LA-UR -80-618

CONF - 800616--4

TITLE: Reaction of Metal Sulfates with Molybdenum Oxide, A High Temperature Reaction Step for Thermochemical Cycles.*

MASTER

AUTHOR(S): C. M. Hollabaugh, T. C. Wallace, M. G. Bowman, and W. M. Jones

SUBMITTED TO: To be presented at the 3rd World Hydrogen Energy Conference 23-26 June 1980, at Tokyo, Japan, and to be published in the Proceedings. (uncl.)

*Work completed under the auspices of the U.S. Department of Energy.

DISCLAIMER

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

Form No. 836 R4
St. No. 2629
12/78

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG-36

REACTION OF METAL SULFATES WITH MOLYBDENUM OXIDE, A HIGH TEMPERATURE REACTION STEP FOR THERMOCHEMICAL CYCLES

C. M. Hollabaugh, T. C. Wallace, Sr., M. G. Bowman, and W. M. Jones
University of California, Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545 USA

ABSTRACT

The reaction of sulfates with molybdenum oxide at high temperature was studied to determine the feasibility of using these reactions in a thermochemical process for making hydrogen. The experiments were performed by heating the blended powders to temperatures of 1075 K and higher and analyzing the evolved gas for acid content.

It was found that the reaction rate over the first few minutes increased with both temperature and MoO_3. The fraction of sulfate reacting in the first 5 minutes varies with cation used. At 1125 K and for a molar ratio of sulfate ion/MoO_3 of 0.5, the fraction reacted was 0.29 for $BaSO_4$, 0.32 for $CaSO_4$ and 0.82 for $La_2(SO_4)_3$.

These results are encouraging and indicate that an alternative means to sulfuric acid drying and decomposition is feasible using a mixed sulfate/oxide system to lower the effective decomposition temperature of the insoluble sulfate.

KEYWORDS

Calcium sulfate, barium sulfate, lanthanum sulfate, molybdenum trioxide, hydrogen, thermochemical, kinetics, decomposition.

INTRODUCTION

Hydrogen production by splitting water thermochemically is a proven concept that is being developed and researched in several laboratories throughout the world. A common step in many of these cycles is production of an aqueous sulfuric acid intermediate which for cyclic use must be evaporated and thermally decomposed to water and sulfur trioxide. The sulfur trioxide is further decomposed to sulfur dioxide and oxygen (Parker, 1979; Rosenbrugh, 1979; and Van Velzen, 1979). These high temperature concentration and decomposition steps impose a severe corrosive environment requiring expensive materials of construction.

An alternative (Bowman, 1974) solution to the problems of handling and decomposing sulfuric acid is the introduction of an insoluble metal sulfate into the cycle. This could be done by contacting sulfuric acid with a metal oxide to produce the

appropriate metal sulfate which, being insoluble, is separated from solution by filtration. The sulfate is decomposed to the metal oxide, sulfur dioxide and oxygen. Cox, Jones and Peterson (1980) have presented experimental results for the bismuth sulfate and bismuth oxysulfate systems and discuss the ramifications of using these and similar sulfates in a thermochemical cycle.

Other less expensive insoluble sulfates, such as calcium sulfate, could also be used except that their decomposition temperatures may be too high. We have found that the effective decomposition temperature for these sulfates can be lowered by adding molybdenum oxide. A typical cycle using this concept may be illustrated by the following equations:

$SO_2 + 2H_2O = H_2SO_4 + H_2$	Electrochemical	350 K	(1)
$H_2SO_4 + CaMoO_4 = CaSO_4 + MoO_3 + H_2O$		350 K	(2)
$CaSO_4 + MoO_3 = CaMoO_4 + SO_3$		1200 K	(3)
$SO_3 = SO_2 + 1/2O_2$		1150 K	(4)

Reaction 1 was originally studied by Bowman and Onstott (1974) and is presently being researched together with reaction 4 at Westinghouse by Parker (1979). The kinetics of reaction 2 are not yet known but our preliminary results indicate reasonable reaction rates at 300 K in 1.0 M acid. This paper reports our study of reaction 3 using calcium, barium and lanthanum sulfates and molybdenum oxide.

EXPERIMENTAL

The course of the reaction of three metal sulfates (barium sulfate, calcium sulfate and lanthanum sulfate) with molybdenum oxide was determined by rapidly heating a mixture of the desired compounds to a selected temperature above the melting point of molybdenum oxide (1068 K), holding them at that temperature and absorbing the product gas in an aqueous solution. The product gases are composed mainly of sulfur trioxide with smaller amounts of sulfur dioxide and oxygen present. The absorbent solution was continuously titrated with 1.0 N sodium hydroxide to maintain the solution at pH = 10.0. The reaction results derived from the titration are expressed as the fraction of $SO_4^=$ reacted.

