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Hydrogen Production Based On Magnetic Fusion

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Introduction

Studies have been underway for the past two years at the Lawrence Livermore National Laboratory (LLNL) to interface a Tandem Mirror Reactor (TMR) fusion energy source to thermochemical hydrogen cycles. The cycle currently under study is the General Atomic (GA) Sulfur-Iodine Cycle, which is being adapted to match the heat output of a TMR blanket design. Other participants in this study are the University of Washington (UW) with contributions in the areas of reactor physics and blanket design, and the General Atomic Company with contributions in the area of chemical engineering of the thermochemical cycle. In addition to this LLNL study, the national program sponsored by the DOE Office of Fusion Energy includes separate studies at the Brookhaven National Laboratory on hydrogen production by high temperature electrolysis of steam based on a Tokamak fusion reactor energy source.

Aspects of the work that will be reported on here are (1) a brief summary of the status of TMR blanket design studies as an energy source for thermochemical cylces, (2) a joule-boosted decomposer concept for SO_3 decomposition, and (3) some of the details of the thermodynamics of boiling of the H₂SO₄ azeotrope and the enthalpy of the resulting vapor as a function of temperature.

Blanket Studies

In blanket studies at LLNL, we initially investigated a Li-Na cauldron blanket design, where Na boils from a Li-Na pool and transfers heat to a heat exchanger. Currently we are looking at a liquid Li-Pb blanket that uses heat pipes for heat removal. At UW, a design has recently been investigated that involves a flowing bed of Li₂O microspheres of about 0.4 mm in diameter.

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Further blanket design: are being explored at both LLNL and UW. Details of these various designs will not be presented here, but suffice it to say that the design of blankets for fusion reactors is quite complex. The problems are least severe for TMR blankets because of a relatively open structure in the TMR design and the ease of access into the blanket region. Some of the important technical issues in blanket design concern corrosion, heat transfer, material creep strengths, radiation damage, activation, and safety. Although further work is necessary before suitable blanket concepts can be selected, progress is being made in this area, and we anticipate that blankets will be designed in the future that will deliver high pressure helium process fluid at about 1000-1200 K.

Joule-Boosted Decomposer

One of the new concepts explored during the past year at LLNL was the concept of using a joule-boosted decomposer to carry out the decomposition of SO_3 as the high temperature step of the GA Sulfur-Iodine Cycle. By jouleboosting, we refer to utilization of electrically heated SiC furnace elements in place of a heat exchanger for SO_3 decomposition. Since only about 25% of the total energy for the GA Cycle is required for this high temperature step, the use of electricity does not seriously reduce the overall cycle efficiency. Also, some surplus electrical power at high conversion efficiency should be available for cycle use from direct converters in the TMR. A very important advantage of joule-boosting from a cycle standpoint is the considerable savings in cost by replacing expensive heat exchangers for SO_{2} decomposition with inexpensive SiC heating elements. Use of SiC heating elements further permits the attainment of higher temperatures (to \sim 1250 K) and hence increases the yield for SO₂ decomposition, reduces the amount of recycle required for 50_3 decomposition, and eliminates the need for a catalyst for 50_3 decomposition. Yet, a further and very important advantage from the TMR blanket standpoint is that the temperature requirements for the blanket are reduced by about 150-200 K. This greatly reduces the severity of a number of materials problems for the blanket especially in regard to materials corrosion and materials creep strengths. We believe that this will permit blanket designs to be developed on the basis of relatively conventional materials.

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H_SO_ Thermodynamics

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When the H_2SO_4 azeotrope is boiled (at 680 K and 8 atm pressure) in the GA Cycle, it produces a mixture of gaseous H_2SO_4 , H_2O , and SO_3 as the main species. Molecular H_2SO_4 gradually decomposes into H_2O and SO_3 with increasing temperature, approaching complete decomposition at ~ 1000 K. Assuming that SO_3 does not itself decompose into SO_2 and O_2 , we have calculated the enthalpy changes associated with the boiling of the azeotrope and heat up of the resultant gas mixture. (In practice, the enthalpy change associated with SO_3 decomposition would of course be added at the appropriate temperature.) These calculations have been carried out for a total of one mole of $H_2SO_4 + SO_3$.

