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THE COMPOSITION OF THE EVOLVED GASES FROM THE THERMAL DECOMPOSITION OF CERTAIN METAL SULFATES

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ABSTRACT

By the use of TG–MS, the thermal dissociation of anhydrous $CuSO_4$ and $Al_2(SO_4)_3$ was found to proceed according to the reactions:

$$CuSO_4 \rightarrow CuO + SO_3$$

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$$

followed by the reactions:

$$SO_3 \rightleftharpoons SO_2 + \tfrac{1}{2}O_2$$

$$SO_2 \xrightarrow[\text{chamber}]{\text{ionization}} SO^+ + O^-$$

No SO_3 was indicated in the dissociation of alunite. The sulfate ion appears to dissociate by at least two different mechanisms although the parameter which controls the mechanisms has not been elucidated.

INTRODUCTION

Although the composition of the evolved gases formed during the thermal dissociation of metal sufates has been determined by a number of investigators, there are still many unresolved problems. Recent discussions in the literature illustrate the disagreement amongst the investigations not only concerning the evolved gas composition but also the reaction kinetics. The main controversy over the former is a result of the lack of experimental evidence for SO_3 in the mass spectrometry data. Johnson and Gallagher[1,2], studying the thermal dissociation of $Al_2(SO_4)_3$, maintain that the absence of the SO_3^+ species in the mass spectrum of the evolved gases does not preclude the possibility that SO_3 is the primary sulfur oxide involved in the dissociation reaction. On the other hand, Papazian et al.[3,4] suggest that since no

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SO_3^+ ion is detected and an inordinate quantity of SO_3^+ is observed in the mass spectra, the primary product is SO with sulfur dioxide (SO_2) formed as an association product on the surface of the solid residue.

Langer and Gohlke[5] studied the mass spectra of fuming sulfuric acid and the dissociation products of certain metal sulfates. They found that there was no ion molecule formed at $m/e = 80$ (i.e. SO_3^+), which is in disagreement with the work of Wendlandt and Southern[6].

In this investigation, the evolved gases from the thermal dissociation of $CuSO_4 \cdot 5H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$ and alunite were analyzed mass spectrometrically in order to qualitatively determine their composition. A computerized TG–MS system was used to obtain a complete mass spectrum (to $m/e = 100$) at 5°C intervals and to generate product gas evolution curves using all of these data points. These curves, which were obtained by introducing the evolved gases directly into the mass spectrometer ionization chamber with no intermediate trapping step, were used to deduce the mode of dissociation of the metal sulfates.

EXPERIMENTAL

Chemicals

The $CuSO_4 \cdot 5H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ used in this study were Baker Analyzed Reagent quality chemicals. The alunite was a sample from a deposit which has been reported in Arizona[7].

Thermal analyzer/mass spectrometer/computer system

This system has been described previously[7]. A heating rate of 6°C min^{-1} was used with a mass spectrometer scan rate of 1.2 min^{-1}.

RESULTS AND DISCUSSION

Gaseous products evolved during the thermal dissociation of $CuSO_4 \cdot 5H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, and alunite in vacuo were determined qualitatively through computer analysis of the mass spectra obtained at 50 sec intervals. Since the sulfur oxide gases formed in the dissociation of the sulfate radicals were of primary interest, peak intensities were measured as a function of temperature for m/e values of 80, 64, 48 and 32 corresponding to the ion molecules of SO_3, SO_2, SO and S or O_2, respectively. The total gas evolution curve and the water evolution curves were also obtained in some cases to aid in the interpretation of the dissociation processes. It should also be noted that each curve was individually normalized with the most intense peak adjusted to 100%. Therefore, comparisons of concentrations or quantities based on the relative peak amplitudes will not reflect the actual concentrations unless the peaks are part of the same evolved gas curve. No quantitative comparison of one gas evolution curve with another curve can be considered valid.

Gas evolution curves were obtained for each compound at mass spectrometer ionization potentials of 7 and 15 eV, but due to the normalization procedure, there was no significant difference between these data. However, there were differences in the relative peak intensities within each mass spectrum. Therefore, selected spectra were printed in normalized digital form for both ionization potentials to facilitate quantitative comparisons of peak intensities and ratios. The data and results obtained in this study are discussed for each compound individually.