The apparatus consisted of a quartz reaction chamber which could be rapidly inserted into a preheated tube furnace so that the reaction temperature was reached in 3-4 minutes. It appeared that little or no reaction occurred until the molybdenum oxide melted. The initial solid sample was contained in a platinum boat held in the reaction chamber. A 25 cm^3/min. helium carrier gas flow was maintained over the sample to prevent back diffusion of the product gas. Because the vapor pressure of molybdenum oxide at the experimental temperatures is significant (43.4 Torr at 1175 K), provision had to be made for its condensation in a cooler portion of the delivery tube so that the tube would not plug.

The experimental variables investigated in this work were: reaction temperature and reactant ratio (SO_4/ MoO_3). For calcium sulfate and barium sulfate the selected temperatures were 1125, 1175 and 1225 K and the specified reactant ratios 0.5, 1.0 and 2.0. With lanthanum sulfate, however, it was found that the inital reaction rate was so rapid that part of the melt was blown out of the platinum boat at the higher temperature. Therefore, only two lower temperatures were chosen, 1075 and 1125 K.

Results and Discussions

Barium sulfate. The results obtained in the reaction of molybdenum oxide with barium sulfate at 1125 K are shown in Fig. 1, a plot of the fraction of $SO_4^=$ reacted as a function of time. The three curves are for reactant ratios of 0.5, 1.0 and 2.0. Similar results are shown in Figs. 2 and 3 at temperatures of 1175 and 1225 K, respectively. For all cases, the results show that the reaction rate increases as molybdenum oxide is added to the system. The reaction sequence appears to be the dissolution of the sulfate in molten molybdenum oxide and later reaction to form sulfur trioxide and barium molybdate. The latter dissolves in the reaction melt.

The effect of temperature on the reaction was as expected. Both the initial reaction rate and the total quantity of sulfate that reacted by the end of the experiment increased with temperature. At 1225 K and a reactant ratio of 2.0, the oxide was consumed in roughly 25 minutes. The fraction of sulfate consumed during this period was less than half because of the loss of part of the molybdenum oxide by evaporation. At lower temperatures, the reaction did not proceed to the depletion of the molybdenum oxide reactant.

Calcium sulfate. The results for calcium sulfate are more complex. It reacts faster than barium sulfate and as a result the molybdenum oxide was depleted at a reactant ratio of 2.0 at the three temperatures. These results are shown in Figs. 4, 5 and 6 at temperatures of 1125, 1175 and 1225 K, respectively. Again we note that the fraction of sulfate consumed was less than 0.5 because of molybdenum oxide evaporation.

At a reactant ratio of 0.5, the reaction rates were high initially (over 30% in 3 minutes), however, only at 1225 K did the rate remain high until most of the sulfate had reacted. At the two lower temperatures an adverse effect occurred when less than half of the sulfate had been consumed. The cause for this effect is not yet known, however, we speculate that calcium sulfate dissolves faster and is more soluble than barium sulfate in the reaction melt. When an excess of molybdenum oxide is present, all the calcium sulfate dissolves in the first 10 minutes causing its activity (in the melt) to decrease as its concentration decreases slowing the reaction rate abruptly as seen in Figs. 4 and 5. It appears, therefore, that a reactant ratio between 0.5 and 1.0 may produce a higher reaction yield, particularly at the lower temperatures.

Lanthanum sulfate. As stated earlier, the reaction of lanthanum sulfate with molybdenum oxide was extremely rapid making it difficult to contain the liquid reaction mixture in the platinum boat. Consequently, experimental results were only obtained at two lower temperatures, 1075 and 1125 K seen in Figs. 7 and 8, respectively. At the highest reactant ratio, 2.0, the initial reaction rate is higher at 1125 K but the fraction of sulfate that had reacted after 60 minutes was the same for both temperatures. The reason for this anomaly is unknown. At the other reactant ratios, both the rate and fraction reacted increased with temperature as expected.

Approximately 90% of the lanthanum sulfate was decomposed in less than 5 minutes at 1125 K, the fastest rate of the three sulfates studied. Compared to calcium sulfate, which showed the next fastest rate, lanthanum sulfate offers an advantage of about 100 K lower temperature for equivalent rates.

Although these results are encouraging from a reaction rate standpoint, we recognize the difficulties in utilizing such materials in a practical cycle. On the one hand, the use of a liquid such as molybdenum oxide as a reactant and reaction

medium would raise heat transfer rates at high temperature, further the handling of a liquid is much easier than that for a solid. On the other hand, one would be faced with the problem of the phase transition from solid to liquid coupled with the subsequent cooling and solidification of the reaction melt in the cycle. Materials handling during these transitions may prove to be difficult from a practical viewpoint.

