Effusion Studies of the Decomposition of $CuSO_4$ and $CuO{\cdot}CuSO_4$

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Both the torsion–effusion technique and high-temperature mass spectrometry were used to study the thermal decomposition of the copper sulfate and oxysulfate phases $CuSO_4$ and $CuO{\cdot}CuSO_4$ at about 700–780 K. The decomposition processes are retarded kinetically; SO_3 is the primary gaseous product, rather than the dominant equilibrium products SO_2 and O_2. Significant orifice size effects were observed for both salts. Although the extrapolated SO_3 pressure at zero orifice area for $CuO{\cdot}CuSO_4$ agrees closely with that calculated from accurate calorimetric data for the process $CuO{\cdot}CuSO_4(s) = 2CuO(s) + SO_3(g)$, the corresponding SO_3 pressure for $CuSO_4$ is more than a factor of 3 higher than that calculated from presumably reliable thermodynamic data. Pt powder, found to be an effective catalyst for the decomposition of magnesium and zinc sulfates at higher temperatures, showed no detectable effect on the decomposition pressures of the copper sulfates, although the effusing gas was converted to the $SO_2 + O_2$ equilibrium mixture. Results are compared with effusion studies on other sulfate systems.

Introduction

Our previous effusion studies of metal sulfate decomposition processes have shown variable and complex kinetic behavior.[1-4] Since it is a dynamic method, with vapor continually withdrawn from the system, the effusion technique is especially sensitive to kinetic limitations associated with the vaporization process. For those metal sulfates vaporizing by decomposition to a metal oxide solid phase and gaseous SO_3, SO_2, and O_2, the situation is particularly interesting, since the earlier effusion studies[1-4] have shown that full equilibrium with respect to gas-phase composition is only achieved under effusion conditions at temperatures above about 1000 K. Both $BaSO_4(s)$ at about 1500 K[5] and $CaSO_4(s)$ at about 1200 K[6] follow the decomposition pathway

$$MSO_4(s) = MO(s) + SO_2(g) + {}^1\!/_2O_2(g) \quad (1)$$

with extrapolated equilibrium pressures in good accord with values calculated from established thermodynamic data. With $MgSO_4(s)$ at 1000 K,[1] vapor molecular weights and derived pressures indicated the process to be

$$MSO_4(s) = MO(s) + SO_3(g) \quad (2)$$

at moderate to large effusion orifice areas, with a trend toward reaction 1 at the smallest orifice sizes. For $ZnSO_4(s)$ and $ZnO{\cdot}2ZnSO_4(s)$ at 800 to 900 K,[4] vapor molecular weight measurements showed conclusively that reaction 2 was the dominant process for all effusion orifice sizes. At equilibrium, reaction 1 should predominate for both magnesium and zinc sulfate systems, with $P(SO_2)/P(SO_3) > 20$ in all instances. There is clearly a substantial kinetic barrier associated with these lower temperature sulfate decompositions, with the evidence indicating release of SO_3 in the initial decomposition step. In some instances ($CaSO_4$, $BaSO_4$), this initial step is apparently closely coupled with a subsequent $SO_3 \rightarrow SO_2$ conversion step and near-equilibrium behavior is observed. For the others, however, direct desorption of SO_3 occurs, and even though subsequent conversion to SO_2 and O_2 may occur as SO_3 diffuses through the porous product oxide layer, this conversion is decoupled from the initial decomposition step. In this latter instance, the observed effusion pressure corresponds to reaction 2 even though the effusing gas may have the equilibrium $SO_2 + O_2$ composition.

