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AUTHOR(S) Edward I. Onstott and Derik de Bruin

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

THERMOCHEMICAL HYDROGEN PRODUCTION WITH THE SULFUR DIOXIDE-IODINE CYCLE BY UTILIZATION OF DIPRASEODYMIUM DIOXYMONOSULFATE AS A RECYCLE REAGENT

E. I. Onstott and Derik de Bruin

Chemistry Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545, U.S.A.

ABSTRACT

Insoluble, dipraseodymium oxide-sulfite-sulfate-hydrates were prepared by reaction of dipraseodymium dioxymonosulfate with sulfur dioxide in aqueous media at 340K. These compositions reacted with iodine to yield sulfate in the solid phase and hydrogen iodide in the gas phase. High yields of hydrogen iodide were measured at 770K for a reaction time of ten minutes. Yields also depended on the sulfite content of the hydrate compositions, and were highest when the dipraseodymium dioxymonosulfate was 60 percent neutralized with sulfurous acid. An increased yield of hydrogen iodide was obtained by a second iodine oxidation after separation of the first gaseous products. A water splitting thermochemical cycle utilizing these reactions is described in which hydrogen is produced by catalytic decomposition of hydrogen iodide, and oxygen results from thermal decomposition of the solid product, that also yields sulfur dioxide and dipraseodymium dioxymonosulfate for recycle.

KEYWORDS

Thermochemical hydrogen; water splitting; synthetic fuel; sulfur dioxide; iodine; hydrogen iodide; dipraseodymium dioxymonosulfate; dipraseodymium oxide-sulfite-sulfate-hydrates; sulfur dioxide-iodine process.

INTRODUCTION

In previous work we demonstrated that dilanthanum dioxymonosulfate can be converted to partially neutralized, insoluble sulfite-sulfate-hydrates that react with iodine at elevated temperatures to yield sulfate in the solid phase and hydrogen iodide in the gas phase (Onstott and co-workers, 1984; Haas, Peterson, Onstott, 1985). Thus the iodine oxidation reaction and hydrolysis reaction can proceed concurrently without injection of steam or separation of the solid phase prior to the hydrolysis reaction. A water evaporation step of the aqueous phase in the cycle is eliminated for better heat efficiency. Mason and Bowman (1984) have recently evaluated heat requirements for water evaporation in a cycle.

In this paper we present results on a sulfur dioxide-iodine cycle that utilizes a dipraseodymium oxide-sulfite-sulfate-hydrate prepared at 340K. A suitable procedure for preparation of hydrates of praseodymium at 295K was not found, but the procedure at 340K is superior to the procedure that was developed previously for preparation of dilanthanum oxide-sulfite-sulfate-hydrate compositions. In addition, the smaller hydrate numbers are more desireable for better water management in the cycle.

EXPERIMENTAL

Materials. Water was double distilled. Anhydrous sulfur dioxide (Matheson) and anhydrous praseodymium sulfate (Research Chemicals, 99.9 purity) were used. Iodine and sodium thiosulfate analytical concentrates and reagent barium chloride (J. T. Baker) were used, as was reagent starch (Mallinckrodt).

Preparation of reactant. The reactant material was made by thermal decomposition of anhydrous praseodymium sulfate in a quartz vessel, either in air or by pumping the gaseous products. A batch of 50g was obtained in 5 hr at 1350K in air, and weight loss ceased under these conditions.