$CuSO_4 \cdot 5H_2O$

The gas evolution curves for $CuSO_4 \cdot 5H_2O$ in vacuo are presented in Figs. 1 and 2. The water evolution curve in Fig. 1 confirms that the major portion of the hydrated water was lost between 100 and 300°C, although water remained in the system until the analysis was terminated at 1000°C. The appearance of water in the

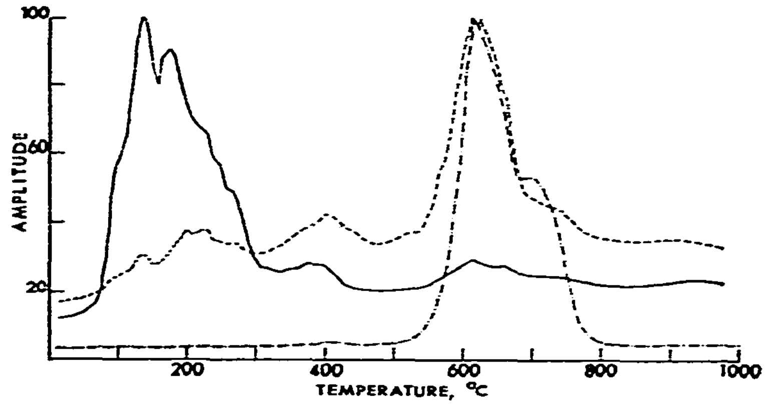

Fig. 1. Mass spectrometric evolved gas curves for $CuSO_4 \cdot 5H_2O$. (———) H_2O; (— — —) total gas pressure; (—·—·—) O_2.

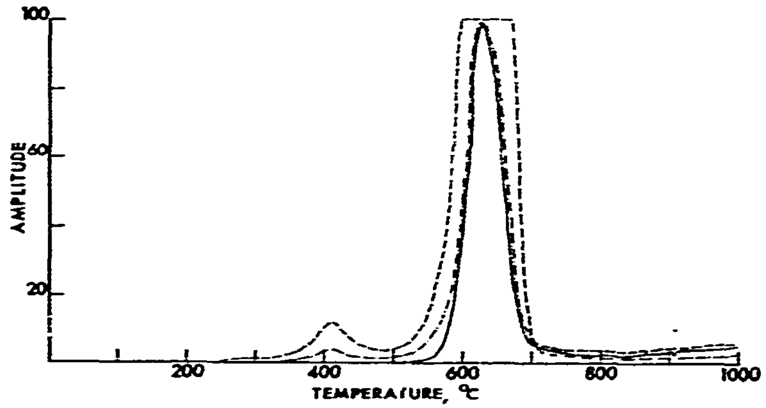

Fig. 2. Mass spectrometric evolved gas curves for $CuSO_4 \cdot 5H_2O$. (———) SO_3; (— — —) SO_2; (—·—·—) SO.

spectra above 300°C is due to its condensation in the cooler parts of the system and to a high vapor pressure which hinders removal by the vacuum system.

Dissociation of anhydrous $CuSO_4$ begins at about 500°C although traces of some sulfur oxides are detectable at lower temperatures. Sulfur dioxide first appears at about 250 and sulfur monoxide at 350°C, as shown in Fig. 2. During this interval preceding the major dissociation process, sulfur dioxide is probably the primary gaseous evolution product with the sulfur monoxide being formed in the ionization chamber as a fragmentation product. In the 250 to 350°C region, the quantity of SO_2 was so minute that the SO fragment was produced in concentrations too small to be detected. Sulfur trioxide could also have been present in quantities too small to be detected in the 250 to 500°C region.

Substantial quantities of SO_3, SO_2 and SO can be detected as $CuSO_4$ decomposed between 500 and 700°C. The SO_3 peaks at $m/e = 80$ were of sufficient intensity to produce a smooth evolution curve, as shown in Fig. 2. Since the SO_3, SO_2 and SO peaks coincide with the sulfate decomposition region, a plausible explanation for the composition of the decomposition products is:

$$CuSO_4 \rightarrow CuO + SO_3$$

$$SO_3 \rightleftharpoons SO_2 + \tfrac{1}{2}O_2$$

$$SO_2 \xrightarrow[\text{chamber}]{\text{ionization}} SO + O$$

The oxygen evolution curve (Fig. 1) also supports this mechanism. Intensity measurements of the P+2 isotope peaks were used to confirm that the $m/e = 80$, 64 and 48 peaks were definitely due to SO_3, SO_2 and SO, respectively.