These same studies[1-4] have shown that addition of small amounts of certain metal and metal oxide powders will catalyze the $SO_3 \rightarrow SO_2$ conversion[3] and may also in some instances effect a dramatic increase in the decomposition pressure of the metal sulfate.[1,2,4] The noble metals Pt, Ir, and Ru were effective as catalytic additives, along with p-type transition-metal oxides such as Cr_2O_3, Mn_2O_3, Fe_2O_3, CuO, CoO, and NiO on occasion. Pt powder was generally most effective, especially at the lower temperatures.[4]

$CuSO_4$ and $CuO{\cdot}CuSO_4$ have somewhat higher decomposition pressures than $ZnSO_4$ and $ZnO{\cdot}2ZnSO_4$ and it was therefore of interest to see if the copper salts exhibit any significant differences in vaporization/decomposition behavior. Additionally, the product oxide CuO shows catalytic activity as noted above, and the possibility of a "built-in" catalyst is also of interest. As another important feature, the relevant thermodynamic properties of the copper sulfates have been determined calorimetrically and are presumably known with reasonable accuracy,[6] so that reliable equilibrium decomposition pressures can be calculated for comparison with the experimentally derived values, greatly aiding the interpretation of the results. In the studies described here, decomposition pressures of the copper sulfates were measured by the torsion–effusion method and vapor composition was determined both by mass spectrometry and by molecular weights evaluated from simultaneous torsion–Knudsen measurements.

Experimental Section

We have described the torsion–effusion[1,7,8] and high-temperature mass spectrometric[9] methods in previous publications. Mass spectrometric studies were performed not only with the magnetic sector instrument described previously, but also with a quadrupole mass filter[3] equipped with a high-temperature beam source of similar design. The experimental procedure closely followed that employed in the earlier sulfate studies,[1,4] including the use of alumina effusion cells for both torsion–effusion and mass spectrometric studies. Accuracy of the effusion pressure measurements is about 5%, as corroborated by runs with laboratory vapor pressure standards. Vapor molecular weights are also accurate to within 5%.

Baker reagent grade anhydrous copper sulfate was dried under N_2 at 600 K for several hours prior to the measurements. Residual water adsorbed by the copper sulfate during transfer to the apparatus was removed by dehydration under vacuum at 650 K until the sample mass was constant. Basic copper sulfate was prepared by the thermal decomposition of anhydrous copper sulfate in air

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TABLE I: Decomposition Pressure of $CuSO_4$ (Torsion-Effusion Method)

T, K	$P \times 10^7$ atm	T, K	$P \times 10^7$ atm
	Cell 7		
704.5	6.74	746.8	58.5
713.2	10.6	754.2	83.7
723.8	18.5	756.1	89.2
728.9	23.7	762.8	126
732.9	28.6	764.7	136
740.9	44.0	770.3	177
742.8	47.8		
$\log P$ (atm) = (10.47 ± 0.03) − (11726 ± 28)/T			
	Cell 3		
705.7	3.09	726.1	9.02
707.4	3.36	727.2	10.4
708.3	3.60	728.0	10.7
711.5	4.32	729.6	11.6
713.2	4.74	732.6	13.6
717.4	5.95	733.3	14.1
719.9	6.77	735.8	16.1
720.6	7.10	739.8	19.6
722.3	7.77	743.1	23.2
724.5	8.97		
$\log P$ (atm) = (10.94 ± 0.11) − (12321 ± 79)/T			
	Cell 2		
684.8	0.443	712.4	2.33
697.9	0.988	714.4	2.79
704.1	1.55	719.9	3.81
704.6	1.67	726.6	5.45
$\log P$ (atm) = (11.66 ± 0.24) − (13022 ± 170)/T			
	Cell 5		
690.7	0.379	729.5	3.19
696.0	0.475	732.4	3.59
698.4	0.545	733.1	3.89
702.4	0.699	733.3	3.95
709.7	1.06	735.3	4.20
720.2	1.89	736.9	4.76
728.0	2.83	739.6	5.47
728.3	2.94	743.1	6.36
728.8	3.06		
$\log P$ (atm) = (10.38 ± 0.11) − (12316 ± 77)/T			
	Cell 1		
691.2	0.323	718.0	1.60
704.0	0.706	722.8	2.10
714.4	1.30		
$\log P$ (atm) = (11.10 ± 0.02) − (12851 ± 11)/T			

