gested that this quenching takes place by metal ions situated at any of the 6 nearest phosphate groups to ethidium bromide excited state. The 6 nearest phosphate groups to intercalated ethidium bromide are the 2 adjacent groups and the 4 groups one base pair away. The distance between the ethidium bromide and a metal ion at a phosphate group one base pair away is roughly 1 nm, if we take the radius of the helix as 1 nm and the base pair separation as 0.34 nm. Thus we have electron transfer across this distance with a rate of ca.  $2 \times 10^8 \text{ s}^{-1}$ . Again this must be taken as an approximation. In fact there is a tendency for the rates to increase in the order Cu<sup>2+</sup> < Co<sup>2+</sup> < Ni<sup>2+</sup>.

#### Conclusion

For the systems we have studied, we believe we have demonstrated that fluorescence quenching techniques may yield useful information. We have given evidence that under our conditions the majority of metal ions are associated with DNA, and there is an equilibrium between metal bound at the phosphate groups and metal mobile around the helix. We have used our results to place the three metal ions studied in order of increasing mobility as  $Cu^{2+} < Ni^{2+} < Co^{2+}$  and have estimated that the mobility of  $Co^{2+}$ , in DNA, under the stated conditions of salt concentration, is a factor of ca. 20 less than its mobility in water. We also conclude that rapid ca.  $2 \times 10^8 \text{ s}^{-1}$  quenching can occur from metal ions bound to phosphate groups one base their away from intercalated ethidium bromide, a distance of roughly 1 nm.

The equilibrium we are studying may be that between "site bound" and "territorially bound" metal ions as given by polyelectrolyte theory. If so our results suggest a significant degree of site binding for  $Ni^{2+}$  and particularly for  $Cu^{2+}$ . Although this is in contradiction to earlier measurements we would point out that our technique allows for sensitive determination of fast equilibria between the two metal ion populations.

If we convert our results into a "base to base hopping frequency" in the manner of Prusik and Geacintov<sup>2c</sup> this must be somewhere between the lifetime of unquenched ethidium bromide excited state, in order to account for quenching of the slower fluorescence component, and the rate of decay of the fast component, to account for biphasic decay. These considerations give this frequency a value between  $4 \times 10^7$  and  $2 \times 10^8$  s<sup>-1</sup> for each metal studied, at least a factor of 400 greater than the lower limit given previously for Mn<sup>2+</sup> by the above authors.

In the quenching experiments of Baguley and Le Bret,<sup>2f</sup> double-exponential behavior was observed but the slower component of fluorescence decayed at the same rate as the fluorescence in the absence of quencher. With respect to our model we suggest that their quenchers are totally immobile on the time scale of ethidium fluorescence.

Finally we are aware that we have tried throughout to simplify a complex system. For example, we have not considered structural effects on DNA due to salt concentration. However, we feel that our current model explains the data and will help us to predict the behavior of other metal ions and fluorescence probes in the DNA system.

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# GENERAL PHYSICAL CHEMISTRY

### Effusion Studies of the Decomposition of Zinc Sulfate and Zinc Oxysulfate

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The torsion-effusion method has been used to measure the  $SO_3$  decomposition pressure over the crystalline solids  $ZnSO_4$ and  $ZnO\cdot 2ZnSO_4$  in the range of about 800 to 900 K.  $SO_3$  is the only detectable vapor species under these conditions. Vapor composition was verified by mass spectrometry and by molecular weights obtained from simultaneous torsion and mass-loss effusion measurements. The vaporization process is kinetically limited in two respects, since  $SO_2$  and  $O_2$  are the dominant gaseous products at equilibrium and since the  $SO_3$  effusion pressures show a pronounced dependence on orifice size. "Equilibrium"  $SO_3$  pressures over both  $ZnSO_4$  and  $ZnO\cdot ZnSO_4$ , derived by extrapolation of steady-state pressures to zero orifice area, are more than a factor of five lower than values calculated from established thermodynamic data, indicating the likelihood that the product solid phases are formed in a finely divided metastable condition. Addition of a few mole percent of Pt powder to  $ZnO\cdot 2ZnO_4$  led to a dramatic pressure increase and to effusing gas compositions consistent with decomposition to  $SO_2$ and  $O_2$ , while for  $ZnSO_4$  the effusing gas was converted to  $SO_2$  and  $O_2$  but the pressure increase was smaller and not entirely reproducible. The mechanistic implications of these results and correlations with other sulfate studies are discussed.

#### Introduction

Previous studies<sup>1</sup> of the decomposition pressure of  $MgSO_4$  at about 1000 K by the effusion method have shown that gross departures from chemical equilibrium are observed under these

dynamic conditions. In particular,  $SO_3$  is the sole gaseous decomposition product for moderate to large effusion orifices, whereas  $SO_2$  and  $O_2$  are the dominant equilibrium products in this system, with the equilibrium pressure ratio  $[P(SO_2)/P(SO_3)]$  $\simeq 100$  in the range of our measurements. It was also found that several metal and metal oxide additives are effective catalysts for the MgSO<sub>4</sub> decomposition, leading to substantial increases in observed pressure, and conversion of gaseous products to SO<sub>2</sub> and

<sup>(1)</sup> Lau, K. H.; Cubicciotti, D.; Hildenbrand, D. L. J. Chem. Phys. 1977, 66, 4532.