Preparation of compounds. Convenience and rapidity were prime considerations for recycling. Two methods were tested. The first was patterned after the method for synthesis of variable-compositions of dilanthanum oxide-sulfite-sulfate-hydrate at room temperature (Haas, Peterson, Onstott, 1985) that utilized a closed manifold and reaction vessel in which the sulfur dioxide supply was fixed. This apparatus proved to be awkward because of the need for elevated temperatures and vigorous stirring. The second method used flowing sulfur dioxide from a dip tube at constant temperature. This procedure proved to be practical and reproducible. For low sulfite coefficients the reaction was stopped with a vigorous stream of helium in the reaction medium. A convenient temperature was 340K where the sulfur dioxide concentration was 0.20 molar at 0.76 atm (Los Alamos pressure). Preparative details are as follows: 0.5 liter of water in a 1 liter flask with a small neck was heated to 340K on a hot plate (magnetic stirring) with the vortex extending to the stirring bar. Sulfur dioxide was added through a dip tube from the start of heating at a rate of 100 cubic centimeters per minute until saturated. Then the reaction was started by adding 10g of reactant through a funnel in the neck of the flask. The reaction was stopped at the appropriate time by substituting helium flow for sulfur dioxide flow at a 20-fold increase in rate. The product settled quickly and was separated by the combination of decantation and filtration. It was washed with cold water. Some praseodymium color remained in the reaction medium. Yields as large as 90 percent were measured.

Analyses. Praseodymium was determined by the procedure of oxalate precipitation followed by ignition at 1200K. Samples of variable-composition dipraseodymium oxide-sulfite-sulfate-hydrates that were ignited at 1350K for 5 hours or more reached constant weight that corresponded to the molecular weight that was obtained by thermal decomposition of the anhydrous sulfate in air under the same conditions (molecular weight 412; calculated 409.88). Dipraseodymium dioxymonosulfate that was obtained at 1375K by partial removal of product gases (sulfur trioxide, sulfur dioxide and oxygen) by pumping had a molecular weight of 409.5. Sulfite in products was done by iodimetry and sulfate as barium sulfate as outlined in Standard Methods (1971). Sulfite was converted to sulfate with bromine prior to the analysis and the sulfate calculated by difference. A thermogravimetric procedure was used for hydrate water determinations. The product was heated in an evacuated ampule with the water allowed to condense in the capillary end at dry ice temperature, then sealed off. Selected product samples were analyzed by standard x-ray diffraction techniques, and by infrared spectroscopy by the KBr pellet technique with a Perkin Elmer 621 instrument.

Iodine oxidation and hydrolysis reactions. The hydrate compositions were reacted with iodine in evacuated and sealed ampules of 20 cubic cm size in a tube furnace. The rate of heating was about 60K per minute. After a predetermined time the ampule was allowed to cool quickly to 500K to quench the reaction. The gaseous products were separated by condensation in the capillary end of the ampule, while cooling with powdered dry ice, and keeping the solid product at 500K. Hydrogen iodide was determined by dilution with water and titration to pH 7 with sodium hydroxide.

RESULTS

At 295K the reaction medium was too stable to yield an insoluble product without solvent removal, but at 340K many insoluble hydrates were obtained with sulfite coefficients in the range of 0.5 to 2. Measurement of the threshold temperature for precipitate formation was not investigated. Mechanisms for product formation included simple neutralization reactions where soluble sulfite-containing species were formed, then crystal hydrate precipitation by removal of excess sulfur dioxide concurrent with the lowering of acidity.

Low sulfite coefficients were obtained in minutes by starting the helium purge before the reactant was added. The stoichiometric composition with 2 sulfites was approached at a reaction time of 1 hour. Many more hours of reaction time were required when the excess of sulfur dioxide was removed by the neutralization reaction in the closed apparatus rather than by gas transport in the purge apparatus.

Sulfate analyses were not accurate enough (standard deviation 5 %) to fix the sulfate coefficient at a number other than one. The oxalate analyses for praseodymium demonstrated a slightly high sulfate deviation from stoichiometry (2 %) in the dipraseodymium dioxymonosulfate reactant when prepared at 1350K instead of 1375K.

The second column in Table 1 shows a correlation of water of hydration with sulfite coefficient, where the ratio is near 2. There is not a correlation of water of hydration with oxide coefficient, nor a correlation with sulfate coefficient.

