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REACTIONS FOR IMPROVING EFFICIENCIES IN THERMOCHEMICAL CYCLES RELATED TO THE SULFUR DIOXIDE-IODINE PROCESS[1]

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ABSTRACT

A modification of the sulfur dioxide-iodine cycle which uses magnesium oxide, magnesium sulfite and magnesium iodide is examined with particular emphasis on decreasing the amount of water employed and thereby increasing the efficiency. The key reaction is that of iodine with magnesium oxide and magnesium sulfite hexahydrate with no additional water. This produces 77% of the total possible sulfate as well as magnesium iodide, hydrogen iodide and hydrogen at 523 K. The efficiency of this cycle varies between 58% and 39% depending on the amount of heat that can be recovered. This is the first example of a cycle where there is no large energy burden due to evaporation.

KEYWORDS

Thermochemical hydrogen, sulfur dioxide-iodine cycle, magnesium oxide, magnesium sulfite, magnesium iodide, magnesium sulfate, hydrogen iodide.

INTRODUCTION

The concept of hydrogen production through splitting water into hydrogen and oxygen by means of several chemical reactions with accompanying recycling of all the intermediates has been studied for some years (Funk and Reinstrom, 1966). Although many such processes have been experimentally verified (Besenbruch and co-workers, 1980) and some closed-loop systems are in operation (Van Velzen and Langenkamp, 1980), the efficiency of such processes is usually of the order of 40-50%.

One recurring problem which decreases the efficiency of all suggested thermochemical processes centers around the need for drying aqueous solutions. This paper considers the relationship between evaporation and efficiency and examines experimentally an adaptation of the sulfur dioxide-iodine cycle where little water needs to be evaporated or condensed.

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If we consider a thermal efficiency (or figure of merit) of 40% to be the lower limit of practicality of a thermochemical hydrogen producing process, then the maximum amount of heat available is 715 kJ (286/0.4). Each mole of water evaporatively removed requires 44 kJ of heat. Thus we can plot the heat required to remove n moles of water expressed as a percentage of the maximum heat permitted (715 kJ) against n. This is shown in Fig. 1. At some other stage in the cycle, this water will be recondensed releasing an equivalent amount of heat which may be partially applied to the evaporation step, and is also shown in Fig. 1 as a percentage of the heat recovered. This figure clearly illustrates the large percentage of the available heat utilized evaporatively. Thus when none of the heat is recovered, 18% of the available heat is used to evaporate 3 moles of water and when 75% of the heat is recovered, this same heat will remove 12 moles of water. In general, therefore, there is an upper limit on the amount of water which can be used, the exact value of which will depend on the specifics of a cycle.