 $O_{2}$ .<sup>2</sup> Additionally, the catalytic activity of a number of these metals and oxides for reduction of  $SO_3$  to  $SO_2$  in the absence of condensed metal sulfate phases has been investigated;<sup>3</sup> as expected, each of the additives found to be an effective catalyst for MgSO<sub>4</sub> decomposition was likewise effective for SO<sub>3</sub> reduction, although there was a considerable spread in the threshold temperatures for catalytic activity. In the SO<sub>3</sub> reduction studies, Pt powder proved to be one of the most effective and reproducible catalysts, with one of the lowest threshold temperatures.

We felt that it would be illustrative to examine other sulfate systems in the same way to obtain a broader view of sulfate decomposition mechanisms and the related kinetic limitations. The zinc sulfate system is of interest in this regard in that decomposition proceeds in two well-defined steps, first from ZnSO<sub>4</sub> to the oxysulfate  $ZnO-2ZnSO_4$ , and then on to ZnO. Because of higher dissociation pressures, the zinc sulfates are studied some 150-200 K lower in temperature than MgSO<sub>4</sub>, and this may show up some additional kinetic effects. Another important factor here is that the thermodynamic properties of the condensed phasese  $ZnSO_4(s)$ ,  $ZnO-2ZnSO_4(s)$ , and ZnO(s) are known with relatively good accuracy from both heat capacity and reaction calorimetry,<sup>4-7</sup> so that reliable equilibrium dissociation pressures can be calculated. In addition, the dissociation equilibria of ZnSO<sub>4</sub> and ZnO-2ZnSO<sub>4</sub> have been studied by a static pressure method<sup>8</sup> and by an EMF method.<sup>9,10</sup> Comparison with established equilibrium data are useful in indicating possible kinetic barriers to the decomposition processes that would be manifested in the effusion pressure data. Typically, the observed pressure of a kinetically limited vaporization or decomposition process exhibits a marked dependence on effusion orifice area, but it is possible to derive equilibrium pressures by extrapolation to zero orifice area. However, there may be yet other factors such as small particle size or metastability of product phases that complicate the comparison with known equilibrium pressures.

In this paper we report dissociation pressures and vapor molecular weights of the zinc sulfates determined by the torsioneffusion method, along with vapor characterization by mass spectrometry. The results are discussed in terms of mechanistic aspects of the decomposition processes.

#### **Experimental Section**

Anhydrous ZnSO<sub>4</sub> was prepared by dehydration of reagent grade ZnSO<sub>4</sub>·7H<sub>2</sub>O in a stream of argon at 655 K; the X-ray diffraction pattern of the final product showed no trace of the heptahydrate. A sample of the oxysulfate  $ZnO-2ZnSO_4$  was prepared by slow decomposition of ZnSO<sub>4</sub> in air at 950 K, with intermittent monitoring of the ZnSO<sub>4</sub> content by X-ray diffraction. No trace of  $ZnSO_4$  could be detected in the final product, and the diffraction pattern of the resulting oxysulfate was in excellent agreement with published values.8 Several larger batches of ZnO-2ZnSO<sub>4</sub> were prepared by the same procedure and submitted for drop calorimetry,<sup>6</sup> solution calorimetry,<sup>7</sup> and low-temperature calorimetry.<sup>5</sup> Chemical analysis indicated an oxysulfate purity of better than 99.9%.

A description of the torsion-effusion system and associated microbalance has been given in an earlier paper on sulfate studies, along with a description of the experimental technique.<sup>1</sup> The torsion-effusion assembly is basically an effusion manometer, a device with which pressure is evaluated in terms of geometrical and mechanical factors of the system. Alumina effusion cells of

9) Flood, H.; Boye, N. C. Z. Elektrochem. 1962, 66, 184

TABLE I: Total Vapor Pressure above ZnSO4

<i>T</i> . K	$P_{\rm r}$ atm $\times 10^7$	М	T. K	$P \text{ atm} \times 10^7$	м	
	Cell 1			Cell 5		
7794	1 20		788.6	1 30		
788.9	1 99	76 1	784 1	1.82		
795 5	2 77	70.3	789.0	2 34	830	
796.4	2.91	80.2	793 7	2.54	05.7	
801.6	3 75	71.8	797 0	3 47	78.6	
803.6	4.14	76.3	800.0	4.02	823	
808.8	5.37	81.1	802.3	4.61	81.5	
809.2	5.34	83.2	804.8	5.09	78 7	
810.1	5.64	79.9	808.1	6.09	77.6	
log P	(atm) = 10.735 (=	$\pm 0.081$	log P	$(atm) = 10.695 (\pm 10.695)$	0.122)	
0-	- 13757 (±63)/7	r		$-13670 (\pm 96)/T$		
	Cell 2			Cell 3		
778.4	2.48		781.7	4.71	79.1	
781.4	2.88		786.7	6.10	79.8	
786.2	3.64	82.5	793.5	8.56	80.1	
793.2	5.18	82.4	796.6	9.93	82.5	
795.8	5.79		803.7	14.0	80.9	
800.4	7.33		808.4	17.7	77.9	
800.7	7.48		813.7	21.8	79.1	
802.7	8.29	79.8	815.0	24.1	77.7	
809.6	11.4	79.4	log P	$(atm) = 10.859 (\pm 0.00)$	0.122)	
810.5	12.0	76.1		$-13433 (\pm 98)/T$		
log P	$(atm) = 10.668 (= -13448 (\pm 52)/7$	±0.066)				
	Cell 7					
799.9	29.7					
802.9	34.7					
806.6	40.4					
809.7	47.0					
817.7	68.1					
821.3	79.5					
828.0	110					
832.3	132	81.2				
835.5	152	79.3				
$\log P$	(atm) = 11.104 (±	<b>E</b> 0.072)				
	$-13304 (\pm 59)/7$	- <u> </u>				
		orifice	2	$10^2 \sum_{i=1}^{n} fa_i$		
	cell	diameter, c	m²	cm <sup>2</sup>		
	7	0.0485		0.1301		
	3	0.1048		0.8708		
	2	0.1491		2.148		
5		0.1871		3.662		