Table 1 Effect of Sulfite and Hydrate Coefficients and Reaction Conditions on Yields of Hydrogen Iodide.

stoichiometry (Pr=2)			reaction conditions			% yield
oxide	sulfite	water*	K	min	iodine**	HI
1.39	0.61	1.88	650	0.2	5.6	7
1.03	0.97	2.08	660	0.2	3.7	4
0.85	1.15	1.98	660	0.2	1.9	4
0.82	1.18	2.03	660	0.2	2.2	6
0.64	1.36	2.04	660	0.2	1.6	5
0.53	1.47	1.93	660	0.2	1.5	3
0.82	1.18	2.03	660	10	1.8	13
0.82	1.18	2.03	700	10	1.6	10
0.82	1.18	2.03	720	2	2.1	9
0.82	1.18	2.03	720	10	1.7	16
0.82	1.18	2.03	720	40	1.8	20
0.82	1.18	2.03	750	10	1.7	17
1.39	0.61	1.88	770	10	1.6	21
1.03	0.97	2.08	770	10	2.1	14
0.82	1.18	2.03	770	10	1.8	31
0.53	1.47	1.93	770	10	2.6	26
0.03	1.97	2.13	770	10	3.2	20
0.82	1.18	2.03	780	10	1.0	31
0.82	1.18	2.03	800	10	2.0	30

* Ratio of water/sulfite. Sulfate was 1 ± 0.05.

** Ratio of molecular iodine/sulfite.

Powder patterns of compositions in Table 1 had d-spacings typical of stoichiometric dicerium disulfite monosulfate-4hydrate (Peterson, Foltyn, Onstott, 1980) except for one with the lowest sulfite coefficient. This result is a positive indication that the neutralization procedure gave stoichiometric, crystalline dipraseodymium disulfite monosulfate-4hydrate on dipraseodymium dioxymonosulfate as a substrate. Infrared spectra of these compositions showed bands more typical of stoichiometric dicerium disulfite dioxymonosulfate-4hydrate than bands typical of dilanthanum oxide-sulfite-sulfate-hydrate compositions, thus confirming the above conclusion.

Formation of hydrogen iodide by oxidation and hydrolysis of dipraseodymium oxide-sulfite-sulfate-hydrates was much slower than with lanthanum compositions. Figure 1 shows the comparative rates at the optimum temperature of 650K for lanthanum compositions. At 720K, for reaction times of 2, 10, 40 minutes, the yields of hydrogen iodide were, respectively, 9, 16, 20 percent. For experimental expedience, a reaction time of 10 minutes was adopted. Conditions for experiments and yields are listed in Table 1.

Figure 2 shows that the best temperature for high yield of hydrogen iodide was 770K.

Further utilization of sulfite was accomplished by a second batch reaction of the solid product after separation of the gaseous products, then adding iodine and water and reheating. The yield of hydrogen iodide was increased to over 40 percent with one rerun, and to 50 percent by two reruns. Data are in Table 2.

Table 2 Sequential Hydrolysis Reactions for Increased Yields of Hydrogen Iodide. Reaction Time was 10 Minutes.

run number	reactant sulfite	water/ sulfite	iodine/ sulfite	% HI yield	% other*	% not reacted
1	1.18	2.03	2.0	30**	26	44
2	0.52	2	2	14	12	18
3	0.21	3	3	7	6	5

* Other oxidation products were sulfur and probably thiosulfate; these were estimated by difference.

** AT 800K; run 2 and run 3 were at 770K.

Concurrent sulfur formation was confirmed by direct observation and by measurement of sulfite consumed. To account for all of the sulfite consumed, a second sulfur product with low sulfur valence, such as thiosulfate, would have formed also.

Dipraseodymium compositions containing sulfur (other than dioxymonosulfate) decomposed at 1375K to yield the dioxymonosulfate. Thermal decompositions at 1350K gave a sulfate coefficient of 1.02. At 1325K the stable decomposition product had a sulfate coefficient of 1.13. These sulfate coefficients were calculated from data for elemental analyses for praseodymium.

