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TWO BISMUTH SULFATE-SULFURIC ACID HYBRID WATER-SPLITTING CYCLES. PROPOSED ANTIMONYL SULFATE CYCLE

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ABSTRACT

Some experimental work is presented that is related to two hybrid thermochemical cycles for the production of hydrogen which involve bismuth trisulfate and/or bismuth oxysulfates. Omitting statement of the steps for decomposition of SO_3 and the electrochemical formation of H_2 and H_2SO_4 from SO_2 and H_2O, the high and low temperature reactions are:

Cycle I

$$Bi_2(SO_4)_3 = Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ SO_3$$

$$Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ H_2SO_4 = Bi_2(SO_4)_3 + 2.3\ H_2O$$

Cycle II

$$Bi_2O(SO_4)_2 = Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ SO_3$$

$$Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ H_2SO_4 = Bi_2O(SO_4)_2 + 1.3\ H_2O$$

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Equilibrium sulfur trioxide pressures are given graphically for three solid-gas equilibria involving $Bi_2(SO_4)_3$, α- and β-$Bi_2O(SO_4)_2$, and $Bi_2O_2SO_4$. An improved method of carrying out the low temperature step for Cycle I is presented which may provide a remedy to a problem of sorption of sulfuric acid solution by the solids. An antimonyl sulfate - sulfuric acid hybrid cycle is outlined in which SO_2 and O_2 are evolved at different temperatures, simplifying the usual SO_3-SO_2-O_2 separation problem.

KEYWORDS

Thermochemical hydrogen cycles; bismuth sulfate and oxysulfates; sulfur trioxide equilibrium pressures; antimonyl sulfate cycle.

INTRODUCTION

Work on a bismuth sulfate hybrid thermochemical cycle began with the suggestion by M. G. Bowman that some of the problems of heat penalty and corrosion associated with the use of solutions in thermochemical hydrogen cycles might be decreased by the use of solids of low solubility which could be decomposed at high temperature and that this notion could be applied to sulfuric acid cycles by forming a sulfate from the H_2SO_4. Ideally the sulfate should have low solubility, few or no waters of hydration, and decompose at not too high temperatures. Bismuth sulfate seemed suitable for investigation.

Two bismuth sulfate cycles are made possible by the stepwise decomposition of the sulfate-oxysulfate system. Omitting statement of the steps for decomposition of SO_3 and the electrochemical formation of H_2 and H_2SO_4 from SO_2 and H_2O, the high and low temperature reactions are:

Cycle I

$$Bi_2(SO_4)_3 = Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ SO_3$$

$$Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ H_2SO_4 = Bi_2(SO_4)_3 + 2.3\ H_2O$$

Cycle II

$$Bi_2O(SO_4)_2 = Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ SO_3$$

$$Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ H_2SO_4 = Bi_2O(SO_4)_2 + 1.3\ H_2O$$

Cycle I proceeds through the intermediate oxysulfates $Bi_2O(SO_4)_2$ and $Bi_2O_2SO_4$ and Cycle II through $Bi_2O_2SO_4$. Cycle I has the advantage of generating 2.3 moles of H_2 per mole of Bi_2O_3, compared with 1.3 for Cycle II. Published work (Allan, 1902; Urazov, Kindiakov, and Chukan, 1958) on the Bi_2O_3-SO_3-H_2O system shows that $Bi_2(SO_4)_3$ is the stable solid in contact with H_2SO_4 solutions above 52.7 wt%, so that acid of at least this strength would have to be used in Cycle I (see, however, the modification of Cycle I discussed later). Concentrations between about 5 wt% and 52.7 wt% could be used for Cycle II. The efficiency for electrochemical formation of H_2SO_4 and H_2 seems at present to be a maximum at around 30 wt% H_2SO_4.

Some thermodynamic data obtained for individual steps in the decomposition reactions will be presented. An improved method of conducting Cycle I will be discussed which may provide a remedy to a problem of sorption of H_2SO_4 solution by the solids.