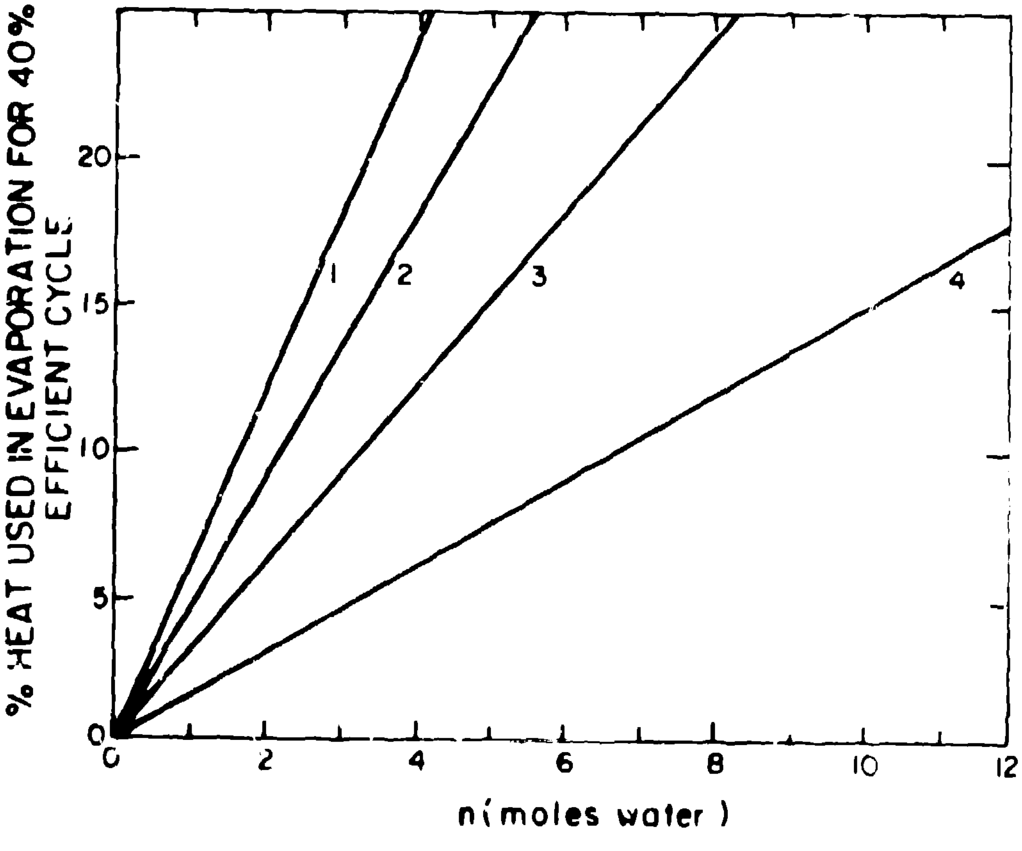

Fig. 1. Heat required to remove n moles of water as a percentage of the maximum heat permitted for different percentages of heat recovered, 1 0%, 2 25%, 3 50%, 4 75%.

The specific cycle studied here can be summarized in the following way:

$$\mathrm{MgO + SO_2 \rightarrow MgSO_3} \qquad (1)$$

$$\mathrm{MgO + MgSO_3 + I_2 \rightarrow MgSO_4 + MgI_2} \qquad (2)$$

$$\mathrm{MgI_2 + H_2O \rightarrow MgO + 2HI} \qquad (3)$$

$$\mathrm{2\,HI \rightarrow H_2 + I_2} \qquad (4)$$

$$\mathrm{MgSO_4 \rightarrow MgO + SO_2 + 1/2\,O_2} \qquad (5)$$

$$\mathrm{H_2O \rightarrow H_2 + 1/2\,O_2} \qquad (6)$$

It was chosen because it offers the possibility of overcoming the drying and separation steps of the SO_2/I_2 cycle:

$$\mathrm{SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI}$$

$$\mathrm{2HI \rightarrow H_2 + I_2}$$

$$\mathrm{H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\,O_2}$$

which has been extensively studied at General Atomic (Norman and co-workers, 1980). Sulfates, in general, are identified (Bowman, 1980) as having thermal decomposition characteristics which are suitable for thermochemical processes. Finally, the magnesium cation was chosen since MgI_2 hydrolyzes readily. The other more promising metal cations for this type of cycle are La and Ti. (Mason and Bowman, 1981a).

THE CYCLE

The cycle is shown in a diagrammatic form in Fig. 2 and can be seen to be conceptually simple. All the solid components are cycled between room temperature and 1350 K with no separations and minimal drying.

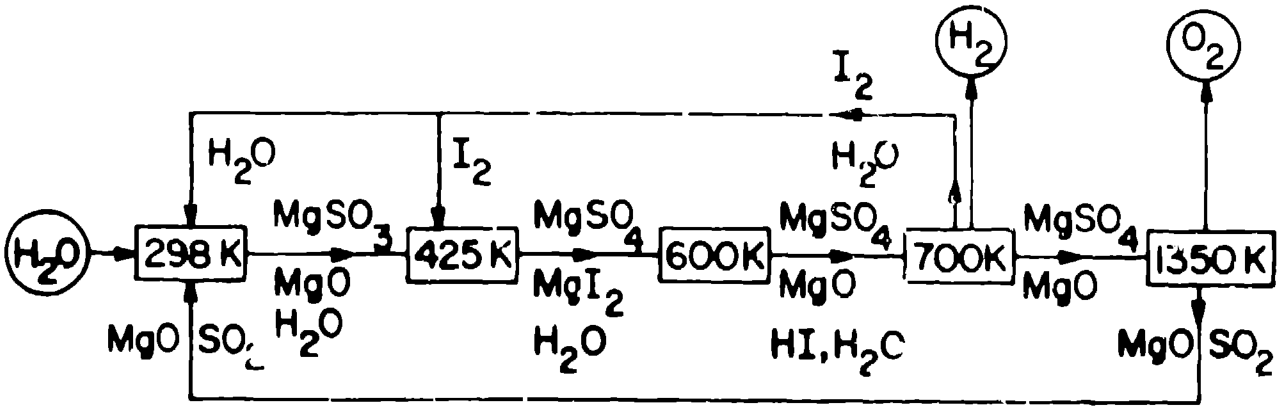

Fig. 2. Schematic Representation of the $MgSO_3/I_2$ cycle.

