SRI International

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

Technical Status Report

October 1979

HIGH TEMPERATURE CHEMISTRY OF HYDROGEN PRODUCTION
CYCLES

Prepared by: D. L. Hildenbrand

Contributions by: K. H. Lau
D. R. Knittel
D. L. Hildenbrand

Prepared for:

DEPARTMENT OF ENERGY
OFFICE OF BASIC ENERGY SCIENCES
Washington, D.C. 20545

Attention: Dr. F. D. Stevenson, Chief
Processes and Techniques Branch

DOE Contract Ey-76-C-03-0114 ⁵ ATO3-76 ER70129
Project Agreement 129

SRI Project PYU 6788

Approved:

R. W. Bartlett, Laboratory Director
Materials Research Laboratory

333 Ravenswood Ave. • Menlo Park, California 94025
(415) 326-6200 • Cable: SRI INTL MPK • TWX: 910-373-1246

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

This report summarizes technical progress for the year ending September 1979 on a DOE-sponsored program concerned with the thermochemistry and kinetics of metal sulfate decomposition processes. These processes are of technological interest in hydrogen thermochemical cycle development, in stack-gas cleanup, in coal-fired MHD power generation, and in hot corrosion technology. However, the thermochemical and, particularly, the kinetic features of most sulfate decomposition processes are not sufficiently well established for efficient process design. The program described here was undertaken to meet some of these needs.

During this period, studies of the catalyzed decomposition of MgSO_4 have been completed and a manuscript describing the work has been prepared. A number of metals and metal oxides were found to be effective catalysts for MgSO_4 decomposition. The most effective catalysts appear to be those with the highest affinity for oxygen chemisorption, and that are generally good oxidation catalysts. In addition, the effects of several catalyst parameters such as particle size and degree of loading were evaluated. All of the results are consistent with a mechanism that involves emission of SO_3 as the primary sulfate decomposition product, followed by conversion to the equilibrium $\text{SO}_2 + \text{O}_2$ composition in the presence of a suitable catalyst, with a substantial increase in pressure to approximately the equilibrium level. Thermochemical data for $\text{MgSO}_4(\text{s})$ have been derived from both the uncatalyzed process yielding SO_3 and the catalyzed process giving $\text{SO}_2 + \text{O}_2$ with good internal agreement.

ZnSO_4 , $\text{ZnO} \cdot 2\text{ZnSO}_4$, CuSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ were also found to yield SO_3 as the sole gaseous decomposition product, although SO_2 should predominate at equilibrium. A reliable mass spectrometric sampling procedure for SO_2 and SO_3 was developed that eliminated spurious SO_2^+ parent signals arising from secondary wall reactions of SO_3 . As with other metal sulfate decompositions, a distinct progression of observed pressure with

effusion orifice area indicates a significant kinetic barrier. Results obtained with the Zn, Cu, and Al sulfates are consistent with the decomposition mechanism postulated for MgSO_4 .

For ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$, derived "equilibrium" pressures indicate that the oxide and basic sulfate reaction products may be formed in a finely divided state of higher surface free energy and slightly lower thermodynamic stability than the normal macrocrystalline phases. None of the semiconducting oxides found to be catalytically effective with MgSO_4 had any detectable effect on the decomposition of ZnSO_4 or $\text{ZnO} \cdot 2\text{ZnSO}_4$, but Pt had a substantial catalytic effect on the basic sulfate and a moderate effect on ZnSO_4 . A sample of $\text{ZnO} \cdot 2\text{ZnSO}_4(\text{s})$ was prepared by thermal decomposition of ZnSO_4 and submitted to Lawrence Livermore Laboratory for measurement of high temperature heat content by drop calorimetry; a second sample has been prepared and submitted for low temperature and solution calorimetry at the Albany Metallurgy Research Center of the Bureau of Mines.

With CuSO_4 , the solid phase decomposition product was found to be CuO rather than the $\text{CuO} \cdot \text{CuSO}_4$ phase reported in static experiments, and the pressures for moderate to large orifices are converging on the SO_3 equilibrium pressure when extrapolated to zero orifice size. For the smallest orifice sizes, there appears to be a partial catalysis of SO_3 to SO_2 and O_2 by the CuO product.