DISCUSSION

The composition with the best sulfite coefficient for hydrogen iodide production was 60 percent neutralized with a coefficient of 1.2 as shown in Figure 2. In Figure 4 is the cycle for hydrogen production, based on this fractional stoichiometry. A 50 percent yield of hydrogen iodide is assumed with an appropriate separation of iodine from hydrogen iodide, and a total of 3 oxidation plus hydrolysis reactions. Splitting of hydrogen iodide according to the method of Shindo and co-workers (1984) would yield hydrogen and iodine for recycle. Thermal decomposition of the solid product would yield sulfur dioxide for recycle, and oxygen for the material balance. Only part of the sulfite is beneficially oxidized to sulfate, so additional heat must be provided for conversion of the solid product back to dipraseodymium dioxymonosulfate for recycle. This heat penalty for unwanted sulfur products would be lessened by burning of the sulfur for heat recovery, and/or injection of sulfur dioxide from pollution sources. The best iodine partial pressure could be utilized, since our results show a relatively low sensitivty of iodine above the stoichiometric requirement.

Water utilization efficiency in this cycle is better than in the dilanthanum cycle because of the factor of 2 in the hydrate number of the oxidation reactant, which also supplies the water for the hydrogen iodide formation.

The starting hydrate composition is easily prepared in 20 minutes, plus the time for removal of unreacted sulfur dioxide. Hydrogen iodide yields were optimum in less than 40 minutes, and the thermal decomposition of hydrogen iodide with a catalyst would be rapid (Shindo and co-workers, 1984). The last reaction in the cycle to yield oxygen at 1350K should be complete within 10 minutes (Hollabaugh and Bowman, 1981). Thus the time interval for one production cycle could be less than 2 hours. Possibly a catalyst material could be incorporated into the dipraseodymium dioxymonosulfate feed material to improve yields of desired sulfur products, and also improve decomposition rates.

An assessment of heat and work requirements for this cycle is in progress.

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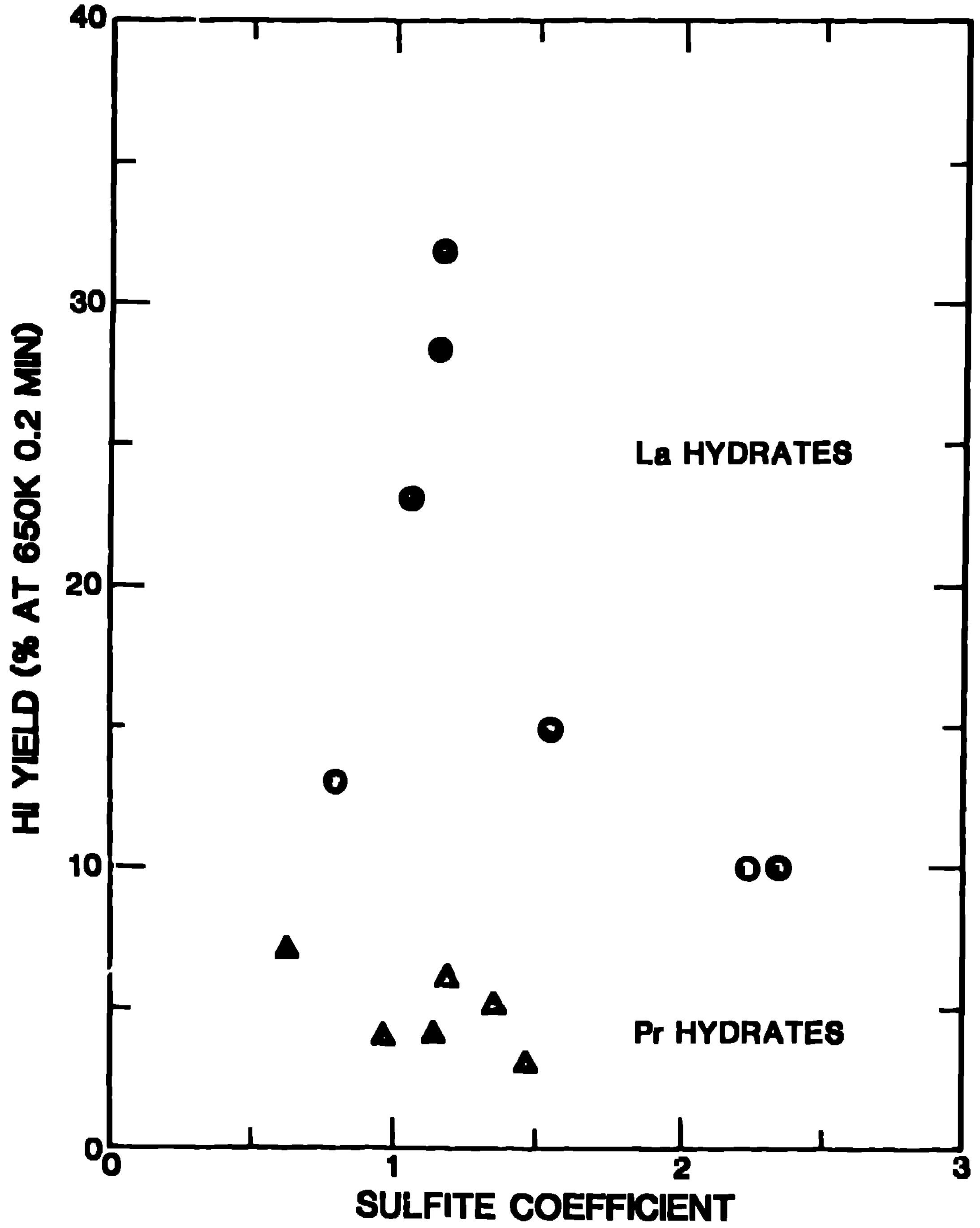