From our previous studies it is known that the reaction represented by equ.(1) will only take place in the presence of water and also that reaction (2) is fast and quantitative in dilute aqueous solution (Mason and Bowman, 1980). The hydrolysis of MgI_2, reaction (3) readily happens in the presence of excess water. The thermal decomposition of HI, reaction (4) occurs in many cycles and has, correspondingly, been studied often (e.g., Takemori, 1978). Finally, the thermal decomposition of $MgSO_4$ occurs quantitatively, albeit slowly, at 1350 K, but can be catalyzed by Fe_2O_3 (Lau, Cubbiciotti and Hildenbrand, 1977). This decomposition has also been suggested as part of a thermal energy storage system by reversible chemical reactions (Ducarrior, Tmar and Bernard, 1980).

Thermodynamically the cycle can be written in the following form where x and y represent the mole amounts of water necessary for fast quantitative reaction yields and square brackets denote nonreactive and noninterfering components:

$$\Delta H^0_{298}\ \text{kJ}$$

$$2\ MgO(s) + SO_2(g) + x\ H_2O(l) \xrightarrow{298K} MgSO_3.yH_2O(s) + (x-y)H_2O(l) + MgO(s) \qquad (1)\ -(109.6 + 15.7y)$$

$$MgSO_3yH_2O(s) + MgO(s) + I_2(g) \xrightarrow{425K} MgSO_4(s) + MgI_2(s) + yH_2O(g) \qquad (2)\ (101.0-59.7y)$$

$$[MgSO_4(s)] + MgI_2(s) + yH_2O(g) \xrightarrow{600K} [MgSO_4(s)] + MgO(s) + 2\ HI(g) + (y-1)H_2O(g) \qquad (3)\ +59.8$$

$$2\ HI(g) \xrightarrow{700K} H_2(g) + I_2(g) \qquad (4)\ +10.4$$

$$MgSO_4(s) + [MgO(s)] \xrightarrow{1350K} 2MgO(s) + SO_2(g) + 1/2\ O_2(g) \qquad (5)\ +390.1$$

$$(y-1)\ H_2O(g) \xrightarrow{375K} (y-1)\ H_2O(l) \qquad (6)\ -(y-1)44.0$$

The noninterference has been shown to be valid since reaction (2) has been carried out in solution and the products slowly heated to 1400 K. Thus, after evaporation, a thermogravimetric curve can be interpreted as going through the solid products $MgI_2.8H_2O$, $MgSO_4.H_2O$, $Mg(OH)I.H_2O$, $Mg_2(OH)_3I$, $MgSO_4$ and finally to MgO exclusively (Mizuta and co-workers, 1980).

The thermodynamic data is calculated from tables in two source books (Parker Wagman and Evans, 1971; Weast, 1974) with the assumption made that the heat associated with each water of hydration is the same. The value of y, the number of moles of water which must be evaporated affects the efficiency greatly. The value of x, the number of moles of water remaining as liquid, is much less significant since $MgSO_3$ is relatively insoluble (1.25 g/100cc) and therefore can be separated by filtration from a saturated solution and necessitates no evaporation except for occluded water.

Figure 3 shows the change in efficiency (defined as $\Delta H^0_{298}/\xi{+}ve\,\Delta H^0_{298}$ cycle) as a function of y for three different percentages (100%, 50%, 0%) of heat recovered from reactions (2) and (6). No heat can be recovered from reaction (1) since it occurs at room temperature.

One may note that there is an initial sharp decline in efficiency when some heat is recovered, but with no heat recovery, the efficiency does not change due to the endothermicity of reaction 2 when $y \leq 1.7$. Even though is is clear that the highest efficiencies occur in the absence of water, it is known experimentally that SO_2 does not react with MgO in the absence of water. Therefore we examined the value of x in reaction (1).