the type described previously<sup>1</sup> were used in the present studies. The operation of the system was checked occasionally with the vapor pressure reference standard KCl; measured pressures are estimated to be accurate to within 5%. Molecular weights of effusing vapors were evaluated from simultaneous measurement of torsion pressures and mass effusion rates. For an effusing vapor containing more than one gasoue species, the molecular weight M is a weight average value defined by the relation

0.2096

$$M = (\sum m_i M_i^{-1/2})^{-2}$$
(1)

4.752

where  $m_i$  and  $M_i$  are the mass fraction and molecular weight of the *i* gaseous species. The magnetic-sector mass spectrometer<sup>11</sup> was used to examine the vapor effusing from  $ZnSO_4$ .

The platinum powder checked for catalytic activity was a -325 mesh sample from Western Gold and Platinum Co.; a few oxide powders used for the same purpose were reagent grade materials.

#### Results

1

ZnSO<sub>4</sub> Decomposition. Decomposition pressures obtained by the torsion method with five different effusion cells are listed in Table I. Orifice diameters ranged from about 0.05 to 0.21 cm, with a length of about 0.1 cm; cell constants are listed in Table I, including the total effective orifice area,  $\sum fa$ , where f, and a are the orifice force factor<sup>12</sup> and geometrical area, respectively.

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<sup>(12)</sup> Searcy, A. W.; Freeman, R. D. J. Am. Chem. Soc. 1954, 76, 5229.



Figure 1. Whitman-Motzfeldt plot for  $ZnSO_4$  decomposition pressures at 800 K.

Coefficients of the vapor pressure expression log P = A - (B/T) obtained by least-squares fitting are also included, along with the derived molecular weights, M, of the effusing vapor evaluated from simultaneous Knudsen and torsion measurements.<sup>1</sup> Pressures were steady and reproducible over the full range of the measurements, which generally covered less than 5% total decomposition.

As can be seen in Table I, the vapor molecular weights, M, averaged 77.4, 80.4, 80.0, 79.6, and 80.2 for the five different cells. These values are in close agreement with the molecular weight of SO<sub>3</sub> at 80.06. Analysis of the effusing vapor by mass spectrometry showed SO<sub>3</sub> to be the only detectable gaseous species, corroborating the molecular weight data. A calculation of the equilibrium composition in this system indicates that SO<sub>2</sub> and O<sub>2</sub> should be the dominant products, with  $P(SO_2)/P(SO_3) > 9$ , and M slightly above 54, in the temperature and pressure range of this effusion study. Clearly, the results indicate a major kinetic barrier to direct evolution of SO<sub>2</sub> and O<sub>2</sub> from the lattice.

As shown by the variation of steady-state pressure with effusion orifice size, there is also a substantial kinetic barrier to the SO<sub>3</sub> evolution step. A Whitman-Motzfeldt<sup>13-15</sup> hole-size plot of the pressure data from the five effusion cells is presented in Figure 1. The correlation of reciprocal pressure with effective orifice area is quite satisfactory, leading to an extrapolated zero hole-size "equilibrium" pressure of  $3.4 \times 10^{-6}$  atm at 800 K. At this temperature, the equilibrium constant for conversion of SO<sub>3</sub> to  $SO_2$  and  $O_2$  is 2.88 × 10<sup>-2.16</sup> The expected  $SO_2$  and  $O_2$  pressures under effusion conditions are  $3.2 \times 10^{-5}$  and  $1.1 \times 10^{-5}$  atm, respectively. If complete equilibration were achieved under our experimental conditions, we would expect to observe M = 56.4instead of about 80. Examination of cell residues by X-ray diffraction showed the oxysulfate  $ZnO-2ZnSO_4$  to be the only new phase present, so that the vaporization process can be expressed as

$$3ZnSO_4(s) = ZnO \cdot 2ZnSO_4(s) + SO_3(g)$$
(2)

Other values for the equilibrium SO<sub>3</sub> pressure over this two-phase system can be evaluated from emf measurements  $(11.0 \times 10^{-6}$  atm<sup>9</sup> and  $9.9 \times 10^{-6}$  atm<sup>10</sup>) and also from static pressure measurements of ZnSO<sub>4</sub> decomposition  $(15.9 \times 10^{-6} \text{ atm})$ ;<sup>8</sup> the direct pressure measurements<sup>8</sup> were extrapolated from results reported over the range 952 to 1122 K. Yet another value for the equilibrium  $P(SO_3)$  of reaction 2 at 800 K can be calculated from thermodynamic data obtained wholly from calorimetric measurements  $(19.5 \times 10^{-6} \text{ atm})$ .<sup>5</sup> It is difficult to put a reliable uncertainty on the calculated thermodynamic value, but it is supported by the emf and static pressure results,<sup>8-10</sup> which differ

TADIE	TT.	Tetel	17	D	- 1	7-0 37-04	2
IADLE	III:	10181	VADOR	Pressure	above	LOUIZED	J.