cell	orifice diam, cm²	$10^2\sum fa$, cm²
7	0.0485	0.1468
3	0.1048	0.9701
2	0.1491	2.361
5	0.1871	3.996
1	0.2096	5.166

at 973 K, as described by Stuve et al.[10] Purity of the resulting basic sulfate phase was verified by X-ray diffraction analysis. No hydration of the basic copper sulfate was observed. The Pt catalytic additive was −325 mesh platinum black powder (Western Gold and Platinum Co.).

Results

A. Decomposition of $CuSO_4$. Torsion–effusion measurements on the pure $CuSO_4$ phase were performed with five alumina cells of varying orifice diameter, from 0.05 to 0.21 cm; the pertinent cell constants including the diameter d and effective orifice area $\sum fa$, where f is the orifice force factor and a the geometrical area, are listed in Table I. Since it was found during trial runs that the decomposition pressure began to decrease slightly after more than 10% mass loss, measurements were confined to the early stages of sample decomposition, when less than 5% decomposition had occurred. The decomposition pressures are summarized in Table I, along with expressions for the temperature dependence obtained by least-squares fitting. All data reported in Table I were taken after stabilization of the total pressure, following a slight increase during the initial stage of decomposition; after this brief initial period, the pressures were quite steady with time. There is a significant dependence of pressure on orifice diameter, as frequently observed for decomposition processes with major structural changes.

TABLE II: Vapor Molecular Weight Determinations (Torsion-Knudsen Method)

cell	T, K	M	cell	T, K	M
			$CuSO_4$		
7	764.6	69.3	5	733.1	71.6
7	770.3	67.1	5	728.0	72.6
7	754.2	70.5	5	732.4	68.1
7	762.8	68.3	3	743.1	65.9
					av 69.2 ± 1.8
			$CuO{\cdot}CuSO_4$		
7	765.4	78.7	1	748.0	70.1
7	776.6	71.1	1	756.3	63.0
7	772.6	79.3	1	746.9	66.1
1	760.9	66.2	2	757.4	75.8
1	752.0	67.8	2	765.0	67.8
					av 70.6 ± 4.5

Vapor molecular weights determined from the simultaneous torsion and mass-loss measurements with several cells are listed in Table II. These values range from 66 to 73, averaging 69.2 ± 1.8, and are intermediate between those expected for effusion of SO_3 (M = 80.1) and $SO_2 + {}^1/_2O_2$ (M = 54.6). There is no clear trend with orifice size as with $MgSO_4$ decomposition,[1] but there was a definite indication of a decrease in M with increasing fraction of decomposition. Since all of the pressure and molecular weight measurements were made after the initial conditioning period at temperature, during which some decomposition occurred, it is likely that the earliest values of M would be near 80, indicating SO_3 to be the initial gaseous decomposition product.

A direct examination of vapor composition was made by mass spectrometry, using the magnetic sector instrument.[9] At a sample temperature of 700 K, only SO_3 was detected in the effusing vapor. Nine measurements of the SO_3^+ intensity over the range 658–767 K yielded a second law slope heat of 208.4 ± 5 kJ mol^{-1} at 700 K. As a further check on vapor composition and its time dependence, the mass spectrum of the effusing vapor was examined with the quadrupole mass filter.[3] Because the ion source of the quadrupole is much more confined and collisions with reducing metal surfaces are more likely, the vapor over $ZnSO_4$(s), which is known to contain only SO_3(g),[4] was examined first as a check. At 16 eV ionizing energy, where both ions should be parents, the ratio SO_3^+/SO_2^+ in the $ZnSO_4$ effusate increased from about 0.5 initially to about 10 on standing overnight. The SO_3^+ signal was relatively steady, while the SO_2^+ decreased continually, showing that SO_2 is generated initially by reduction of SO_3 in the quadrupole ion source but that the surfaces become passivated with time to give a more correct indication of vapor composition. With $CuSO_4$(s), however, the SO_3^+/SO_2^+ ratio at 700 K increased over several hours to a value of about 10, and then decreased steadily to about 0.1 after 15 h. In this latter instance, the SO_3^+ signal continued to drop with time, while the SO_2^+ parent signal remained fairly constant after a few hours.