Fig. 1 Comparison of yields of hydrogen iodide from hydrates of lanthanum and hydrates of praseodymium at the optimum temperature and optimum reaction time for lanthanum compositions

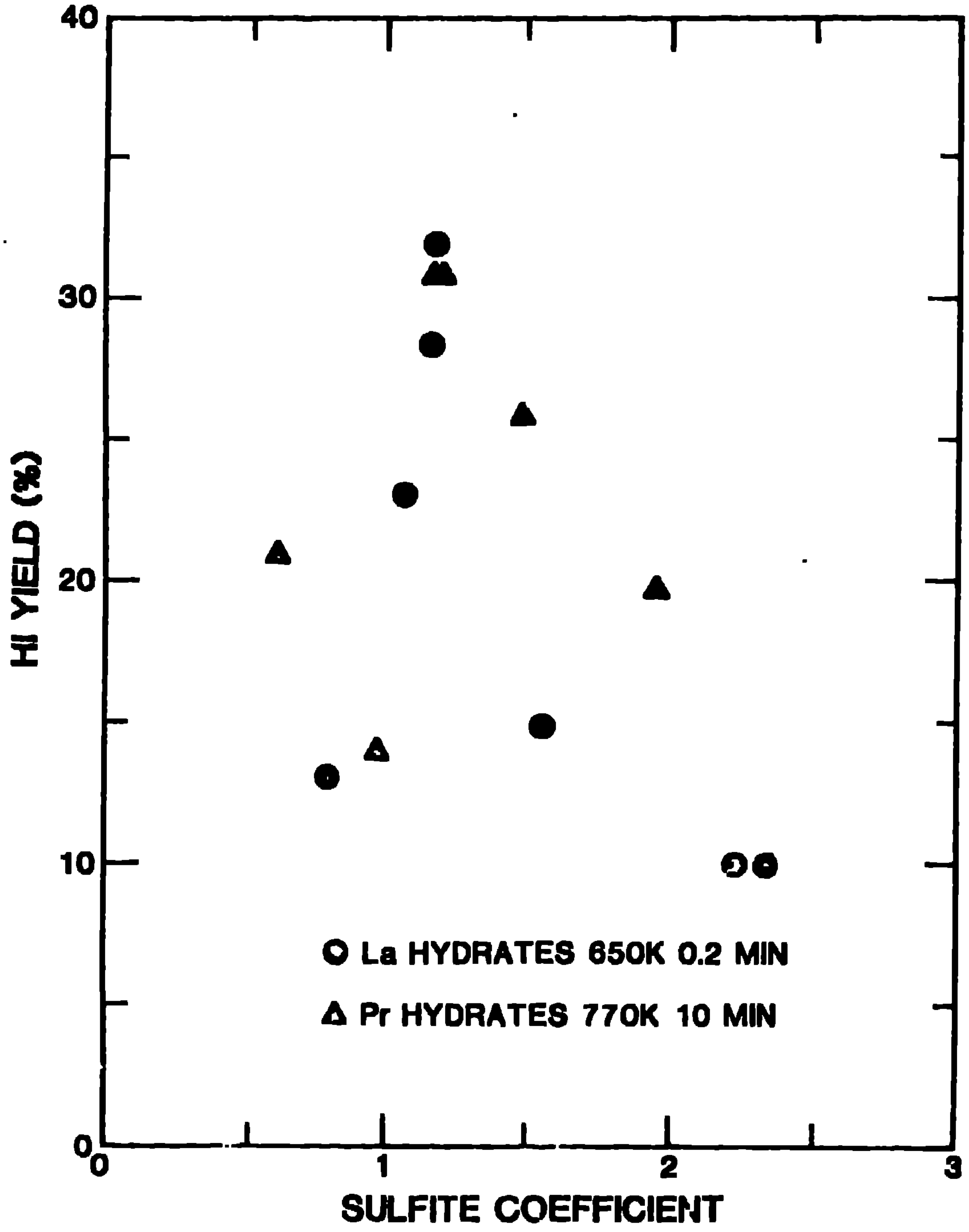

Fig. 2 Comparison of the effect of the sulfite content of hydrates on hydrogen iodide yields at optimum temperatures and near optimum reaction times