EXPERIMENTS

Equilibrium Pressures in the Decomposition of $Bi_2(SO_4)_3$ and α-$Bi_2O(SO_4)_2$

Work has been completed (W. M. Jones, 1982) on determination of equilibrium total pressures in closed systems for the first two stages of dissociation. Platinum black was mixed with the solids to establish equilibrium (1), and the known

$$SO_3 \overset{Pt}{=} SO_2 + 1/2\ O_2 \qquad (1)$$

$$Bi_2(SO_4)_3 = \alpha\text{-}Bi_2O(SO_4)_2 + SO_3 \qquad \Delta H = 140.6\ kJ \qquad (2a)$$

$$Bi_2(SO_4)_3 = \beta\text{-}Bi_2O(SO_4)_2 + SO_3 \qquad \Delta H = 162.3\ kJ \qquad (2b)$$

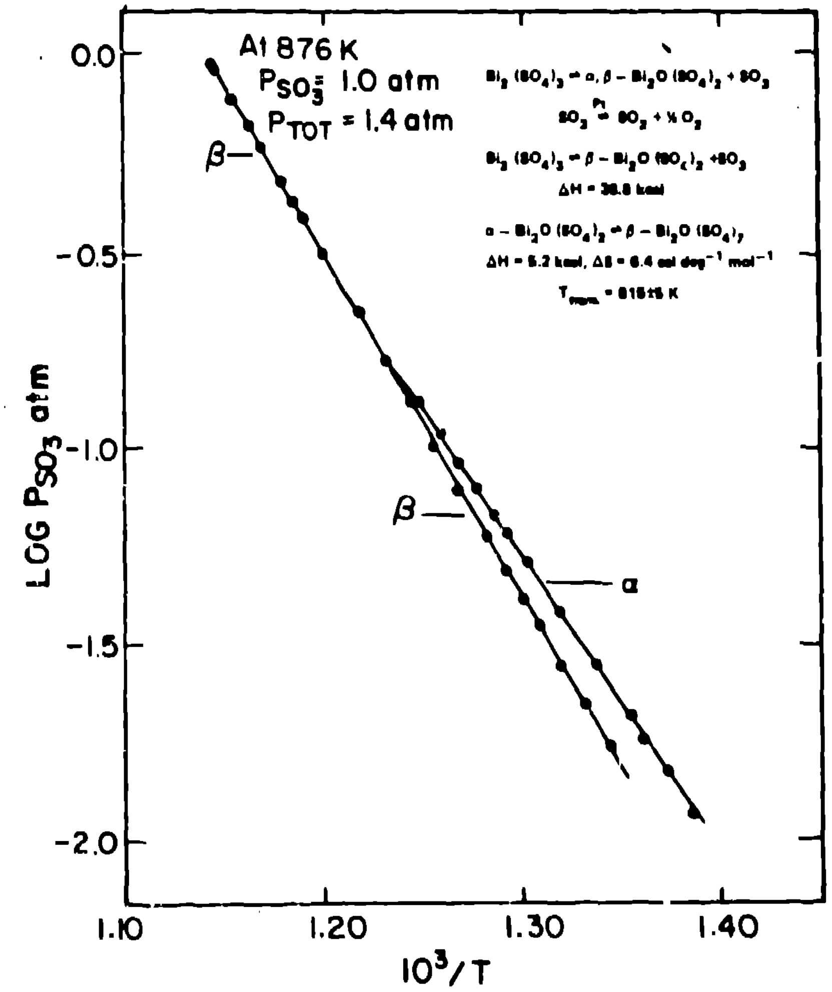
$$\beta\text{-}Bi_2O(SO_4)_2 = Bi_2O_2SO_4 + SO_3 \qquad \Delta H = 174.5\ kJ \qquad (3)$$

$$\alpha\text{-}Bi_2O(SO_4)_2 = \beta\text{-}Bi_2O(SO_4)_2 \qquad \Delta H = 21.7\ kJ \qquad (4)$$

$$\Delta S = 26.8\ J/K$$

$$T_{tr} = 815 \pm 5\ K$$

The data are shown in Figs. 1 and 2. There is a transformation of $Bi_2O(SO_4)_2$ at $T_{tr} = 815 \pm 5$ K between a low temperature α and high temperature β form. The transformation is unusually sluggish, allowing equilibrium pressures for (2b) involving metastable β to be measured below T_{tr}. Pressures for (2a) were obtained after β had very slowly transformed in situ to stable α below T_{tr}. The β form was found from a new x-ray diffraction pattern observed when $Bi_2O(SO_4)_2$ was made outside the equilibrium apparatus by thermal decomposition