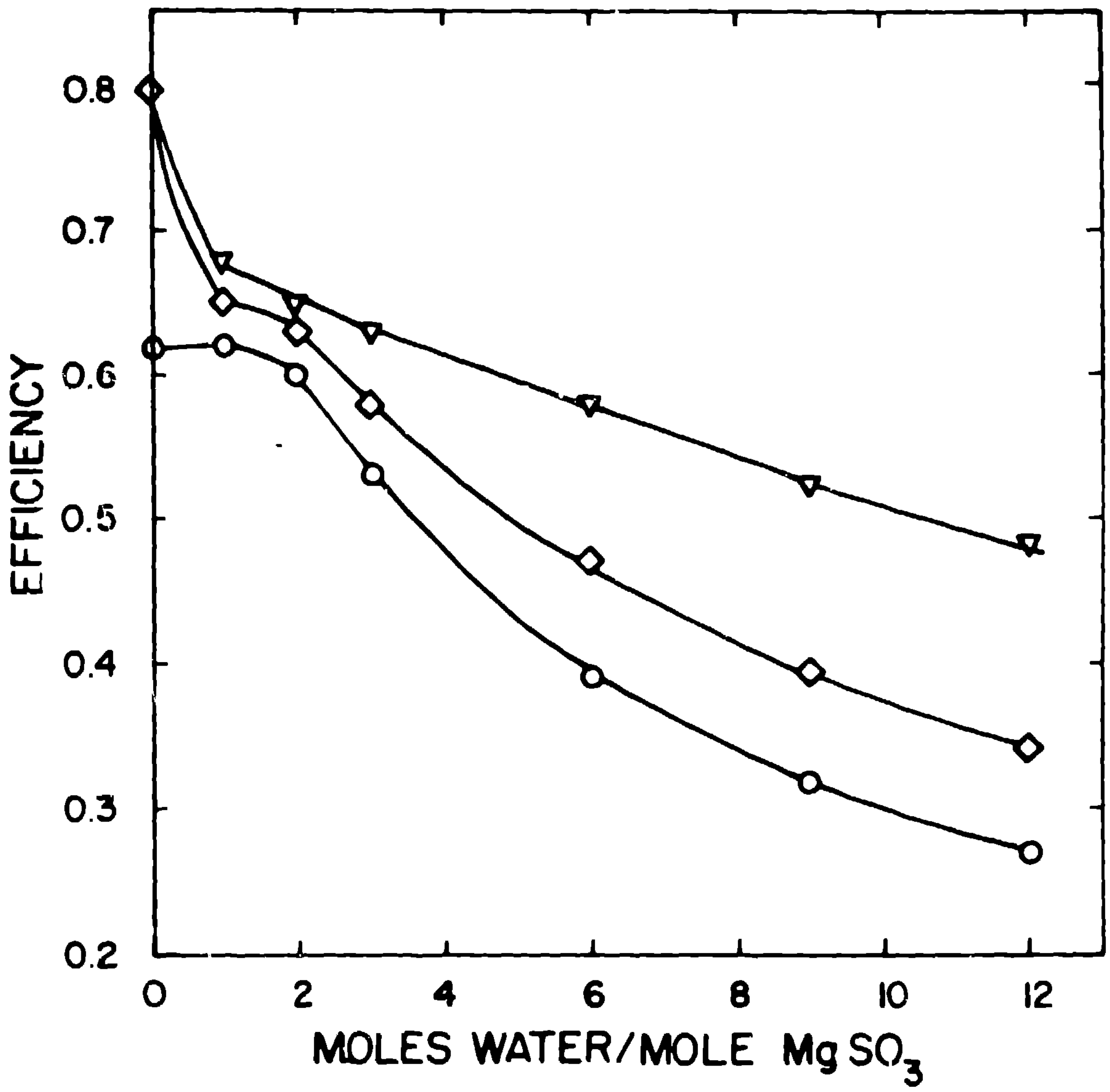

Fig. 3. The effect of the mole ratio of $H_2O/MgSO_3$ on the overall efficiency of three different amounts of heat recovered. ▽ 100%, ◇ 50%, O 0%.