INTRODUCTION

Metal sulfate chemistry is involved in several of the emerging energy technologies, e.g., thermochemical hydrogen generation, stack gas cleanup, and coal-fired MHD power generation. For efficient process design, it is necessary to have reliable kinetic and thermodynamic data for the process steps of interest, but such information is often not available for many metal sulfates of technological concern. In the research program described here, we are studying the kinetics and thermochemistry of metal sulfate decomposition/vaporization processes, a reaction step that is common to most of the technological applications. Our principal experimental techniques are the torsion-effusion method with simultaneous mass-effusion rate measurements for accurate determination of decomposition pressure and vapor molecular weight, and high temperature mass spectrometry for studies of vapor composition and reaction thermochemistry. The torsion-effusion method, in particular, has proven to be a very sensitive and effective technique for the study of dissociative vaporization processes such as those of the metal sulfates. Because it is dynamic in nature, the torsion method yields kinetic as well as thermochemical information.

In earlier studies of metal sulfates vaporizing solely by dissociation to the solid metal oxide and gaseous sulfur oxides, it has been observed that with the more stable sulfates such as CaSO_4 and BaSO_4 , studied at temperatures of 1200 K and above, gas phase equilibrium among the S-O species is readily attained.^{1,2} For CaSO_4 and BaSO_4 , the vapor composition and derived pressure data are in accord with the equilibrium vaporization process

under which conditions the equilibrium partial pressure of SO_2 exceeds that of SO_3 by several orders of magnitude. On the other hand, with

MgSO₄ at 950 to 1050 K, it was found that direct desorption of the non-equilibrium product SO₃ occurred preferentially under the dynamic effusion conditions,¹ and that the observed pressures were primarily characteristic of the process

rather than the thermodynamically-favored process denoted by reaction (1). Later studies on ZnSO₄(s) and ZnO·2ZnSO₄(s) at still lower temperatures of 800 to 850 K showed SO₃ again to be the dominant vaporization product, although at equilibrium the partial pressure of SO₂ exceeds that of SO₃ by more than an order of magnitude. The consequences of this phenomenon are of some significance, since in any practical process for the decomposition of metal sulfates carried out under dynamic conditions, the rate of the nonequilibrium decomposition process (2) will be substantially lower than that of reaction (1), and process efficiency will be affected adversely.

Subsequently it was found that the decomposition of MgSO₄ could be catalyzed by the addition of small amounts of certain metal oxides of the first transition series, leading to pressures and gas phase compositions in accord with reaction (1). Some of the platinum group metals, especially Pt itself, also were found to be effective catalysts for MgSO₄ decomposition. During this past year, we completed a systematic study of the catalyzed decomposition of MgSO₄ and investigated a number of the important catalytic parameters. These studies were then extended to the ZnSO₄ and ZnO·2ZnSO₄ systems for evaluation of possible catalytic activity there. New measurements on CuSO₄ and Al₂(SO₄)₃ were initiated. The combined results of these studies now begin to give a clearer picture of the mechanistic features of the metal sulfate dissociative vaporization process and of the kinetic limitations involved.

TECHNICAL PROGRESS

A. MgSO₄ Decomposition

The effects of certain metal and metal oxide additives on the thermal decomposition of MgSO₄ have been investigated by the torsion-effusion method in the range 900-1000 K. Although the pure material yields SO₃ as the sole gaseous decomposition product, metals such as Pt, Ru, and Ir, and the oxides Cr₂O₃, Mn₂O₃, Fe₂O₃, CoO, NiO, and CuO added at a level of a few mole % apparently catalyze the decomposition process, yielding pressures and effusing gas compositions consistent with the equilibrium process $\text{MgSO}_4(\text{s}) = \text{MgO}(\text{s}) + \text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$. Other additives (TiO₂, Y₂O₃, MgO, Al₂O₃, ZnO, and V₂O₄) were found to have little or no effect on MgSO₄ decomposition. The most effective catalysts seem to be those that have the greatest capacity for oxygen chemisorption and are generally good oxidation catalysts. Several of the catalyst parameters such as particle size and degree of loading have been investigated. All of the various results are consistent with a mechanism in which evolution of SO₃ is the primary step in the decomposition, and the additive simply catalyzes the gas phase conversion of SO₃ to SO₂ and O₂. The catalyzed and uncatalyzed decomposition pressure data are in agreement with a value of -310.2 ± 1.0 kcal/mol for the standard enthalpy of formation of MgSO₄(s) at 298 K.

A manuscript describing this work has been prepared and is being submitted for publication.