Our interpretation of these observations is that decomposition of $CuSO_4$(s) under effusion conditions yields SO_3(g) initially and that the desorbed SO_3 is converted to SO_2 and O_2 at progressively higher levels as the product oxide layer builds up in the decomposing sample. X-ray diffraction analysis of the cell residues at the completion of the measurements identified the product oxide as CuO(s), rather than $CuO{\cdot}CuSO_4$(s), which is slightly more stable thermodynamically. Interestingly enough, the CuO(s) product appeared primarily as a black surface coating over a light-colored $CuSO_4$(s) interior when the residue was removed as a pellet. In one experiment, the surface coating was an orange-yellow, suggestive of $CuO{\cdot}CuSO_4$(s), but XRD showed it to be CuO(s). In any event, CuO(s) is known to catalyze the SO_3

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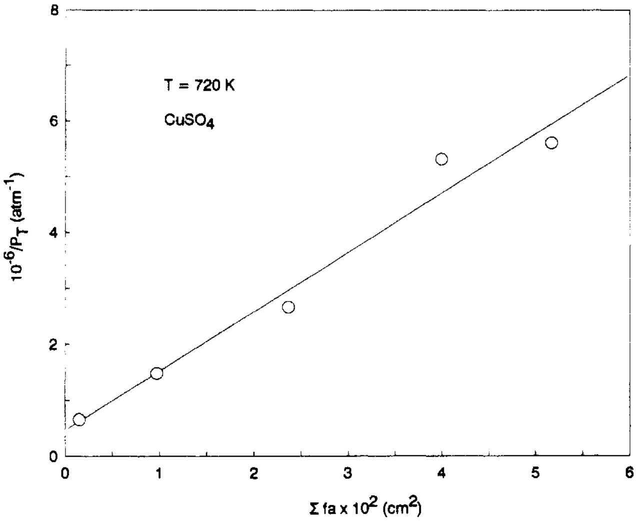

Figure 1. Whitman–Motzfeldt plot for $CuSO_4$ decomposition pressures at 720 K.

to SO_2 conversion,[3] and presumably this effect is responsible for the change in effusing gas composition noted in the mass spectra and molecular weights as the fraction of decomposition increases.

When a few percent of either CuO(s) or Pt powder was added to the starting $CuSO_4$(s) sample, the measured vapor molecular weights dropped immediately into the range 56–58, but the torsion pressures were essentially identical with those observed without the additives. We conclude that the additives as well as the intrinsic CuO(s) decomposition product catalyze the SO_3 to SO_2 conversion as effusion proceeds but that the sulfate decomposition rate itself is unaffected and the measured pressure, regardless of composition, is that associated with SO_3 desorption

$$CuSO_4(s) = CuO(s) + SO_3(g) \qquad (3)$$

Figure 1 shows a Whitman–Motzfeldt plot of the $CuSO_4$(s) torsion pressures, in which reciprocal pressure is shown as a function of effective orifice area, $\sum fa$, at 720 K. The correlation, in which $\sum fa$ is varied by a factor of 37, is quite linear and yields an extrapolated zero hole-size pressure of 2.2×10^{-6} atm at 720 K. Although the established thermodynamic data[6] for reaction 3 yield a calculated SO_3 equilibrium pressure of 6.3×10^{-7} atm, both emf[11] and static pressure measurements[12] yield derived SO_3 pressures of 2.0×10^{-6} atm, the latter in close agreement with our extrapolated equilibrium pressure. If the oxysulfate phase $CuO{\cdot}CuSO_4$(s) were the actual product, the calculated SO_3 equilibrium pressure[6] would be 8.1×10^{-7} atm, only about 30% higher but still well below the experimental values. At 720 K, the Gibbs energy change ΔG for the reaction