RESULTS

Reaction (1)

$$2MgO(s) + SO_2(g) + x\,H_2O(l) \xrightarrow{298K} MgSO_3{\cdot}yH_2O(s) + (x-y)H_2O(l) + MgO(s)$$

Figure 4 shows the results of bubbling an excess of SO_2 ($SO_2/MgO = 8$) through a stirred slurry of MgO in saturated $MgSO_3$ solution at room temperature. The MgO used was formed by decomposition of $MgSO_4$ (reaction (5)) at 1350 K in a stream of N_2 in order to mimic the conditions in the actual cycle. The product was removed by filtration in dilute cases and in concentrated cases it was simply dried before analysis. Identification was by x-ray powder diffraction crystallography. In all cases the product was found to be $MgSO_3.6H_2O$, except at low H_2O/MgO where MgO remained the dominant phase. The amount of $MgSO_3$ formed was measured by thermal decomposition and the SO_2 evolved estimated by iodimetry. From Fig. 4 it can be seen that in order to have 50% of MgO sulfited (that being the necessary amount for the cycle it is required to have about 6 moles H_2O which is also the necessary amount for hexahydrate formation.

Above 40°C, the hexahydrate becomes metastable and the trihydrate is the stable phase (Seidell, 1940). Thus, by carrying this step out at ≥40°C, the trisulfite will be formed which, preliminary experiments suggest will be adequate hydration for reaction (2) (Mason and Bowman, 1981b). However, as will be seen, more recent experiments do not support this conclusion. Since the reaction is exothermic, heat is produced, resulting in temperature increase.

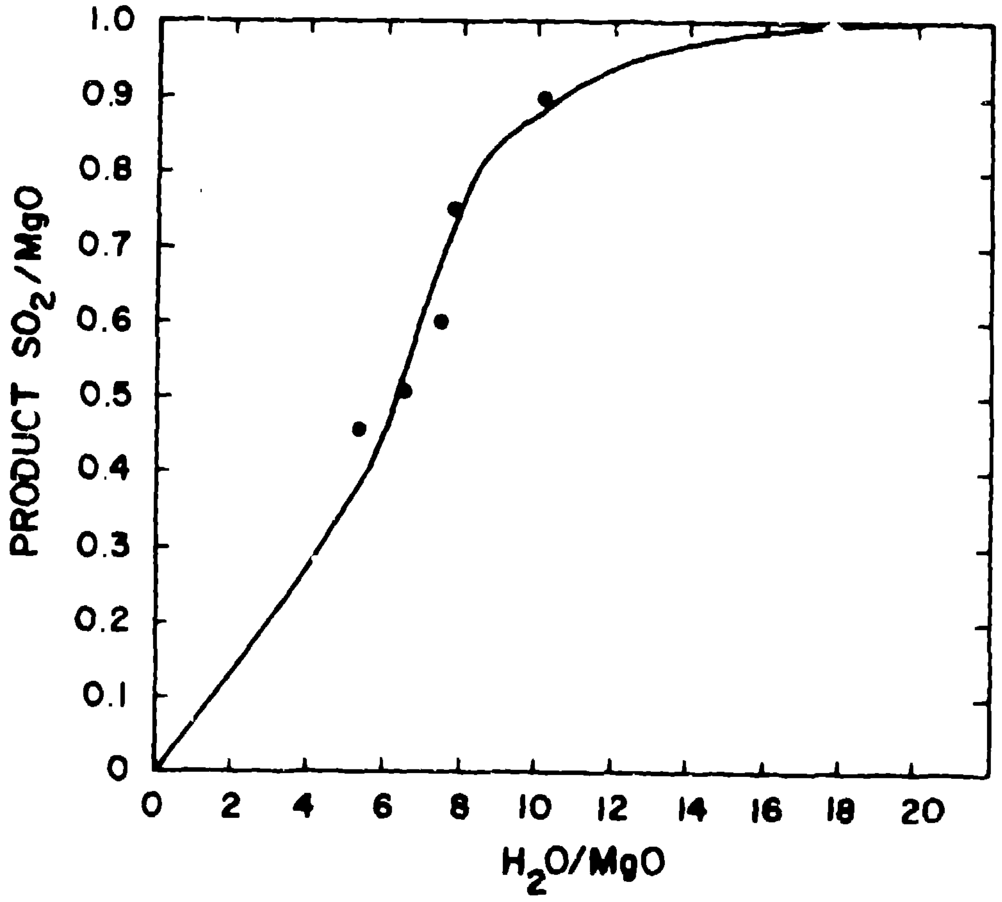

Fig. 4. The amount of MgO sulfited as a function of H_2O present.