IADLE	II: TOTAL VAPOL	rressure	above ZhO	42LIISU4	
<i>T</i> , K	P, atm $\times 10^7$	М	<i>T</i> , K	$P$ , atm $\times 10^7$	М
	Cell 1			Cell 5	
829.5	1.12		799.8	0.30	
832.6	1.30		807.1	0.42	
839.3	1.76		819.0	0.74	
841.5	1.91		825.5	0.98	
844.9	2.25		831.4	1.31	
852.0	3.05	77.6	842.5	2.22	
854.1	3.34	80.5	844.5	2.33	
858.8	4.11		849.5	2.94	
log P (	(atm) = 9.538 (±	0.072)	log P (	atm) = 9.597 (±	0.083)
-	- 13676 (±275)/7	Γ	-	$-13701 (\pm 68)/T$	•
	Cell 2			Cell 3	
825.5	1.60		840.6	4.54	
833.7	2.33		844.8	5.36	
837.2	2.71		851.4	7.04	
845.7	3.89		857.2	9.02	
848.6	4.46		860.0	10.1	80.5
851.4	5.05		863.2	11.5	76.6
855.1	5.96		869.9	15.2	77.0
856.9	6.42	79.1	872.8	17.1	67.6
864.0	8.55		877.4	20.6	77.7
865.7	9.17	82.0	log P (	$atm) = 9.377 (\pm$	0.048)
log P (	$(atm) = 9.582 (\pm$	0.052)	-	$-13219 (\pm 42)/T$	•
-	$-13520 (\pm 44)/T$	•			
	Cell 7				
844.0	8.86				
851.8	13.2				
856.3	16.7				
860.1	19.9				
870.1	31.3				
874.1	35.3				
881.6	49.0	86.4			
885.3	59.3				
892.7	79.0				
$\log P$ (	(atm) = 11.205 (:	±0.20)			
$-14559 (\pm 173)/T$					

by less than a factor of two. Our value of  $P_{800}(SO_3)$  derived from the effusion measurements, however, lies almost a factor of six lower than the calculated thermodynamic result, making it obvious that there is a significant unknown factor affecting the interpretation of the effusion results.

Several runs were made with additions of  $Fe_2O_3$  and Pt powder at a level of a few mole percent to check for possible catalytic activity; both of these materials were found to be highly effective catalysts for MgSO<sub>4</sub> decomposition.<sup>17</sup> In the case of the ZnSO<sub>4</sub>, however,  $Fe_2SO_4$  addition had no detectable effect on decomposition pressure, while Pt yielded erratic and irreproducible pressure increases varying between factors of three to eight times that of the pure material. With the Pt addition, the molecular weight of the effusing vapor dropped to about 52, denoting a shift to the  $SO_2 + O_2$  composition.<sup>1</sup> An increase by about a factor of 20 in pressure would be expected for a fully effective catalyst that would convert reaction 2 to the dominant equilibrium process

$$3ZnSO_4(s) = ZnO \cdot 2ZnSO_4(s) + SO_2(g) + \frac{1}{2}O_2(g)$$
 (3)

Although there is definite evidence that dispersed Pt powder substantially increases the decomposition rate and steady-state effusion pressure of  $ZnSO_4$ , the effect was not explored further because of the difficulty in obtaining reproducible results.

In the course of the mass spectrometric analysis of the effusing vapor from  $ZnSO_4$ , the temperature dependence of the  $SO_3^+$  signal was determined at 17 temperatures over the range 671 to 775 K. Results in this instance were steady and reproducible, yielding the second-law slope heat of 251.1 kJ·mol<sup>-1</sup> at about 725 K, in accord with an average value of 250.9  $\pm$  6.2 kJ·mol<sup>-1</sup> derived from the vapor pressure coefficients in Table I. Both of these values are higher than the equilibrium enthalpy change for reaction 2 calculated from calorimetric data,<sup>5</sup> 232.5 kJ·mol<sup>-1</sup> at 800 K.

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Figure 2. Whitman-Motzfeldt plot for ZnO-2ZnSO<sub>4</sub> decomposition pressures at 800 K: □, pure ZnO·2ZnSO<sub>4</sub>; ◊, ZnO·2ZnSO<sub>4</sub> + 4 mol % Pt.

 $ZnO.2ZnSO_4$  Decomposition. An analogous set of torsioneffusion measurements was made on the oxysulfate ZnO-2ZnSO4 using the same five effusion cells, with the results shown in Table II. As expected, the observed torsion pressures were more than an order of magnitude lower than those of ZnSO<sub>4</sub>, but otherwise the behavior was very similar. Again the measured vapor molecular weights, M, which averaged 79.0, 80.6, 86.4, and 78.0, identify SO<sub>3</sub> as the effusing gaseous species rather than the equilibrium  $SO_2 + O_2$  mixture. The overall vaporization process is therefore taken to be

$$\frac{1}{2}ZnO\cdot 2ZnSO_4(s) = \frac{3}{2}ZnO(s) + SO_3(g)$$
 (4)

since ZnO(s) was identified in the cell residue from its X-ray diffraction pattern. While the pressure and molecular weight measurements with cells 1, 2, 3, and 5 were relatively steady and reproducible from day to day, the results with the smallest orifice (cell 7) showed an increase of about 50% in the observed pressures and a decrease in the molecular weights with time. Only the initial results when  $M \sim 80$  are reported.