CONCLUSIONS

A thermochemical cycle using insoluble metal sulfates mixed with molybdenum oxide to lower their decomposition temperatures appears to be a feasible way to avoid the high temperature drying and decomposition of sulfuric acid. Approximately 90% of the sulfate can be decomposed in less than 5 minutes at 1125 K in the presence of molybdenum oxide so that residence times at high temperature could be short depending on the heat transfer rate. Because the materials are liquid at the decomposition temperature, heat transfer should be rapid.

REFERENCES

Besenbruch, G. and Co-workers (1979). Development of a Sulfur-Iodine Thermochemical Water-Splitting Cycle for Hydrogen Production. Proceedings 14th IECEC, Boston, Massachusetts.

Bowman, M. G. (1974). Fundamental Aspects of Systems for the Thermochemical Production of Hydrogen from Water. Proceedings First National Topical Meeting on Nuclear Process Heat Applications, American Nuclear Society, Los Alamos, New Mexico.

Bowman, M. G. and E. I. Onstott (1974). Hydrogen Production by a Low Voltage Electrolysis in a Combined Thermochemical and Electrochemical Cycle. Proceedings Electrochemical Society Meeting, New York.

Cox, K. E., W. M. Jones and C. L. Peterson (1980). The LASL Bismuth Sulfate Thermochemical Hydrogen Cycle. Proceedings of the 3rd World Hydrogen Energy Conference, Tokyo, Japan.

Parker, G. H. and P. W. T. Lu (1979). Laboratory Model and Electrolyzer Development for the Sulfur Cycle Hydrogen Production Process. Proceedings 14th IECEC, Boston, Massachusetts.

van Velzen, D. and H. Langenkamp (1979). Thermochemical Hydrogen Production by the Mark-13 Process: A Status Report. Proceedings 14th IECEC, Boston, Massachusetts.

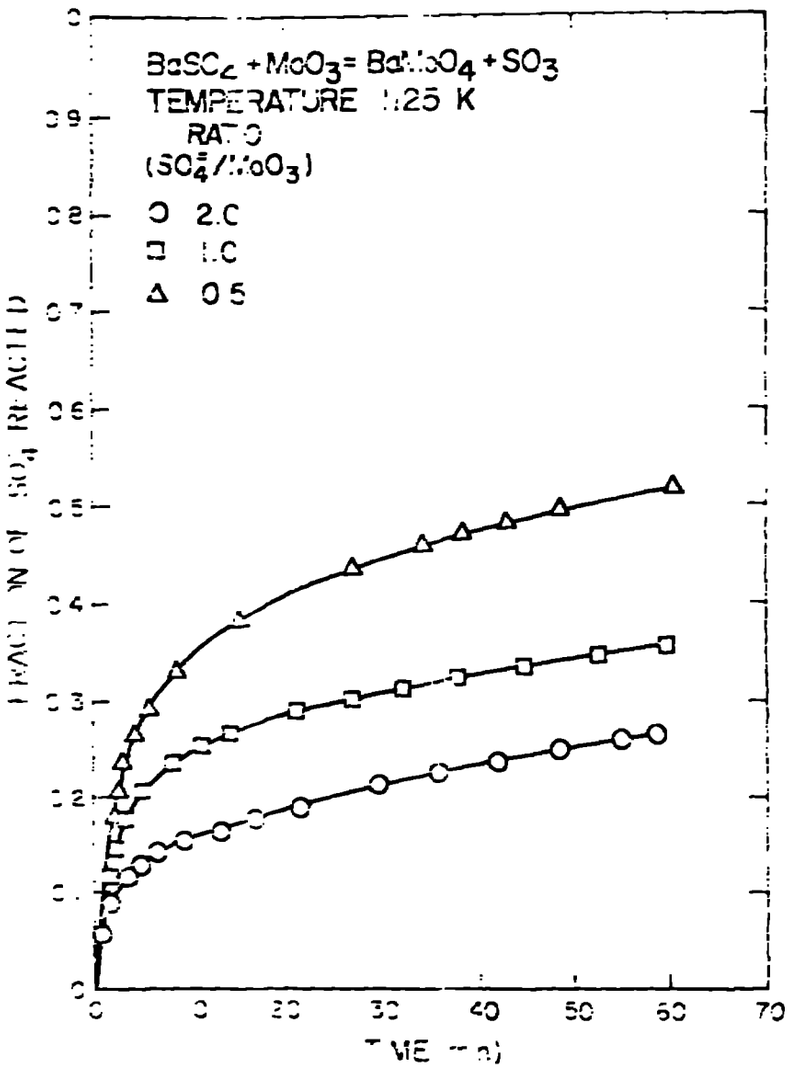

Fig. 1. Reaction of $BaSO_4$ with MoO_3 at 1125 K.