B. Decomposition of ZnSO₄ and ZnO·2ZnSO₄

Torsion effusion decomposition pressure measurements on ZnSO₄ and ZnO·2ZnSO₄ have now been extended down to an orifice size of 0.048 cm diameter, using a newly constructed cell. The measurements on both substances now cover a range of orifice sizes from 0.200 to 0.048 cm diameter,

and they show the decrease in steady state pressure with increasing orifice area found for the other sulfates that is characteristic of kinetically limited vaporization processes. Vapor molecular weight measurements, examination of the vapor by mass spectrometry, and analysis of effusion cell residues establish that the corresponding vaporization processes are

and

When compared with equilibrium data derived from EMF⁴ and static pressure⁵ measurements, our zero orifice-size extrapolated pressures are low by about a factor of three to five. This discrepancy corresponds to a defect of only about 1.5 to 2.0 kcal/mol in the reaction enthalpy change, and could readily be accounted for by the formation of oxide or mixed oxide product in finely divided form of correspondingly high surface free energy. A similar effect was noted with the MgO product of the MgSO_4 decomposition,¹ and it may be common to other sulfate decomposition processes.

The final analysis with the small orifice results leads to the SO_3 pressure ratio $P_4/P_3 \cong 15$ and the Gibbs energy change $\Delta G^\circ/T \cong -3.5$ cal/deg mol for the reaction

at 800 K, essentially the same as that reported earlier from the less complete orifice data. More complete analysis of the results requires standard enthalpy and entropy data on the basic sulfate. We have arranged for the necessary calorimetric measurements, to be carried out at the Albany Metallurgy Research Center of the Bureau of Mines, and have submitted a sample of $\text{ZnO} \cdot 2\text{ZnSO}_4(\text{s})$ prepared by slow thermal decomposition of ZnSO_4 . A smaller sample was prepared earlier and submitted to the

Lawrence Livermore Laboratory for determination of high temperature heat content by drop calorimetry.

None of the metal oxides found to be effective catalysts for MgSO_4 decomposition were found to have a detectable effect on the thermal decomposition of ZnSO_4 or $\text{ZnO} \cdot 2\text{ZnSO}_4$. This may result from the reduced mobility of defects in the semiconducting oxide additives at the lower temperatures of the ZnSO_4 and basic sulfate studies, although in one set of experiments with Cr_2O_3 in $\text{ZnO} \cdot 2\text{ZnSO}_4$, no effect was noted when the pressure was pushed beyond the molecular flow range and into the temperature regime of effective catalysis for MgSO_4 . On the other hand, Pt at the same 4 mol % level led to greater than a factor of ten increase in the $\text{ZnO} \cdot 2\text{ZnSO}_4(\text{s})$ decomposition pressure at 760 to 810 K and a shift in effusing gas composition from SO_3 to $\text{SO}_2 + 1/2 \text{O}_2$. With ZnSO_4 in this same temperature range, however, the catalytic activity of Pt was lower and somewhat erratic, amounting at most to a pressure increase by about a factor of five. Again, vapor molecular weights of 51 ± 2 were obtained with the ZnSO_4 - Pt combination, showing a shift to the $\text{SO}_2 + 1/2 \text{O}_2$ composition. It is significant that the thermal decomposition of $\text{ZnO} \cdot 2\text{ZnSO}_4$ and, to some extent, ZnSO_4 can be catalyzed by Pt, even though none of the oxides appear to be effective. The results indicate that the 750 to 800 K regime may be bordering on the temperature threshold of catalytic activity for SO_3 reduction by these materials. Therefore, it would be worthwhile to investigate the effect of temperature on the catalytic reduction of gaseous SO_3 directly, rather than as the second step of a metal sulfate decomposition.

C. Decomposition of CuSO_4

The thermal decomposition of cupric sulfate, CuSO_4 , previously has been studied in detail only by static methods. This substance is of interest in that it has a lower thermal stability than many other sulfates, and the oxide products CuO and Cu_2O are efficient catalysts for SO_3 reduction at higher temperatures. It is reported that CuSO_4 decomposes through an intermediate basic sulfate $\text{CuO} \cdot \text{CuSO}_4(\text{s})$.