$$CuSO_4(s) + CuO(s) = CuO{\cdot}CuSO_4(s) \qquad (4)$$

is only 1.4 kJ mol^{-1}, and evidently the oxysulfate phase does not nucleate on the time scale of the experiments. The equilibrium $SO_2 + O_2$ pressure, i.e., reaction 1, for $CuSO_4$ is higher than the SO_3 pressure by a factor of 5, but it is clear that full equilibrium is not attained under effusion conditions and that reaction 3 represents the process actually observed. It is worth noting that the tabulated SO_3 equilibrium decomposition pressures for $CuSO_4$(s) given by King et al.[13] are about 50% higher than the later values tabulated by DeKock[6] because of revisions in the enthalpy of formation of $CuSO_4$(s); the later value[6] is presumed to be more reliable.

TABLE III: Decomposition Pressure of $CuO{\cdot}CuSO_4$ (Torsion–Effusion Method)

T, K	$P \times 10^7$, atm	*T*, K	$P \times 10^7$, atm
Cell 7			
744.7	11.9	772.6	49.8
746.0	13.1	780.6	73.8
751.0	17.7	783.3	84.1
756.8	22.7	788.0	105
764.9	33.9		
log *P* (atm) = (11.05 ± 0.13) − (12633 ± 98)/*T*			
Cell 2			
		745.4	2.53
717.7	0.550	751.5	3.55
722.6	0.732	754.6	4.16
726.7	0.925	761.7	5.90
732.2	1.24	765.0	6.88
735.0	1.41		
740.0	1.90		
log *P* (atm) = (10.56 ± 0.07) − (12789 ± 55)/*T*			
Cell 1			
		741.4	1.14
697.4	0.100	741.9	1.12
717.0	0.306	745.8	1.33
719.4	0.343	750.6	1.73
723.5	0.413	754.2	2.28
729.8	0.618	759.1	2.89
730.0	0.537		
735.8	0.777		
log *P* (atm) = (9.87 ± 0.27) − (12476 ± 197)/*T*			

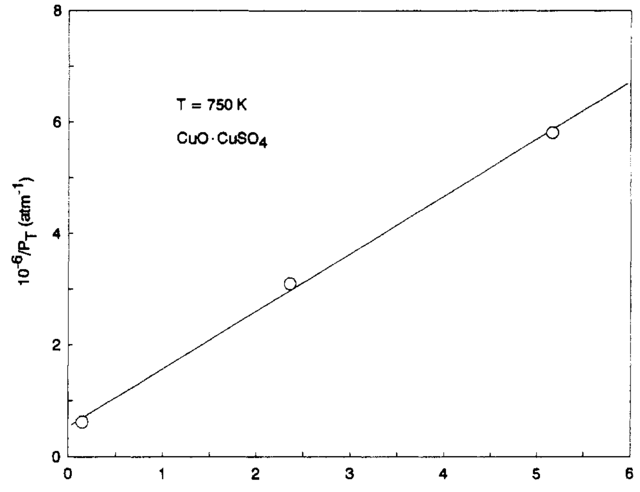

Figure 2. Whitman–Motzfeldt plot for $CuO{\cdot}CuSO_4$ decomposition pressures at 750 K.

B. Decomposition of $CuO{\cdot}CuSO_4$. Decomposition pressures of the oxysulfate phase $CuO{\cdot}CuSO_4$(s) measured with three different effusion cells are listed in Table III, and the corresponding vapor molecular weights are given in Table II. As with $CuSO_4$(s), a substantial orifice-size effect was observed, and the molecular weights ranged from 63 to 79, with an average of 70.6 ± 4.5. From XRD analysis of cell residues, CuO(s) was again identified as the solid decomposition product. Other aspects of the decomposition behavior are quite similar to those observed with $CuSO_4$(s), including a decrease in vapor molecular weight as the decomposition is carried out to an increasingly higher fraction.