The peak intensities of SO_3, SO_2, SO and O_2 were measured at selected temperatures at mass spectrometer ionization potentials of 70 and 15 V and are presented in Table 1. These data show that the SO_3 peak is small but significant over the region of the sulfate decomposition. Also, the SO_2/SO ratio is nearly constant at

TABLE 1

PEAK INTENSITIES FOR O_2, SO, SO_2 AND SO_3 FOR THE THERMAL DISSOCIATION OF $CuSO_4 \cdot 5H_2O$ IN VACUO

m/e	*Ionization voltage*					
	70 V				*15 V*	
	125°C	*215°*	*400°*	*630°*	*625°*	*650°*
32	6.93	10.43	25.36	44.98	17.76	18.79
48	<0.6	1.37	35.98	83.24	34.7	34.33
64	<0.6	3.83	100.0	100.0	100.0	100.0
80	<0.6	<0.6	<0.6	4.13	1.09	1.69

about 2.8 for 70 V and 2.9 for 15 V. Papazian et al.[3] obtained a constant SO_2/SO ratio of about 1. Since the ratio is constant, this implies that one species, the SO_2, is the precursor for the other, SO. The disagreement in the numerical values of the ratio is probably due to difference in the ionization efficiency of the individual mass spectrometers and to the experimental conditions such as temperature, pressure and so on. Also, the ratio will vary if the mass detectors are saturated by large ion currents, as in the spectrum at 630°C, 70 eV, which corresponds to the point of maximum sulfate dissociation. For this situation, relative peak heights are meaningless since the detector output is no longer proportional to the impinging ion current. This saturation effect is also responsible for the flattened SO_2 peak in Fig. 2.

$Al_2(SO_4)_3 \cdot 18H_2O$

The gas evolution curves for this compound are presented in Figs. 3 and 4.

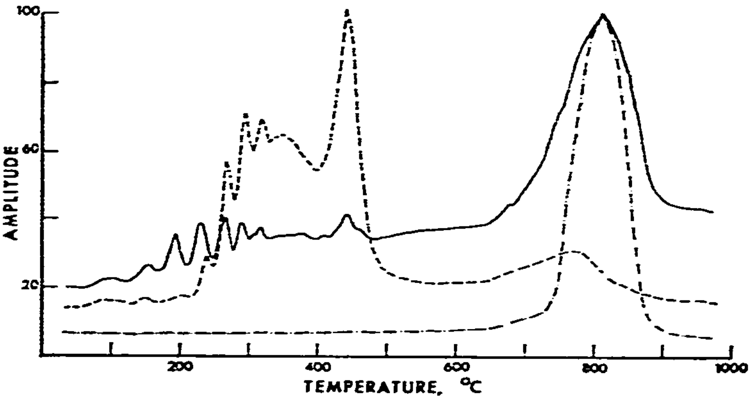

Fig. 3. Mass spectrometric evolved gas curves for $Al_2(SO_4)_3 \cdot 18H_2O$. (———) Total pressure; (— — —) H_2O; (—·—·—) O_2.

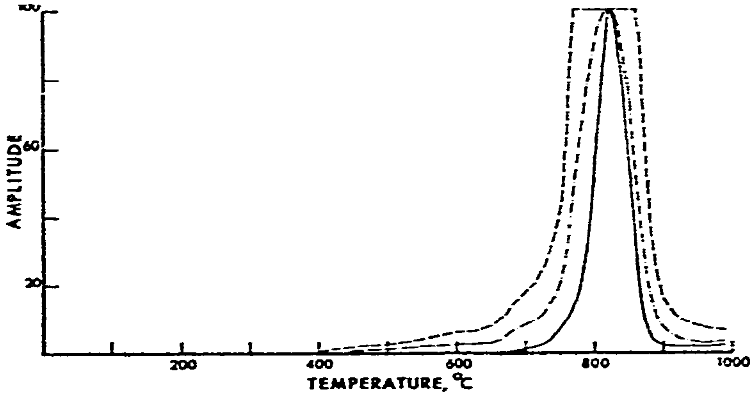

Fig. 4. Mass spectrometric evolved gas curves for $Al_2(SO_4)_3 \cdot 18H_2O$. (———) SO_3; (— — —) SO_2; (—·—·—) SO.

Although large quantities of water were lost during the initial pump-down, these curves show that a substantial amount of water remained strongly attached and was lost in the temperature region of 200 to 500°C. The dehydration is followed by the dissociation of $Al_2(SO_4)_3$ between 700 and 900°C. As in the $CuSO_4$ decomposition, the primary product appears to be SO_3 with SO_2, SO, and O_2 resulting from dissociation or fragmentation. These data agree with and support the following mechanism which has been proposed previously by Johnson and Gallagher[1]:

$$Al_2(SO_4)_3 \rightleftharpoons Al_2O_3+3SO_3$$

$$SO_3 \rightleftharpoons SO_2+\tfrac{1}{2}O_2$$

Intensity measurements of the $m/e = 80$ peak in selected spectra in the sulfate dissociation region yielded values ranging from 2.09 to 21.48. The lower values are probably more realistic since the high values were obtained during periods of detector saturation. However, in both cases the intensity was of sufficient amplitude to indicate that the peak actually existed and was not due to background noise. Also, the P+2 peak was observed in some cases. Previous investigations[3] indicated that the SO_3 peak will always be relatively small even when it is the parent product. The SO_2/SO ratios were approximately the same for the $Al_2(SO_4)_3$ spectra as for the $CuSO_4$ spectra.