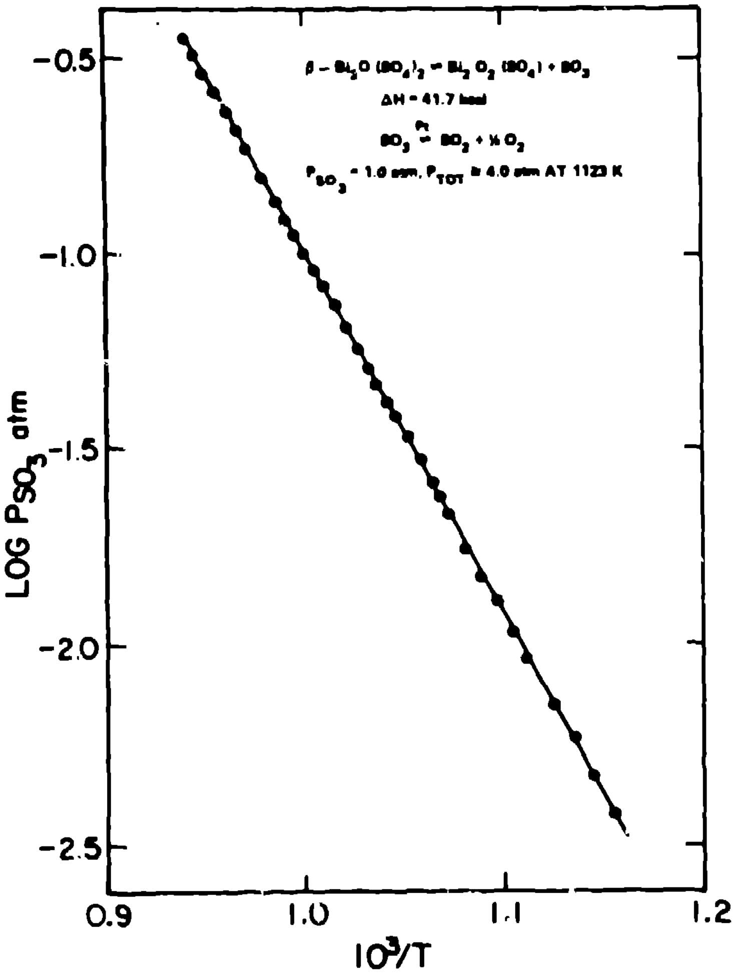


Fig. 2. Equilibrium SO_3 pressures.

of $Bi_2(SO_4)_3$, at a higher than usual temperature. Time-temperature characteristics of the transformation and an independent value of T_{tr} were then determined by annealing and x-ray powder diffraction methods. The β form appears to be stable indefinitely at room temperature. The transformation should not affect a cycle importantly but would have to be allowed for. Additional crystal forms have not been found for the other solids in (2a), (2b), and (3).

Survey Experiments on the Thermal Decomposition of $Bi_2(SO_4)_3$

Survey experiments on the decomposition of $Bi_2(SO_4)_3$ in flowing helium showed breaks in decomposition rate after evolution of one mole of SO_3 at 1050 K and after two moles at 1150 K. At 1240 K the abrupt decrease in rate, after less than two minutes reaction time, took place after evolution of 2.3 moles. Further evolution at 1240 K was very slow, leading to formation of a liquid phase (eventually liquid Bi_2O_3), in agreement with the work of Margulis, Grishankina, and Kopylov (1965); such evolution would require excessive heat input. Process development work at Los Alamos (Cox, Jones, and Peterson, 1980; Hollabaugh, 1980; Peterson and Bowman, 1980) has included the use of a benchscale rotary kiln to study the rapid decomposition reaction of Cycle II and several other decompositions. These experiments, along with the thermodynamic data presented for the enthalpy change will be involved in going from $Bi_2O_2SO_4$ to $Bi_2O_{2.3}(SO_4)_{0.7}$, determine the two cycles that are practically possible.

The gas evolved by the solid at each of the above temperatures was at least 99% SO_3, although extensive dissociation would have taken place at thermodynamic equilibrium. SO_3 is then the species emerging from the normal sulfate and the first two oxysulfates. These solids were not catalysts for SO_3 dissociation within the 0.25 minute residence time, nor would they be for recombination of $SO_2 + 1/2\ O_2$.