Again we interpret the results as showing that SO_3 is released as the primary gaseous product, with some conversion to SO_2 and O_2 as the product oxide builds up in the sample. Just as with $CuSO_4$(s), addition of a few percent of Pt powder led to vapor molecular weights of 55 ± 2, although pressures were unchanged, showing that the $SO_2 + {}^1/_2O_2$ stoichiometry can be achieved without increasing the decomposition pressure by the factor of 7 that would be required if these were the equilibrium products.

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This is a distinct departure from the behavior observed with $MgSO_4$ and $ZnO{\cdot}2ZnSO_4$, where the Pt catalyst effected a large increase in decomposition pressure.

A Whitman–Motzfeldt plot of the orifice data at 750 K is shown in Figure 2; a linear equation fits the data well, leading to an extrapolated pressure of 1.8×10^{-6} atm at 750 K for the process

$$CuO{\cdot}CuSO_4(s) = 2CuO(s) = SO_3(g) \qquad (5)$$

The calculated SO_3 equilibrium pressure for reaction 5, based on calorimetric and other established thermodynamic data,[6] is 2.0×10^{-6} atm, while the recommended value[12] extrapolated from static pressure measurements is 1.5×10^{-6} atm. In contrast to the results for reaction 3, the pressure derived from effusion measurements is in remarkably good agreement with the value calculated from thermodynamic data, which should normally be accurate to within about 20% when the properties are well established. The good agreement can be taken as an indication that the interpretation of the effusion results is essentially correct.

Discussion

The two copper sulfate phases CuO(s) and $CuO{\cdot}CuSO_4(s)$ exhibit yet a different type of decomposition behavior than those observed in effusion studies of the magnesium and zinc sulfates.[1,4] This might be due to the lower temperature regime of the copper sulfate studies. It is very striking that the effusing gas can be readily converted to the equilibrium $SO_2 + {}^1/_2O_2$ composition by either the accumulating CuO(s) product phase or by CuO(s) and Pt powder additions, while neither of these has any detectable effect on decomposition pressure. This behavior is in contrast to that of magnesium and zinc sulfates, where Pt powder addition led to pressure increases of 1–2 orders of magnitude,[1,2,4] approaching $SO_2 + O_2$ equilibrium pressure for the smallest orifice sizes. Although Pt is still a very effective catalyst for the gas-phase $SO_3 \rightarrow SO_2$ conversion at the temperatures and pressures of $CuSO_4$ and $CuO{\cdot}CuSO_4$ decomposition, this process apparently is not coupled to the primary decomposition step in which SO_3 is ejected from the sulfate lattice site. One could rationalize this difference as being due to a lower surface diffusion rate of adsorbed SO_3 from decomposition site to catalytic site. On another aspect, it does seem from the gradual decrease in SO_3 content with time for the pure Cu sulfates that nucleation of a catalytically effective CuO product phase requires considerable atomic migration and rearrangement; addition of bulk CuO to the sample effects an immediate conversion to SO_2 and O_2.

A lesson worth remembering from these results is that, for sulfate decomposition reactions, effusing gas composition may not be a good indicator of the actual chemical process responsible for the decomposition rate and its associated steady-state pressure. We have described several instances in which accumulation of the catalytically active CuO product phase or addition of small amounts of catalytic materials will convert the gas to the $SO_2 + {}^1/_2O_2$ stoichiometry, while the measured pressure is basically that of SO_3, reactions 3 and 5. A similar effect was noted with $MgSO_4$, where buildup of a thick MgO(s) product layer yielded M values of 55–60, although the effusion pressure was only slightly lower than initial values when $M = 80$.[1] In complex kinetically limited situations such as this, the experimenter must use great care in sorting out the results and assigning the correct chemical process.