Alunite

The gas evolution curves for alunite are presented in Fig. 5.

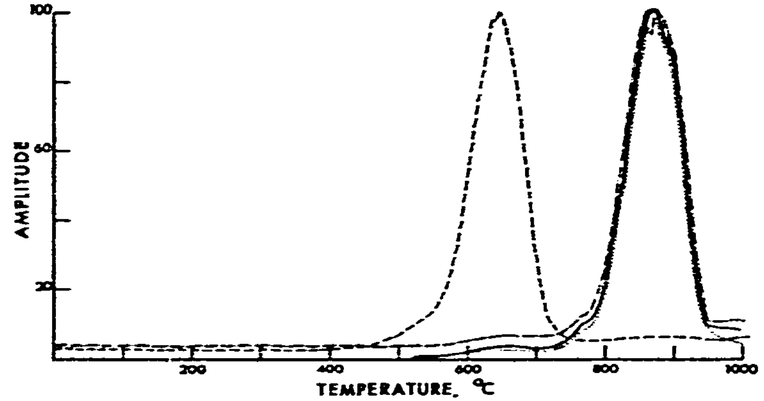

Fig. 5. Mass spectrometric evolved gas curves for alunite. (———) SO_2; (– – –) H_2O; (······) SO; (—·—·—) O_2.

Dissociation of the compound was initiated with the loss of water at 450°C. The remaining anhydrous material decomposed between 750 and 1000°C with the evolution of SO_2, SO and O_2. No SO_3 was detected at any point in the dissociation process. Since several runs were made and no $m/e = 80$ peak appeared in any of the spectra, it seems unlikely that SO_3 was released as a major decomposition product. The crystal structure of alunite may influence the sulfate decomposition by making other modes of dissociation more energetically favorable. No dissociation mechanism can be suggested from the data available. The primary evolution product could be either SO_2 or SO. The SO_2/SO ratio had a smaller numerical value than for the other sulfates and was not a constant. This ratio had values ranging from 2.5 to 0.2.

CONCLUSIONS

Mass spectrometric analysis of the evolved gases indicates that the thermal dissociation reactions for anhydrous $CuSO_4$ and $Al_2(SO_4)_3$ are as follows:

$$CuSO_4 \rightarrow CuO + SO_3$$

and

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$$

These reactions are followed by the dissociation reactions

$$SO_3 \rightleftarrows SO_2 + \tfrac{1}{2}O_2$$

$$SO_2 \xrightarrow[\text{chamber}]{\text{ionization}} SO^+ + O^-$$

The SO_3 peak was well resolved during all runs for both compounds.

The thermal dissociation of alunite was found to produce a different mixture of gaseous evolution products. No SO_3 peak could be detected in any mass spectra of gases evolved from this compound. Since $CuSO_4$ and $Al_2(SO_4)_3$ demonstrated that SO_3 could be detected when it was present in the system, it is unlikely that SO_3 is a decomposition product of alunite. Also, the large increase in the amplitude of the $m/e = 48$ peak, corresponding to SO, and the variable SO_2/SO ratio seem to indicate a dissociation process which is different from that of $CuSO_4$ and $Al_2(SO_4)_3$.

The thermal dissociation of the sulfate radical seems to occur through two or more different mechanisms. The parameters, which influence the mechanism preferred for a particular compound, have not been determined. However, it was established that one dissociation mechanism produces SO_3, SO_2 and SO while another produces only SO_2 and SO.

ACKNOWLEDGEMENT

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REFERENCES

1 D. W. Johnson and P. K. Gallagher, *J. Amer. Ceram. Soc.*, 54 (1971) 461.
2 D. W. Johnson and P. K. Gallagher, *Thermochim. Acta*, 6 (1973) 333.
3 H. A. Papazian, P. J. Pizzolato and R. R. Orrell, *Thermochim. Acta*, 4 (1972) 97.
4 H. A. Papazian, P. J. Pizzolato and R. R. Orrell, *Thermochim. Acta*, 6 (1973) 337.
5 H. G. Langer and R. S. Gohlke, in W. Lodding (Ed.), *Gas Effluent Analysis*, M. Dekker, New York, 1967, Ch. 3.
6 W. W. Wendlandt and T. M. Southern, *Anal. Chim. Acta*, 32 (1965) 405.
7 E. K. Gibson, *Thermochim. Acta*, 5 (1973) 243.