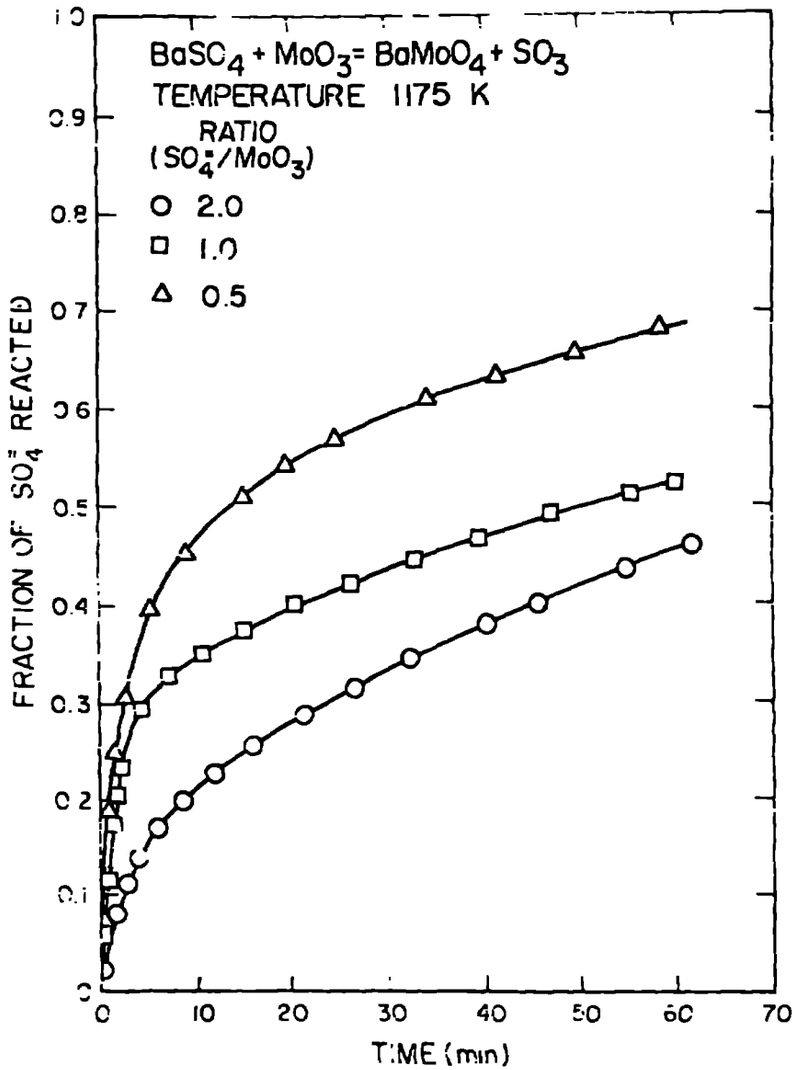

Fig. 2. Reaction of $BaSO_4$ with MoO_3 at 1175 K.

