chemistry can be better defined. The thermochemical water-splitting route, in

theory, is more efficient than current electrolysis pathways to hydrogen. However, considerable effort is needed to see whether this promise can be translated into practical operating systems. A 3-stage system employing Calcium-Bromine combined with electrolysis offers a potentially attractive route to the early deployment of this technology. As successful hydrogen producing thermochemical cycles emerge, 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.

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