The azeotrope relations are defined as follows:

$$\kappa_{eq} = (p_{SO_3})(p_{H_2O})/(p_{H_2SO_4})$$

$$\kappa_{H_2SO_4} = (p_{H_2SO_4} + p_{SO_3})/(p_{H_2SO_4} + p_{H_2O})$$

$$r_{tot} = p_{H_2SO_4} + p_{SO_3} + p_{H_2O}$$

From data supplied by Dr. John Norman of GA, we assume a composition of 89.9 mol % H_2SO_4 for the $H_2O-H_2SO_4$ azeotrope at 680 K and 8 atm. From this and the azeotrope relations, we obtain the vapor composition given by

 H_2SO_4 (2, azeotrope) + 0.112354 H_2O (2, azeotrope) \longrightarrow 0.665462 $H_2SO_4(g)$ + 0.334538 $SO_3(g)$ + 0.446892 $H_2O(g)$,

where additional significant figures are given for convenience in calculations. The enthalpy change for this boiling process is calculated to be

$$\Delta H_{680}^{\circ}$$
 (boiling of azeotrope) = 86.46 kJ/mol.

This value is derived from data for H_2SO_4 (pure liquid) and for gaseous H_2SO_4 ,

 SD_3 and H_2O from the JANAF Tables (with supplements through September 30, 1977), data for liquid H_2O from NBS-TR-270-3 plus the Steam Tables, and an estimated value of -0.94 kJ/mol for the enthalpy of mixing of $H_2SO_4(1)$ and $H_2O(1)$.

In order to determine the enthalpy required to heat up the gas produced by boiling of the azeotrope, we first calculate the composition of the gas as a function of temperature (see Table 1). We than separately calculate the enthalpy increments as a function of temperature for each of the gaseous species and combine them (see column 2, Table 2) to obtain the sensible heat contributions. The decomposition enthalpy is next accounted for as shown in column 3 of Table 2. Finally the sensible heat and decomposition enthalpy contributions are combined (column 4, Table 2) to obtain the total enthalpy increments. Table 1. Composition as a Function of Temperature of the Vapor Produced by the 680 K, 8 Atm $H_2O-H_2SO_4$ Azeotrope. Calculations are based on Data given in the JANAF Tables. It is Assumed that SO_3 does not Decompose.

Moles per total of 1 mole SO ₂ + H ₂ SO ₄			
<u>T,K</u>	moles SO3	moles H ₂ SO ₄	moles H ₂ 0
	-		-
6 80	0.33454	0.66546	0.44689
700	0.41894	0.58106	0.53128
750	0.63255	0.36745	0.74490
800	0.79619	0.20381	0.90853
850	0.89373	0.11986	1.00607
900	0.94380	0.05620	1.05614
950	0.96924	0.03076	1.08159
1000	0.98222	0.01778	1.09457
1050	0.98925	0.01075	1.10160
1100	0.99317	0.00683	1.10553
1150	0.99547	0.00453	1.10782
1200	0.99692	0.00308	1.10926
1250	0.99782	0.00218	1.11016
1300	0.99842	0.00158	1.11076

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Table 2. Calculated Enthalpy Increments for Vapor Produced by the 680 K, 8 Atm $H_2O-H_2SO_4$ Azeotrope. Calculations are based on One Total Mole of H_2SO_4 + SO₃, and it is Assumed that SO₃ does not Decompose.

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	^H T ^{-H} 680,	$\Delta n \times \Delta H^{\circ}_{decomp}$.	Total enthalpy increase above
<u>T, K</u>	kJ/mol	kJ/mol*	<u>680 K, kJ/mol</u>
680	0.000	0.000	0.000
700	2.074	7.959	10.033
750	7.285	28.103	35.388
800	12.439	43.535	55.974
350	17.912	51.452	69.364
9 00	23.542	57.455	80.997
950	29.425	59.854	89.279
1000	35.367	61.079	96.446
1050	41.477	61.741	103.218
1100	47.602	62.111	109.713
1 1 50	53.857	62.328	116.185
120 0	60.117	62.464	122.581
1250	66.486	62.549	129.035
1300	72.860	62.606	135.466

* Δn is the integrated number of moles of $H_2SO_4(g)$ decomposed at temperatures above 680 K.

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