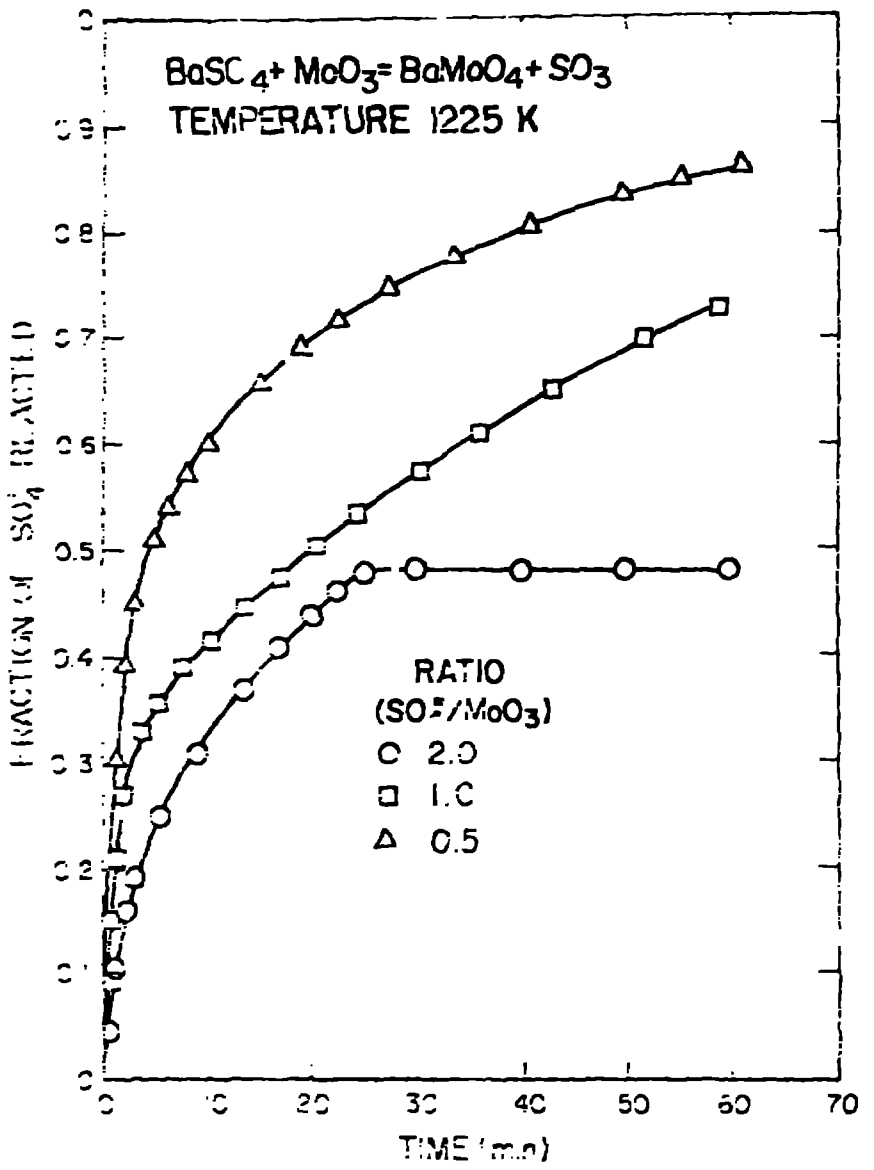

Fig. 3. Reaction of $BaSO_4$ with MoO_3 at 1225 K.