To date, effusion studies on $\text{CuSO}_4(\text{s})$ have been carried out over a range of effusion orifice sizes, and vapor composition has been determined by mass spectrometry and vapor molecular weight measurements. Thus far, SO_3 is the only detectable vaporization product for all but the smallest effusion orifice of 0.048 cm diameter; the mass spectrometric analysis was quite clear on this point. And, contrary to the results of the static pressure⁶ and EMF⁴ investigations carried out at somewhat higher temperatures, CuO rather than $\text{CuO} \cdot \text{CuSO}_4$ was the product phase identified by X-ray diffraction analysis of cell residues. Under the dynamic conditions of the effusion process, decomposition proceeds by way of the reaction.

over the range 680 to 770 K. As with all the other sulfates studied, the observed pressures show a distinct progression with orifice size, indicating a kinetic barrier to the decomposition process. However, the pressures obtained with the larger effusion orifices seem to be converging on the equilibrium pressure of Reaction (7), as calculated from calorimetric data.⁷ The mass spectrometric second law study of the SO_3^+ intensity yielded a slope enthalpy of 49.8 kcal/mole at 700 K, compared to the equilibrium value⁷ of 50.8 kcal/mole for Reaction (7). With the smallest effusion orifice, vapor molecular weights of 70 ± 2 and observed pressures slightly higher than the calculated SO_3 equilibrium values indicate a small amount of SO_2 in the effusing gas and a shift toward the overall equilibrium composition at which $P(\text{SO}_2)/P(\text{SO}_3) \cong 10$. This effect is similar to that observed with MgSO_4 ,¹ and may indicate some slight catalytic reduction of SO_3 by the product oxide CuO as the system approaches zero orifices area. Again, the results indicate that kinetic effects are likely to be significant in a CuSO_4 decomposition process carried out on a practical scale.

D. Decomposition of $\text{Al}_2(\text{SO}_4)_3$; Mass Spectrometric
Detection of SO_2 and SO_3

With all of the pure metal sulfates decomposing below 1000 K we have consistently observed SO_3 rather than SO_2 as the sole gaseous product, although the equilibrium ratio $P(\text{SO}_2)/P(\text{SO}_3)$ is > 1 for temperatures above 600 K. In contrast to these observations, Knutsen and Searcy⁸ report that mass spectrometric analysis of the vapor effusing from a cell containing $\text{Al}_2(\text{SO}_4)_3$ at 673 K shows the attainment of SO_2 - SO_3 gaseous equilibrium, with $P(\text{SO}_2) \cong P(\text{SO}_3)$ at several different orifice sizes. This is an important point since it represents a major departure from the behavior observed with other low temperature sulfate decompositions (MgSO_4 , ZnSO_4 , $\text{ZnO} \cdot 2\text{ZnSO}_4$, CuSO_4), and may signify a different decomposition mechanism.

Although we had not intended originally to study $\text{Al}_2(\text{SO}_4)_3$, it seemed important to check the findings of Knutsen and Searcy. A vacuum dehydrated sample of $\text{Al}_2(\text{SO}_4)_3$ was placed in an alumina effusion cell and the composition of the effusing vapor was determined by high temperature mass spectrometry. Both SO_2^+ and SO_3^+ parent ion signals were observed at about 700 K, but only the SO_3^+ signal showed the characteristic sharp response to movement of the neutral beam defining slit. The results show that only SO_3 is present in the cell beam, and that the SO_2 observed is a background gas, most likely the secondary product of the reaction of SO_3 with metal beam source components. We conclude that the earlier report⁸ of equilibrium decomposition of $\text{Al}_2(\text{SO}_4)_3$ is in error because of beam sampling difficulties, and that a mechanism involving emission of SO_3 as the primary decomposition product is consistent with our new measurements on this substance. The clarification of the mass spectrometric sampling and detection procedure is quite important, since elucidation of the mechanistic features is critically dependent on this information.

REFERENCES

1. K. H. Lau, D. Cubicciotti, and D. L. Hildenbrand, J. Chem. Phys. 66, 4532 (1977).
2. P. Mohazzabi and A. W. Searcy, J. Chem. Soc. Faraday Trans. I 72, 290 (1976).
3. D. L. Hildenbrand, Technical Status Report, "High Temperature Chemistry of Hydrogen Production Cycles," DOE Contract Ey-76-C-03-0115, Sept. 1978.
4. J. M. Skeaff and A. W. Espelund, Can. Met. Quart. 12, 445 (1973).
5. T. R. Ingraham and H. H. Kellogg, Trans. AIME 227, 1419 (1963).
6. T. R. Ingraham, Trans. AIME, 233, 359 (1965).
7. JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Govt. Printing Off., Wash., D.C., 1971.
8. G. F. Knutsen and A. W. Searcy, J. Electrochem. Soc. 125, 327 (1978).
9. K. H. Lau, D. Cubicciotti, and D. L. Hildenbrand, J. Electrochem. Soc. 126, 490 (1979).