Here, too, a significant variation of pressure with effusion orifice area was observed, showing again that the direct SO<sub>3</sub> vaporization process is retarded kinetically. From a Whitman-Motzfeldt<sup>13-15</sup> analysis of the data, shown plotted in Figure 2, the extrapolated pressure at zero hole size and 850 K is found to be  $1.29 \times 10^{-6}$ atm. This value derived from the effusion data is well below others for reaction 4 evaluated from emf data  $(6.2 \times 10^{-6} \text{ atm})$ ,<sup>10</sup> from the static pressure measurements  $(5.9 \times 10^{-6} \text{ atm})$ ,<sup>8</sup> and from thermodynamic calculations based on calorimetric data (6.7  $\times$ 10<sup>-6</sup> atm).<sup>5</sup> This comparison again suggests a major systematic difference between the results of the dynamic effusion measurements and the null or static equilibrium measurements.<sup>5,8,10</sup>

The effect of additions of a few mole percent of several potential catalytic additives on ZnO-2ZnSO4 decomposition was investigated.  $Cr_2O_3$  has no apparent effect on the decomposition pressure, while CuO yielded an increase by about a factor of two. With Pt powder at the 4 mol % level, however, the results were very striking, leading to increases in the total decomposition pressure by factors of 12 to 25, depending on effusion orifice size. In contrast to the erratic behavior observed with ZnSO<sub>4</sub>, the decomposition pressures of the Pt-catalyzed ZnO-2ZnSO<sub>4</sub> samples were entirely steady and reproducible. Results obtained at four different effusion orifice sizes are shown in Table III. Vapor molecular weights determined with three of the cells averaged 50.4, 53.2, and 55.4, clear evidence that the gas composition has shifted from SO<sub>3</sub> to SO<sub>2</sub> + 1/2O<sub>2</sub>; the calculated *M* for the latter is 54.6. The pressure data for the samples with Pt additive showed a very satisfactory correlation with orifice size, as seen in Figure 2.

In Table IV the pressures of pure and Pt-catalyzed ZnO- $2ZnSO_4$  are compared at 800 K; also shown is the ratio of the two pressures for each cell. This pressure ratio increases significantly with decreasing orifice size. Interestingly enough, the

TADLE III. TAAL V. -- -

IADLE	in: iotal vapo	or Pressure	above ZnC	J-22nSU4 (4 Wt %	PT)
<i>T</i> , K	P, atm $\times 10^7$	М	<i>T</i> , K	P, atm $\times 10^7$	М
	Cell 1			Cell 2	
763.8	0.648		767.6	1.46	
768.0	0.808		770.9	1.73	
770.5	0.880		774.4	2.03	
771.8	0.967		777.0	2.31	
777.7	1.32		779.2	2.58	
778.8	1.33		782.2	2.94	
782.7	1.55		786.5	3.62	
784.2	1.75		790.1	4.24	
789.6	2.29		793.1	4.90	
792.7	2.65		797.7	6.15	
796.2	3.11		803.6	8.19	
799.3	3.65	48.6	806.5	9.35	
803.6	4.52		808.7	10.3	
806.6	5.06		$\log P$ (	$atm) = 9.867 (\pm 0.000)$	).074)
807.0	5.14	52.2	-	$-12824 (\pm 59)/T$	,
807.5	5.36	50.3			
812.2	6.71			Cell 7	
$\log P$ (	atm) = 9.831 (±	0.109)	789.5	23.0	
-	$-13005 (\pm 88)/7$	r í	791.7	24.9	
			795.3	29.6	
	Cell 3		796.4	31.4	
771.7	3.22		797.7	32.8	
776.9	4.18		799.0	34.5	
779.8	4.66		801.9	40.1	
782.7	5.45		804.7	45.6	
784.0	5.80		805.3	47.4	
786.8	6.60		808.4	53.2	
788.8	7.21		814.0	68.3	
790.2	7.76		816.8	76.4	
793.9	9.28		819.6	84.3	
796.9	10.7		821.0	92.3	
799.7	12.1		823.2	98.1	
804.2	15.0		825.7	11.1	53.7
806.0	16.1	52.7	827.7	12.0	
808.1	17.9		829.9	13.3	57.0
810.5	19.8	51.8	830.5	13.5	
812.3	21.5	51.6	833.8	15.3	
813.8	23.0	54.5	$\log P$ (	$atm) = 9.992 (\pm 0)$	).066)
816.9	26.8	55.4	-	$-12342 (\pm 52)/T$	
$\log P$ (a	atm) = 10.101 (=	<b>⊧</b> 0.022)		·	
-	- 12808 (±39)/7	-			

TABLE IV: Comparison of ZnO-2ZnSO<sub>4</sub> Decomposition Pressures at 800 K with and without Catalyst

cell	$P(\text{uncat}) \times 10^{7,a} \text{ atm}$	$P(\text{cat}) \times 10^{7,b} \text{ atm}$	P(cat)/ P(uncat)	calcd equil ratio
equilibrium	1.12	33.0	29.5	37.2
7	1.02	36.7	36.0	38.4
3	0.71	12.3	17.3	43.3
2	0.48	6.9	14.4	49.4
1	0.28	3.8	13.6	59.1

<sup>a</sup> Without Pt additive. <sup>b</sup> With 4 mol % Pt additive. <sup>c</sup> Extrapolated by the Whitman-Motzfeldt method.

ratio of 36.0 at 800 K with the smallest orifice is quite close to the value of 38.4 calculated as the expected equilibrium pressure increase in shifting from reaction 4 to the reaction

$$\frac{1}{2}$$
ZnO·2ZnSO<sub>4</sub>(s) =  $\frac{3}{2}$ ZnO(s) + SO<sub>2</sub>(g) +  $\frac{1}{2}$ O<sub>2</sub>(g) (5)