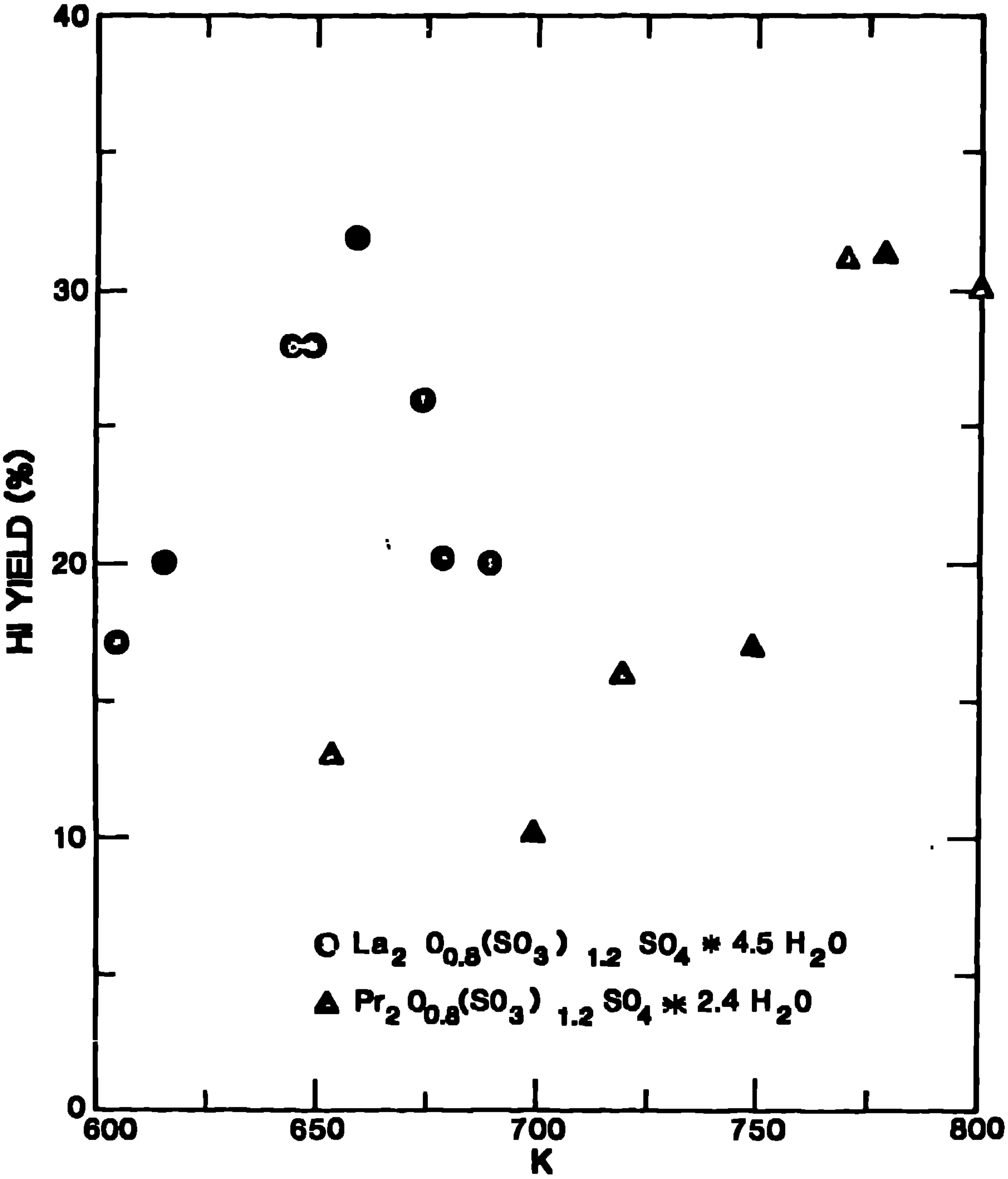

Fig. 3 Effect of temperature on reactivity of hydrates that gave maximum yields of hydrogen iodide

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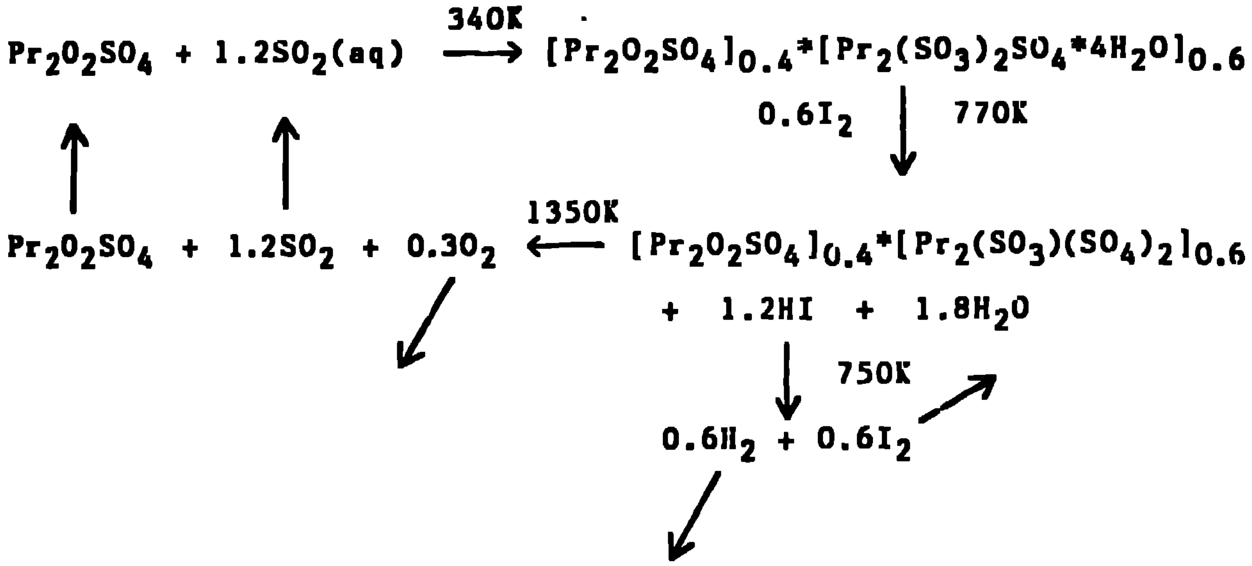

Fig 4 Thermochemical hydrogen cycle with fractional stoichiometry that utilizes dipraseodymium dioxymonosulfate. A 50 percent yield of hydrogen iodide is assumed. Only the iodine consumed and starting hydrate water are included in the material balance.