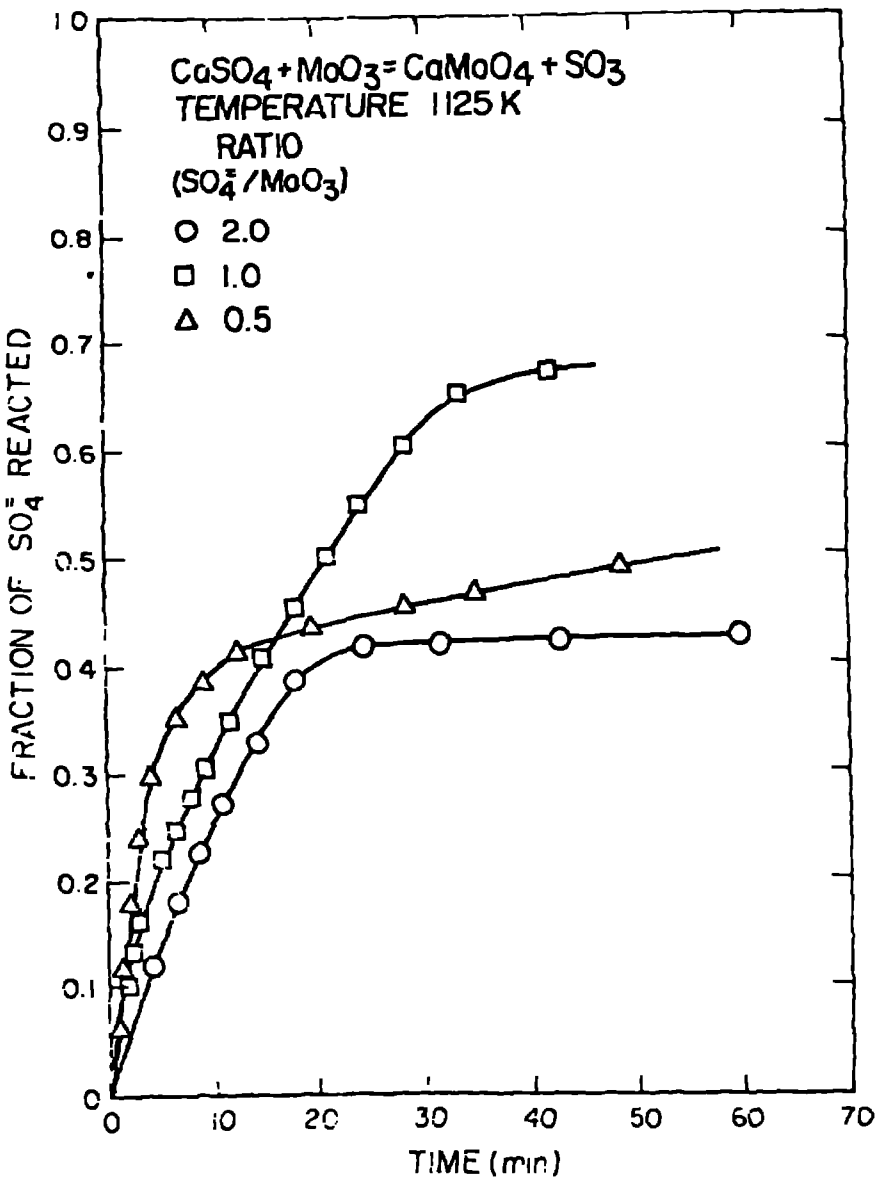

Fig. 4. Reaction of $CaSO_4$ with MoO_3 at 1125 K.

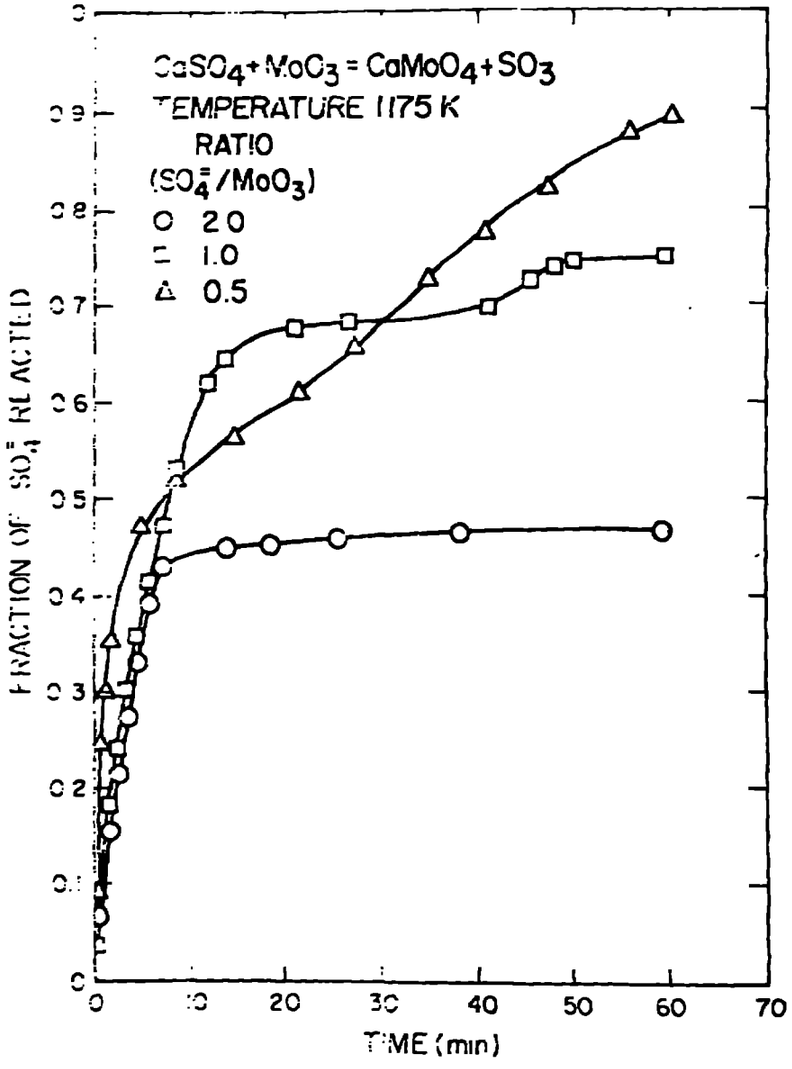

Fig. 5. Reaction of $CaSO_4$ with MoO_3 at 1175 K.