This calculated pressure increase is that to be expected for conversion to the equilibrium gas composition from each steady-state  $SO_3$  pressure under effusion conditions. Observed ratios for the larger orifice cells were all substantially lower than those expected for equilibrium attainment, as appears reasonable for such a kinetically retarded vaporization process. The results with cell 7, which are shown by the Whitman-Motzfeldt analysis to lie close to the equilibrium values, strongly suggest that the Pt powder effectively catalyzes the full attainment of equilibrium in reaction

#### Discussion

It is quite evident from the vapor composition and effusion hole-size results that both sulfate decomposition processes are

TABLE V: Comparison of Measured and Derived SO<sub>3</sub> Equilibrium Pressures of Zinc Sulfates

investigators	method	$\frac{\text{ZnSO}_{4}}{P_{800}(\text{SO}_{3}), \text{ atm}}$	$ZnO-2ZnSO_4$ , $P_{850}(SO_3)$ , atm
Flood and Boye <sup>a</sup>	emf	$11.0 \times 10^{-6}$	
Skeaff and Espelund <sup>b</sup>	emf	9.9 × 10⁻⁴	$6.2 \times 10^{-6}$
Ingraham and Kellogg <sup>c</sup>	static press.	15.9 × 10 <sup>-6</sup>	5.9 × 10 <sup>-6</sup>
Beyer <sup>d</sup>	thermodyn data	$19.5 \times 10^{-6}$	6.7 × 10⁻⁴
this work <sup>e</sup>	effusion	$3.4 \times 10^{-6}$	$1.3 \times 10^{-6}$

<sup>a</sup>Reference 9. <sup>b</sup>Reference 10. <sup>c</sup>Reference 8. <sup>d</sup>Reference 5. <sup>e</sup>Derived from Whitman-Motzfeldt extrapolation.

severely hindered kinetically. The initial decomposition step in the crystal yields gaseous SO<sub>3</sub> rather than the dominant equilibrium products  $SO_2$  and  $O_2$ , but even the  $SO_3$  evolution process exhibits a substantial kinetic barrier. As noted earlier,<sup>1</sup> this could well arise from the major orientational changes associated with conversion of the tetrahedral lattice sulfate ion to the planar symmetric SO<sub>3</sub> gas molecule. Because of this relatively large kinetic barrier, the nature of the sulfate ion decomposition process is highly temperature dependent. Whereas effusion studies of BaSO<sub>4</sub> decomposition near 1500  $K^{17}$  and CaSO<sub>4</sub> at about 1200  $K^1$  both show direct decomposition to gaseous SO<sub>2</sub> and O<sub>2</sub>, similar studies of MgSO<sub>4</sub> near 1000 K<sup>1</sup> indicate direct desorption of SO<sub>3</sub> from the solid for large ratios of effusion orifice area to cell cross sectional area a/A, with a partial transition to SO<sub>2</sub> and O<sub>2</sub> for smaller values of a/A. For MgSO<sub>4</sub>, this type of behavior yielded an unusual Whitman-Motzfeldt plot showing two distinctly different slopes as the steady-state pressures approached first the  $SO_3$  equilibrium value and then that for  $SO_2$  and  $O_2$ .

The effusion results from this research on ZnSO<sub>4</sub> and ZnO- $2ZnSO_4$  at 800-900 K show yet another type of behavior, with SO<sub>3</sub> as the only detectable gaseous decomposition product over the same range of orifice sizes used in the MgSO<sub>4</sub> work. On this basis, one would expect that other metal sulfates decomposing at still lower temperatures would also yield only SO<sub>3</sub>. In contrast to this trend, Knutsen and Searcy<sup>18</sup> reported the detection of equilibrium abundances of  $SO_3$  and  $SO_2$  over  $Al_2(SO_4)_3$  at 625 to 725 K, as observed by mass spectrometry. Because of this unexpected result, we reinvestigated Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> decomposition by mass spectrometry and found only SO3 in the effusing molecular beam.<sup>19</sup> Although a parent SO<sub>2</sub><sup>+</sup> signal was indeed observed, the profile of the neutral beam yielding this signal was very much broader than the typical effusion beam profile, indicating that parent  $SO_2^+$  did not originate in the cell. Related studies<sup>3</sup> have clearly indicated to us that SO3 is easily reduced to SO2 on collision with metal surfaces, so that the SO<sub>2</sub><sup>+</sup> signals observed by Knutsen and Searcy<sup>18</sup> probably arose from secondary reaction of SO<sub>3</sub> with some part of the ion source structure. Quantitative measurement of  $SO_2$  in the presence of  $SO_3$  is clearly a difficult operation, and our experience has been that neutral beam profiles determined with the movable beam defining slit provide the surest means for differentiating between primary and secondary  $SO_2$  signals. The weight of evidence to date favors the concept that attainment of SO<sub>3</sub>-SO<sub>2</sub> equilibrium under dynamic conditions becomes increasingly difficult with decreasing temperature. We expect that effusion studies of other metal sulfates at temperatures comparable to the zinc sulfate range or lower would likewise show only SO<sub>3</sub> emission, as long as there is no change in the oxidation state of the metal.