Hydrates. Sorption of H_2SO_4 Solutions by the Solids. Possible Improvement of the Cycles

The conclusion of Urazov, Kindiakov, and Chukan (1958) was initially accepted that anhydrous $Bi_2O(SO_4)_2$ was the stable phase in contact with H_2SO_4 solutions between about 3 wt% (about 5 wt% according to Allan, 1902) and 52.7 wt%, although previous preparative work (Skramovsky and Vondrasek, 1937) indicated that mono and trihydrates could be formed. Later, two new x-ray patterns were observed with samples of $Bi_2O(SO_4)_2$ known to have been exposed to moisture. A sample of $Bi_2O(SO_4)_2$ prepared from Bi_2O_3 in 1-2 M H_2SO_4 and dried with acetone and by mild heating in vacuum (preparation by C. L. Peterson) showed one of these patterns. This pattern was changed to the second pattern after evolution of two moles of water at 275°C. After much slower evolution of a third mole of water at 275°C the pattern was that of anhydrous α-$Bi_2O(SO_4)_2$. The trihydrate is regularly formed in preparations from Bi_2O_3 and 3M H_2SO_4 for kiln decompositions(Peterson and Bowman, 1980). The monohydrate (probably a hydroxysulfate) forms very readily at room temperature in room air from anhydrous material of high specific area.

The writer had earlier drawn attention to occlusion of H_2SO_4 solutions by $Bi_2O(SO_4)_2$ (actually by the trihydrate) when the latter was formed by adding Bi_2O_3 powder to stirred 1M H_2SO_4; the observed final 0.8 M H_2SO_4 corresponded to the expected reaction. After centrifuging, the solid was dried at 280°C to constant weight. The final weight and x-ray diffraction pattern unexpectedly corresponded to $Bi_2(SO_4)_3$. Estimates showed that about 10% more H_2SO_4 had been present in the wet solid than was necessary, upon concentration during heating, to give trisulfate. Since the sorbed solution had about 75 moles H_2O per mole of solid, the behavior had no value as a method for making trisulfate. Later, C. L. Peterson, in making material under approximately the same conditions for decomposition in a fluidized bed, was able to reduce the amount of sorbed solution greatly, in one case to 8.8 moles H_2O per mole of solid. If we assume that incorporation of only 8 moles of H_2O per mole of product can be achieved - three as hydrate and five as sorbed solution - then if the solution were 11.1 m (52.1 wt%), enough H_2SO_4 would be present to give trisulfate for a Cycle I process. Heat would have to be provided to vaporize 9 moles of water, including that from H_2SO_4, or 4.5 moles per mole of H_2. A major advantage of this way of implementing Cycle I would be the elimination of the sorbed solution problem, with its heat penalty, since observation indicates that $Bi_2(SO_4)_3$ formed directly from sufficiently strong H_2SO_4 would also sorb solution.

It would be necessary that the $Bi_2O(SO_4)_2$ trihydrate formed from the high temperature product $Bi_2O_{2.3}(SO_4)_{0.7}$ be sufficiently active to react with the sorbed H_2SO_4 to give trisulfate before vaporization of the acid. Too fast a heating rate would have to be avoided. The [illegible] large particle size of $Bi_2O(SO_4)_2$ developed by Peterson at Los Alamos to give good characteristics for kiln operation came from a filter cake of trihydrate with about 10 moles of water per mole of solid (Peterson and Bowman, 1980). The sorbed solution corresponded to seven waters and 0.36 H_2SO_4's per mole of solid (2.88 m, 22 wt% final H_2SO_4). If this H_2SO_4 had all reacted to form trisulfate after concentration during heating, the final composition of the solid would have been $Bi_2O_{3-x}(SO_4)_x$ with $x = 2.36$. In practice x varied from 2.00 to 2.14. Apparently the morphology and relatively large size of these particles did not allow much reaction before H_2SO_4 vaporized. However, the emphasis was on kiln performance and no attempt was made to maximize x. [A slight reinterpretation of the data of Table 1 of Bowman and Peterson (1980) by the writer gives 9.0 ± 0.5 as the average number of waters per mole of dried product (water of hydration, from sorbed solution, and the H_2O of H_2SO_4 itself). The maximum fraction of sorbed H_2SO_4 reacting to give trisulfate was 0.475].

A Cycle I carried out as suggested above might also be superior to Cycle II. The heat penalty associated with sorbed solution would be allocated to 1.77 (= 2.3/1.3) times as many moles of hydrogen in Cycle I. The dependency on the acid concentration of the efficiency of electrolysis and the volume of solution sorbed per mole of trihydrate might lead to optimum behavior at some intermediate acid concentration corresponding to a combination of Cycles I and II.