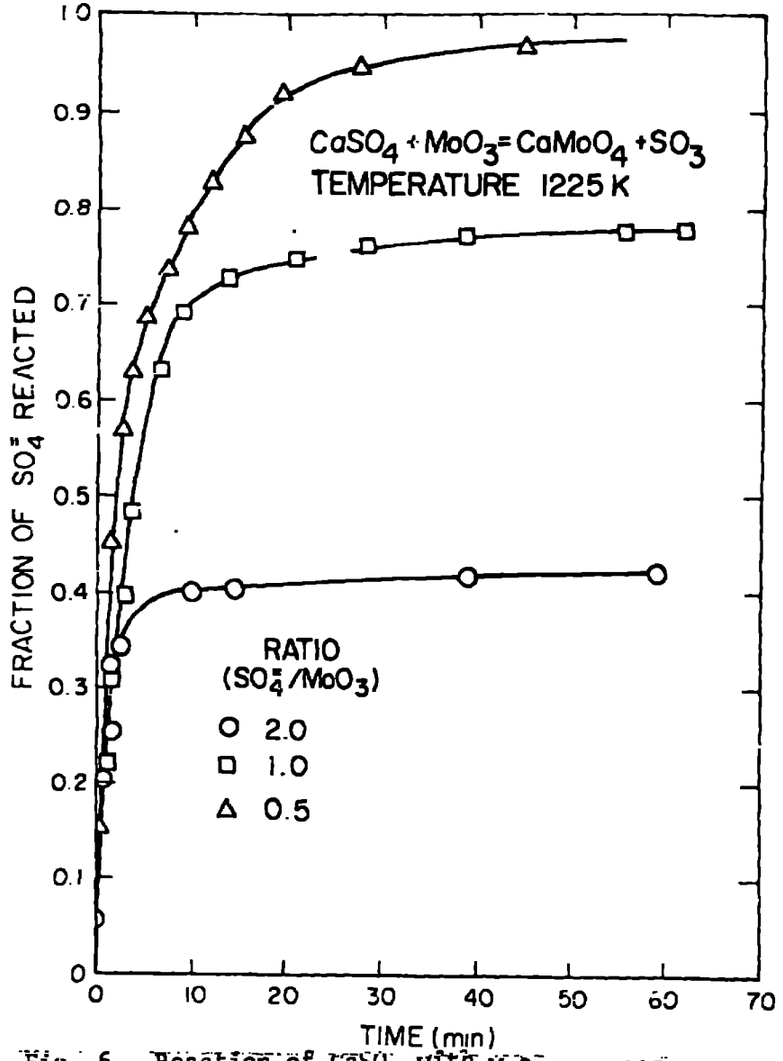

Fig. 6. Reaction of $CaSO_4$ with MoO_3 at 1225 K.