The comparison of extrapolated zero hole-size pressures for ZnSO<sub>4</sub> and ZnO-2ZnSO<sub>4</sub> with both calculated and measured equilibrium values for reactions 2 and 4 presents an interesting situation. These values are summarized in Table V. Although the emf and static pressure values of  $P(SO_3)$  agree with the values calculated from thermodynamic data to within a factor of two or better, the effusion values are unmistakably low by a factor

of five or more. This is certainly not due to an inherent limitation of the effusion method or to the orifice extrapolation procedure, since other studies have shown that reliable results can be obtained on well-characterized systems. With CaSO<sub>4</sub>, for example, the extrapolated equilibrium effusion pressure at 1200 K lies within 15% of calculated and measured  $SO_2 + O_2$  pressures in this system.<sup>1</sup> It seems much more likely that the difference results from formation of the solid product phases in some metastable form of higher energy content than normal macroscopic phases. Giauque<sup>20</sup> recognized this possibility a number of years ago in regard to the equilibrium

$$Mg(OH)_2(s) = MgO(s) + H_2O(g)$$
 (6)

in stating: "For example, it seems probable that anhydrous salts, or the lower hydrates of salts, formed by the decomposition of multihydrated forms, in the absence of a solution, can be expected to produce finely divided material. The higher free energies of substances in this form should give lower decomposition pressures than do macroscopic phases." Not only did static pressure measurements<sup>20,21</sup> of reaction 6 yield finely divided MgO(s) with an excess enthalpy of about 3.7 kJ·mol<sup>-1</sup> at 298 K, but subsequent effusion studies<sup>22</sup> of the same reaction gave evidence for still greater departures from bulk phase behavior with extrapolated zero orifice-size pressures about 10<sup>4</sup> times smaller than established equilibrium pressures. Beruto et al.<sup>23</sup> have determined recently the enthalpy of solution of MgO(s) as a function of oxide surface area and found excess enthalpies as large as 73 kJ·mol<sup>-1</sup>, more than enough to account for the low H<sub>2</sub>O decomposition pressures observed in the effusion experiments.<sup>22</sup> In the case of the two zinc sulfates, the factor of five lowering of the pressure is equivalent to an excess enthalpy of formation of about 12 kJ·mol<sup>-1</sup>, for the product oxide or oxysulfate. Although we have no direct evidence in terms of measured particle size and its relation to excess enthalpy, we believe that small particle size effects of this type are responsible for the low effusion pressures. It seems likely that this type of solid product mestastability might be rather common in effusion studies of decomposition reactions at 1000 K or below and the possibility of its occurrence should be kept in mind.

We have no ready explanation as to why dispersed Pt powder is an effective and reproducible catalyst for decomposition of  $ZnO-2ZnSO_4$  but is only marginal and erratic for  $ZnSO_4$ . Despite the erratic behavior with ZnSO<sub>4</sub>, Pt does clearly catalyze the decomposition of the solid. On the other hand, Fe<sub>2</sub>O<sub>3</sub> had no effect on the decomposition pressure of  $ZnSO_4$  near 800 K, while  $Cr_2O_3$ similarly had no observable effect on ZnO-2ZnSO<sub>4</sub> at about 850 K and CuO had only a small effect. These observed effects correlate reasonably well with our earlier work<sup>3</sup> on the catalytic reduction of SO<sub>3</sub> in the range 600–1000 K and pressures of  $10^{-7}$ to  $10^{-6}$  atm. In this pressure range, Pt is an effective catalyst for  $SO_3 \rightarrow SO_2$  conversion at temperatures above about 750 K, while this threshold temperature is about 900 K for  $Fe_2O_3$  and  $Cr_2O_3$ , and 850 K for CuO. On this basis one can rationalize the observed behavior of Pt, Cr<sub>2</sub>O<sub>3</sub>, and CuO. It would seem that there must be a strong relationship between threshold temperature, catalyzed decomposition pressure, and the kinetics of the overall surface chemisorption/desorption processes that are involved in the SO<sub>3</sub>  $\rightarrow$  SO<sub>2</sub> catalytic conversion. It is known already from studies of the catalyzed decomposition of  $MgSO_4^2$  near 1000 K that there is a considerable spread in total decomposition pressures with the various additives even where all are effective for  $SO_3 \rightarrow SO_2$ conversion. Furthermore, the results seem not to be strongly dependent on catalyst concentration or particle size. Thus it seems that a critical step must be reduction of the local SO<sub>3</sub> partial pressure near the lattice decomposition site, so that  $SO_3 \rightarrow SO_2$ chemisorption/desorption steps on each specific catalyst surface may be controlling. A possible chemisorption type mechanism for catalytic conversion of SO<sub>3</sub> to SO<sub>2</sub> by Pt and metal oxides has

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<sup>(21)</sup> Giauque, W. F.; Archibald, R. C. J. Am. Chem. Soc. 1937, 59, 561.
(22) Kay, E.; Gregory, N. W. J. Phys. Chem. 1958, 62, 1079.
(23) Beruto, D.; Rossi, P. F.; Searcy, A. W. J. Phys. Chem. 1985, 89, 1695.