Finally, it is possible that the formation of the trihydrate, although not of the monohydrate, could be avoided with the more concentrated H_2SO_4 for a Cycle I, as indicated by the experiments in Table 1. The avoidance would be for kinetic reasons. It is assumed that $Bi_2O_{2.3}(SO_4)_{0.7}$ would behave like the Bi_2O_3 and $Bi_2O(SO_4)_2$ in Table 1. The heat penalty associated with two H_2O's of hydration would be eliminated and the water (in all forms) would be reduced from 4.5 to 3.5 moles per mole of H_2. However, sorption characteristics of the monohydrate might be different from those so far observed, which pertain to the trihydrate.

TABLE 1 Hydration of $Bi_2O_3\cdot 2SO_3$ in More Concentrated H_2SO_4

Initial Solid	H_2SO_4 Concentration	Time	Temp., °C	Product
1. Bi_2O_3	50 wt % (44 wt% final)	3 h	25-40	$Bi_2O_3\cdot 2SO_3\cdot(1.06\ H_2O)$, from initial weight and product after EtOH extraction of H_2SO_4 and drying 6 h at 228°C
2. α-$Bi_2O_3\cdot 2SO_3$	50 wt %	40 min	25-40	$Bi_2O\cdot 2SO_3\cdot(0.97\ H_2O)$; monohydrate x-ray pattern.
3. α-$Bi_2O_3\cdot 2SO_3$	50 wt %	6 h	75	$Bi_2O_3\ 2SO_3\cdot(1.21\ H_2O)$; monohydrate x-ray pattern
4. α-$Bi_2O_3\cdot 2SO_3$	50 wt %	5 h	100	$Bi_2O_3\cdot 2SO_3\cdot(1.88\ H_2O)$; trihydrate and monohydrate x-ray patterns.
5. α-$Bi_2O_3\cdot 2SO_3$	1 m followed by 44 wt %	10 min 5 h	25 75	$Bi_2O_3\cdot 2SO_3\cdot(3.1\ H_2O)$; trihydrate x-ray pattern

A PROPOSED ANTIMONYL SULFATE -SULFURIC ACID HYBRID CYCLE

As will be seen, this cycle offers the possibility of greatly simplifying the SO_3-SO_2-O_2 separation problem. Sulfuric acid-solid sulfate (or oxysulfate) cycles in which the metal ion can have variable valence have the possibility of forming SO_2 and a higher valence state oxide. The conditions on the sulfate outlined in the Introduction and decomposition of the oxide at reasonable temperatures to oxygen and a lower valent oxide (for reaction with H_2SO_4) would be necessary. Decomposition of the sulfate to give both SO_2 and SO_3, as is found with some first transition series sulfates, would not be of interest. This indicates the need to match the number of sulfates (say by choosing an oxysulfate) to the available change in oxidation number of the metal ion. One possibility is antimonyl sulfate.

$$Sb_2O_2SO_4 = Sb_2O_4 + SO_2 \qquad 900\ K \tag{1}$$

$$Sb_2O_4 = Sb_2O_3 + 1/2\ O_2 \qquad 1300\ K \tag{2}$$

$$Sb_2O_3 + H_2SO_4 = Sb_2O_2SO_4 + H_2O \tag{3}$$

The temperature for (1) is suggested by the "glowing red" temperature at which Metzl (1906) decomposed $Sb_2(SO_4)_3$ to SO_3 and Sb_2O_4. Detailed conditions of the experiment were not given. No mention was made of SO_2 formation, Sb_2O_3 was apparently sometimes present, and some of the Sb_2O_4 could have been formed by air oxidation of sesquioxide. However, preliminarily considering $Sb_2O_2SO_4$ decomposition to give Sb_2O_3 and SO_3, calculations show that SO_3 should oxidize Sb_2O_3 to Sb_2O_4, allowing (1) to be achieved as written. The different temperature ranges of (1) and (2) should permit SO_2 and O_2 to be evolved separately. The vapor pressure of $Sb_2O_3(l)$ is relatively high at the temperature of (2); avoidance of back reaction and recovery of the heat of condensation would be necessary.

Hintermann and Venuto (1968) report that anhydrous $Sb_2O_2SO_4$ can be formed in boiling 6.5 M H_2SO_4 (9.0 m, 47 wt%). The definite compound $Sb_6O_7(SO_4)_2$, or Sb_2O_3 2/3 SO_3 (Bovin, 1976; Hintermann and Venuto, 1968), forms in the range 4.3 to 6.9 M at room temperature or in 2.0 to 6.5 M in the boiling acid (Hintermann and Venuto, 1968). If the solids sorb the H_2SO_4 solution, it might be possible to handle this problem, and perhaps use weaker acid then otherwise, as suggested for the bismuth cycles.

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