Reaction 2

$$MgSO_3yH_2O(s) + MgO(s) + I_2(g) \longrightarrow MgSO_4(s) + MgI_2(s) + yH_2O(g)$$

Previous experiments (Mason and Bowman, 1981b) using a system where I_2 was passed through a preheated bed of $MgSO_3.6H_2O$ and MgO have established that at 423 K, 67% of the total possible $MgSO_4$ (based on the stoichiometry) was formed. At this temperature it was estimated that between 2 and 3 moles o hydration remained.

In the present study, a different approach was taken. The reaction was carried out in a teflon cylinder in an evacuated closed pressure vessel which precluded the possibility of removing any reactants or products. The results are shown in Table 1.

In most cases, traces of $Mg(OH)I.H_2O$ were found (identified by x-ray powder diffraction patterns). The stainless steel vessel was heated to the temperature indicated and maintained there for 40 min. Gas analyses were carried out both before and after cooling. The estimation of $MgSO_4$ was carried out gravimetrically and that of MgI_2 using a specific iodide electrode after removing excess I_2 and HI by heating the solid product. It can be seen that, the total amount of sulfate formed was 77%. This occurred 100° higher than in the flow experiments, presumably due to the fact that water vapor was not removed from the reaction site. Palladuim was added as it is known (Takemori, 1978) to catalyze the decomposition of HI, thereby forcing the preceding equilibria to favor product formation.

Table 1 Results of reacting I_2 with $MgSO_3.6H_2O$ and MgO
$MgSO_3.6H_2O = 9.8 \times 10^{-3}M$, $MgSO_3 : MgO : I_2 = 1 : 1 : 1$

Temperature K	Products (expressed as a % of the total possible stoichiometric amount)	
	$MgSO_4$	MgI_2
523	54	30
523	50	27
523	77	24
473	54	18
423	48	9
373	12	4

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[1] Carried out in presence Pd black, Pd/MgO=0.1

The experiments were repeated using the 3-hydrate in place of the 6-hydrate. These are shown in Table 2. In all cases less reaction occurred than previously. Thus experimentally it is shown that for optimal reaction, y 3. Since the 3 and 6 hydrates are the known stable hydrates, it appears that the cycle should be carried out with the 6-hydrate, this being the smallest amount of water which gives acceptable product yields.

TABLE 2 Results of reacting I_2 with $MgSO_3.3H_2O$ and MgO
$MgSO_3.3H_2O = 1.1 \times 10^{-2}M$, $MgSO_3 : MgO : I_2 = 1 : 1 : 1$

Temperature K	Products (expressed as a % of the total possible stoichiometric amount)	
	$MgSO_4$	MgI_2
523	34	1
473	28	1
423	34	1

Unlike the room temperature aqueous solution reaction, there is no stoichiometric equivalence between $MgSO_4$ and MgI_2. This is mainly due to the concurrent hydrolysis of MgI_2 which, at 523 K, was measured to be 44%; and also, in small measure to incomplete hydrolysis:

$$MgI_2 + H_2O \rightarrow Mg(OH)I + HI.$$

In addition, it is due to some H_2 formation and furthermore to air oxidation of MgI_2 during the removal of I_2 and HI:

$$2MgI_2 + O_2 \rightarrow 2MgO + 2I_2.$$

There are also some minor side reactions of which the most important is the disproportionation of $MgSO_3$:

$$MgSO_3(s) \rightarrow 3/4\ MgSO_4(s) + MgS(s),\ \Delta H_{298} = -41.9\ kJ$$

which is followed by hydrolysis of MgS.

$$MgS(s) + H_2O(l) \rightarrow MgO(s) + H_2S(g),\ \Delta H^o_{298} = +\ 9.9\ kJ$$

and reaction with I_2:

$$MgS(s) + I_2(g) \rightarrow MgI_2(s) + S(s),\ \Delta H^o_{298} = -74.8\ kJ$$

Although no S was detected, the presence of CS_2 and COS (from the gas analysis) show that it is present at some stage. Worth considering in the same context is the direct oxidation of $MgSO_3$ with H_2O:

$$MgSO_3(s) + H_2O(g) \rightarrow MgSO_4(s) + H_2(g),\ \Delta H^o_{298} = -34.7\ kJ$$

Althougn this is thermodynamically favored, it has never been observed to happen (Mason and Bowman, 1980). It is possible I_2 catalyzes this reaction, but it is minor since little H_2 is found.