 TABLE VI: Measured Slope Enthalpies<sup>a</sup> of Zinc Sulfate Decompositions

	ZnSO4		ZnO•2ZnSO4		$ZnO-2ZnSO_4$ + 4% Pt	
cell	$\Delta H^{\circ}_{G}$	$T_{\rm av}/K$	$\Delta H^{o}_{T}$	$T_{\rm av}/{\rm K}$	$\Delta H^{\circ}_{T}$	$T_{\rm av}/{\rm K}$
7	254.7	817	278.7	868	236.4	812
3	257.2	800	253.0	860	245.2	796
2	257.4	796	258.8	848	245.6	787
5	261.7	795	261.8	831	249.0	789
1	263.4	799	262.3	844		
equilibrium	232.5 <sup>b</sup>	800	220.9°	850	213.0 <sup>d</sup>	800
6 I. 1. I 1-1	h D +			1 d D		

<sup>a</sup> In kJ·mol<sup>-1</sup>. <sup>b</sup> Reaction 2. <sup>c</sup> Reaction 4. <sup>d</sup> Reaction 5.

been discussed in another paper,<sup>2</sup> with reference to a similar mechanism for N<sub>2</sub>O decomposition. It is worth noting here that Skeaff and Espelund<sup>10</sup> found that additions of a few mole percent of Fe<sub>2</sub>O<sub>3</sub> or Mn<sub>3</sub>O<sub>4</sub> were required in order to obtain steady and reproducible emf data on ZnSO<sub>4</sub> and ZnO·2ZnSO<sub>4</sub>, presumably because of induced catalytic effects. Although Fe<sub>2</sub>O<sub>3</sub> and other transition-metal oxides were found to be ineffective in our studies at 800–900 K, the emf measurements extended into the range 1000–1200 K.

One can estimate the so-called vaporization coefficients associated with the several decomposition processes from the slope of the Whitman-Motzfeldt<sup>13-15</sup> plots. When the reciprocal of observed pressure is plotted against effective orifice area,  $\sum fa$ , the intercept is the reciprocal of the equilibrium pressure,  $P_e$ , and the slope is  $(\alpha AP_e)^{-1}$  where  $\alpha$  is the vaporization coefficient and A is the sample surface area according to this approximate analysis. It is difficult to specify the true value of A, but if the cell cross sectional area is taken as a lower limit, then upper limit values of  $\alpha$  at 800 K are calculated to be  $5.3 \times 10^{-3}$  for reaction 2,  $1.5 \times 10^{-2}$  for reaction 4, and  $6.0 \times 10^{-3}$  for the Pt-catalyzed results on ZnO-2ZnSO<sub>4</sub>. The kinetic barrier to the vaporization processes is such that the free surface vaporization fluxes of these materials would be lower than the maximum kinetic theory values by approximately the derived values of  $\alpha$ . These  $\alpha$  values found in the present work are very similar in magnitude to those found for MgSO<sub>4</sub> decomposition.<sup>1</sup>

In Table VI, the slope enthalpies derived from least-squares fitting of the vapor pressure data (where coefficient  $B = \Delta H/$ (2.303R)) for the three different samples are compared with each other and with the equilibrium values for the various reactions calculated from calorimetric and other thermodynamic data. Standard deviations for slope enthalpies can be derived from those for the B coefficients reported in Tables I-III; the values range from 0.75 to 5.3 kJ·mol<sup>-1</sup> with a mean of 1.65 kJ·mol<sup>-1</sup>. With the exception of the smallest orifice (cell 7) data for ZnO-2ZnSO<sub>4</sub>, the results generally show a decreasing  $\Delta H^{o}_{T}$  with decreasing hole size, in line with expectations as equilibrium is approached. Note, however, that all values of  $\Delta H^{\circ}_{T}$  are significantly larger than the equilibrium values, indicating the likelihood of a slow or ratelimiting step preceding the desorption of gaseous products in the decomposition process. This seems reasonable in view of the structural rearrangements associated with emission of SO<sub>3</sub> or SO<sub>2</sub> and  $O_2$  from the sulfate ion decomposition site. It may be significant that this difference between equilibrium and observed slope enthalpies was much smaller for  $MgSO_4$  at 1000 K and that these processes with significant activation energies will manifest themselves increasingly at the lower temperatures. It should be noted that the true equilibrium enthalpies for the several decomposition reactions are probably larger than the values in Table VI by 10 to 12 kJ·mol<sup>-1</sup> due to the expected small particle sizes as mentioned earlier, but this correction accounts for only a small part of the differences shown there.

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**Registry No.** ZnSO<sub>4</sub>, 7733-02-0; ZnO-2ZnSO<sub>4</sub>, 12037-14-8; Pt, 7440-06-4; CuO, 1317-38-0.

## A Lie Approach to Global Sensitivity Analysis of Systems Described by Ordinary Differential Equations

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A new form of global sensitivity analysis, based on Lie algebraic and group methods appropriate to many problems of chemistry, physics, and engineering, is outlined. An algorithm is provided that enables one to systematically determine, exactly or approximately, *operators* that convert solutions of ordinary differential equations containing parameters into families of solutions that arise when the parameters in the equation are changed in value. These techniques differ from conventional sensitivity analysis in that the new solutions generated by the present methods are guaranteed to satisfy the transformed differential equation. For example, if one knows a solution valid for some nonzero but restricted range of a parameter in the differential equation, then the operators can be used to obtain solutions valid outside of this range when such exist. If one knows a single solution valid for all values of the parameters. The operator determining equations of the present method are shown to reduce to those of conventional sensitivity analysis under appropriate restrictive conditions.

#### I. Introduction

Most problems in chemistry, physics, and engineering may be expressed in terms of differential equations. The solutions to these equations, or their functionals, are quantities of physical interest. Typically, the underlying differential equations contain a number of parameters used to establish the physical model. In some cases the model may be well-defined with parameters having essentially no uncertainty. In more typical circumstances, the model parameters have significant uncertainties. Under both these conditions one would frequently like to know as much as possible about the solutions of the differential equations as functions of the parameters. In the first case, the issue is not parameter uncertainty, but rather the desire to understand which portions of the model are responsible for particular aspects of the observables. The second case involves the determination of the probability

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