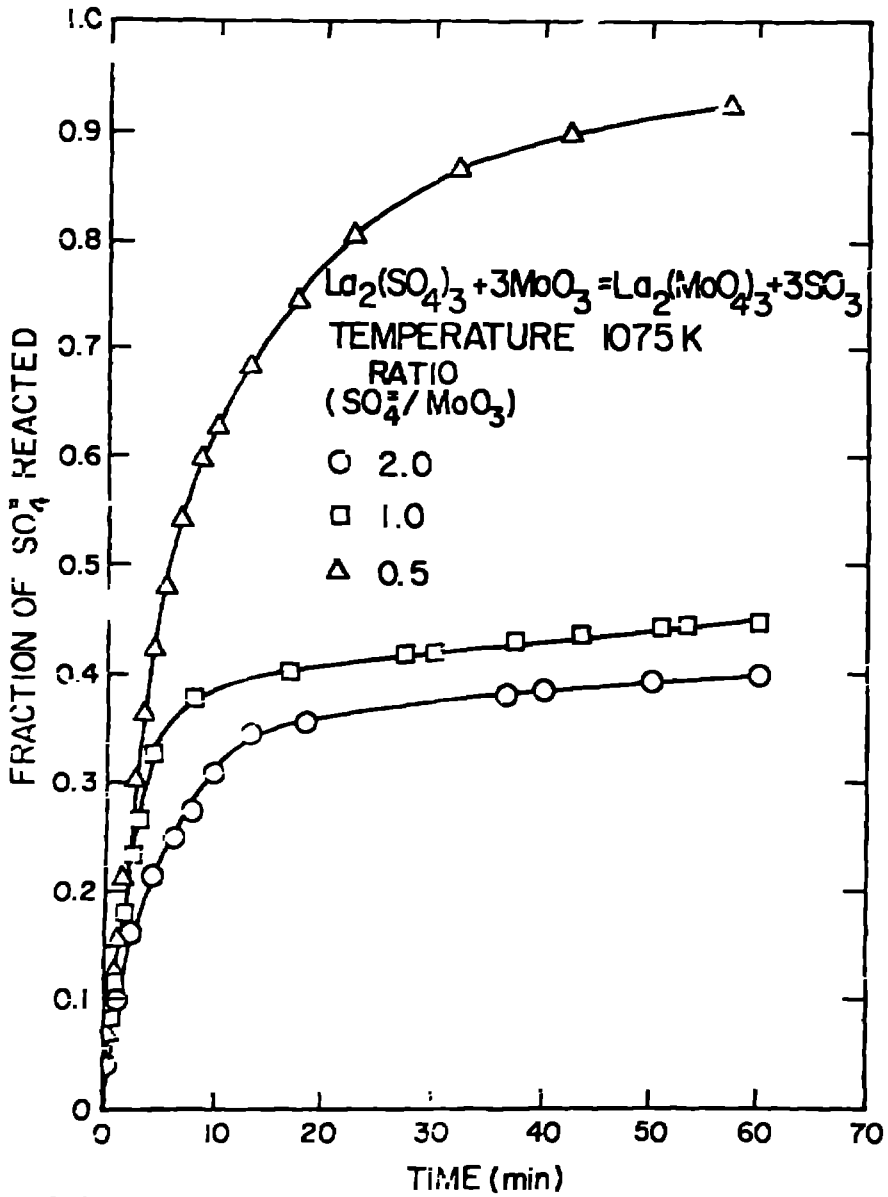

Fig. 7. Reaction of $La_2(SO_4)_3$ with MoO_3 at 1075 K.

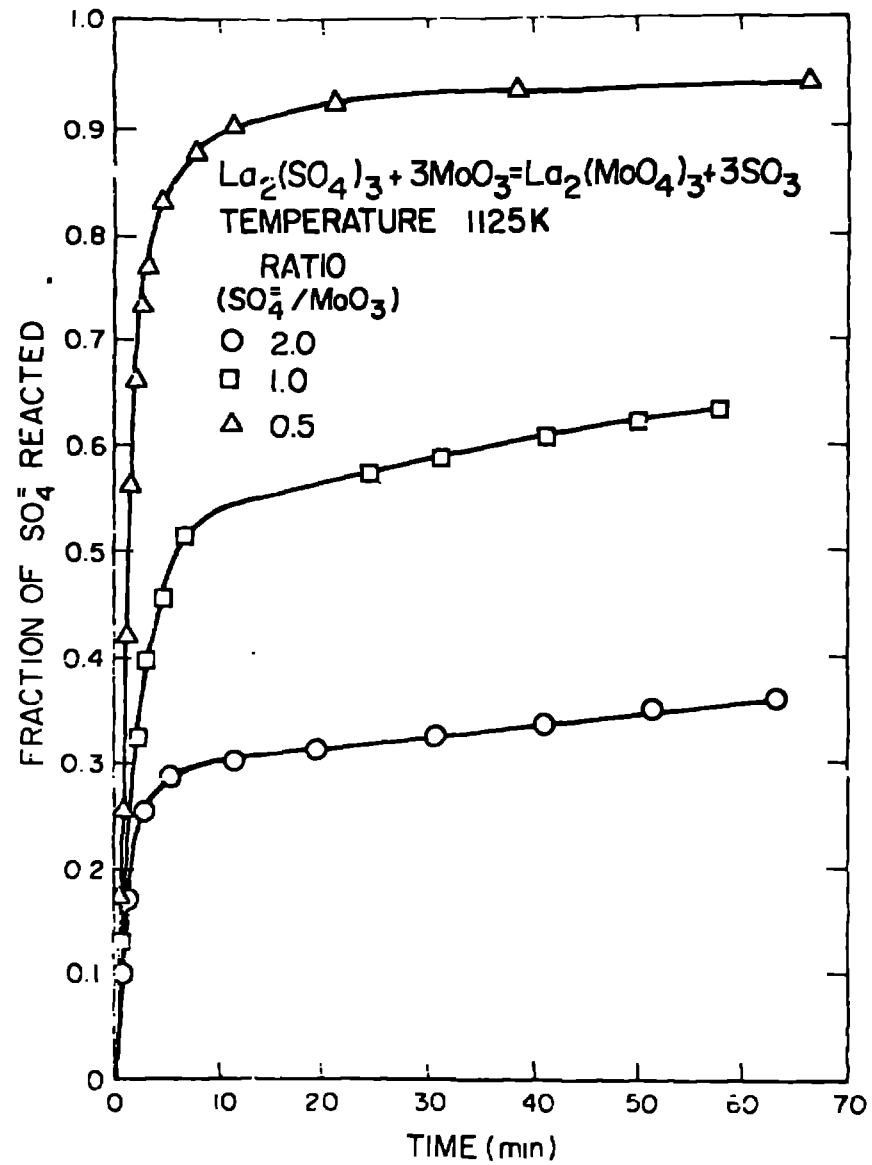

Fig. 8. Reaction of $La_2(SO_4)_3$ with MoO_3 at 1125 K.