Mass spectrometric gas analyses gave the same general result whether the gases were removed before or after cooling showing that there are no significant reactions on cooling. The major constituent was found to be CO_2 (~90 2 x 10^{-3}M) with small amounts of CO (~5%), N_2(~2%), H_2(~1%), CH_4(<1%), O_2(<1%) and traces of CS_2 and COS.

The formation of CO_2 was unexpected and, after further analysis, was found to be due to the contamination of $MgSO_3$ by $MgCO_3$(10 wt. %). The results in Tables 1 and 2 have been corrected to account for this. The temperature is low for $MgCO_3$ decomposition (Stern and Weise, 1969) but apparently sufficient:

$$MgCO_3 \rightarrow MgO + CO_2$$

A possible reaction, forming CO is

$$MgSO_3 + MgCO_3 \rightarrow MgSO_4 + MgO + CO$$

Again the temperature is low, ($\Delta G \leq 0$ at $T > 780$ k).

A more likely mechanism for CO formation is the water gas reaction:

$$CO_2 + H_2 \rightarrow H_2O + CO$$

Hydrogen can also reduce CO_2 to CH_4:

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2H_2O$$

Consideration of these reactions together with the H_2 analysis itself puts an upper limit on the amount of H_2 formed based on the initial stoichiometry at 2%. Although the actual amount of H_2 evolved is small, this will be increased with increase in temperature due to large amount (44%) of HI formed.

DISCUSSION

The concurrent formation of MgI_2, HI and H_2 shows that reactions 2), (3), and (4) occur simultaneously and that with increase in temperature (up to 1350 K for $MgSO_4$ decomposition) amounts of H_2 should be obtained up to the equilibrium amount of HI decomposition corresponding to 77% formation of $MgSO_4$. Side reactions do occur but these appear to be minimal since no S or H_2S were found although traces of COS and CS_2 were seen.

The experimentally determined critical amount of water for high product yield is 6. This gives an efficiency of 58% with total heat recovery, dropping to 39% with zero heat recovery. As well as simplicity and relatively high efficiency, another advantage this cycle possesses is the lack of corrosivity in the high temperature step which contrasts favorably with those cycles involving sulfuric acid decomposition.

The main drawbacks to this cycle involve the problems associated with handling solids and the high temperature necessary for decomposing $MgSO_4$. An investigation into high temperature solids handling (Peterson and Bowman, 1980) has shown that some sulfate decompositions, most notably $Bi_2(SO_4)_3$ and $ZnSO_4$, take place rapidily indicating heat transfer to and from the solid is also rapid.

Since it is possible that 1350 K may be an unrealistically high temperature for available heat, we carried out a search for alternative metals which fit the following criteria:

a) sulfate must decompose in the temperature range availalbe (<1300 K),
b) iodide must hydrolyze easily, and
c) salts must not be rare, toxic, or expensive.

Two metals fit these criteria, they are lanthanum and titanium. For lanthanum, the triiodide hydrolyzes readily only as far as the oxyiodide and lanthanum trisulfate decomposes to lanthanum dioxymonosulfate at 1270 K. For titanium, in the tetravalent state, the iodide will be in the liquid or vapor phases (mp 423 K, bp 650 K) and hydrolyzes to TiO_2 ($\Delta G^o = 0$ at 430 K). Titanium sulfate is reported to decompose to TiO_2 and SO_3 at 870 K (Stern and Weise, 1966).

CONCLUSION

The $MgSO_3/MgI_2$ cycle has been shown experimentally to require minimal amounts of water for high yields of reaction products. It therefore opens up new possibilities in thermochemical H_2 cycles where efficiencies will be higher due to the elimination of solution chemistry.

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