For both $CuSO_4(s)$ and $CuO{\cdot}CuSO_4(s)$, the decomposition processes are kinetically limited in two respects. First, equilibrium levels of SO_2 and O_2 are not attained, as discussed above, and second, the measured SO_3 decomposition pressure shows a substantial orifice-size dependence. The latter is not unexpected for a process of this type in which considerable bond rearrangement and orientation accompanies the release of a planar symmetric SO_3 molecule from the tetrahedral lattice sulfate ion SO_4^{2-}. This orifice-size effect gives a qualitative feel for the magnitude of the kinetic barrier. According to the Whitman–Motzfeldt model of the effusion process,[14–16] the slope of a plot of reciprocal observed pressure against effective orifice area is in first approximation equal to $(\alpha A P_e)^{-1}$, where α is the vaporization coefficient (equal to unity when there is no kinetic retardation), A is the vaporizing surface area, and P_e is the equilibrium pressure; the intercept is of course P_e^{-1}. With the usual simplifying assumption that the sample chamber cross-sectional area can be taken as a lower limit to A, then upper limit values of α are found from the results to be 4.5×10^{-3} for $CuSO_4$ at 720 K and 5.3×10^{-3} for $CuO{\cdot}CuSO_4$ at 750 K. The interesting point is that these values are quite comparable to corresponding results found earlier for the magnesium[1] and zinc[4] sulfates, ranging from 3×10^{-3} to 4×10^{-2}. This implies that the actual surface vaporization flux of SO_3 molecules from the decomposing sulfates will be several orders of magnitude smaller than that calculated from kinetic theory and the equilibrium SO_3 pressure.

The calculated SO_3 equilibrium pressure for $CuO{\cdot}CuSO_4$, reaction 5, is within 8% of the value extrapolated from the effusion data. It may be significant that our extrapolated zero hole-size SO_3 pressure for reaction 3 agrees closely with values derived from the emf[11] and static pressure measurements[12] but is a factor of 3.5 higher than the value calculated from presumably well-established thermodynamic data.[6] One might infer a possible error in the tabulated[6] thermodynamic properties of $CuSO_4(s)$. One would tend to suspect the standard enthalpy of formation rather than the entropy or Gibbs energy function, but the discrepancy would imply an error of about 7.5 kJ mol^{-1} in $\Delta H_f{}^\circ$, far outside the stated error limit of ± 1.3 kJ mol^{-1}. Therefore an error of this sort seems unlikely. Contrary to the experimental evidence, if the oxysulfate $CuO{\cdot}CuSO_4$ is really the solid-phase product of $CuSO_4$ decomposition rather than CuO, then the calculated SO_3 pressure increases only by 28% and is still a factor of 2.7 lower than the extrapolated effusion result as well as the two other experimental values. Also, if the solid-phase reaction product in our study were metastable, the experimentally derived pressures would be too low rather than too high. At the moment, we have no reasonable explanation for the discrepancy in $CuSO_4(s)$ decomposition pressures.

Although the mass spectrometric second law slope measurements on SO_3^+ yielded an enthalpy change $\Delta H^\circ_{700} = 208.4 \pm 5$ kJ mol^{-1}, as compared to the tabulated value[6] of 214.2 kJ mol^{-1}, the total pressure slopes from the torsion–effusion data in Tables I and III are uniformly 15–35 kJ mol^{-1} higher than the values derived from calorimetric data.[6] Again, this is very similar to the corresponding behavior noted in the $ZnSO_4$ and $ZnO{\cdot}2ZnSO_4$ decomposition reactions.[4] With the large kinetic barriers involved, the slope enthalpies must reflect a significant activation energy contribution and are understandably higher than the equilibrium enthalpies.

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Registry No. $CuSO_4$, 7758-98-7; $Cu_2O(SO_4)$, 12015-77-9; Pt, 7440-06-4.

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