Kinetics of the thermal decomposition of zinc sulfate

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Résumé. Cinétique de la décomposition thermique du sulfate de zinc. Le pourcentage de poids perdu par les échantillons de ZnSO₄ pur, ZnO·2ZnSO₄ et le produit de la réaction de NH₄HSO₄ avec ZnO a été mesuré en fonction de la température entre 900°C et 980°C. Pour ZnSO₄ pur, la décomposition thermique a lieu en deux paliers. Pour ZnO·2ZnSO₄ et pour le produit de la réaction, la décomposition s'effectue en un seul palier. Le taux de décomposition suit une équation dérivée de la loi linéaire de formation de noyaux. Les constantes de taux et les énergies d'activation d'Arrhenius sont calculées pour chaque réaction de décomposition. Les résultats concordent avec la conclusion suivante : la décomposition de ZnSO₄ en ZnO entraîne la formation de ZnO·2ZnSO₄ en tant qu'intermédiaire. La décomposition du produit de la réaction de NH₄HSO₄ est uniquement qualitativement similaire aux décompositions de ZnSO₄ et ZnO·2ZnSO₄ et la nature de ce produit n'est pas claire.

Summary. The rates of weight loss from samples of pure ZnSO₄, pure ZnO·2ZnSO₄, and from samples of the product of the reaction of NH₄HSO₄ with ZnO have been measured as a function of temperature over the range 900 - 980°C. For pure ZnSO₄, the thermal decomposition occurs in two steps. For pure ZnO·2ZnSO₄ and for the reaction product, thermal decomposition occurs in a single step. The rates of decomposition follow a rate equation derived from the linear law of nucleation formation. Rate constants and Arrhenius activation energies are calculated for each decomposition reaction. The data are consistent with the conclusion that the decomposition of ZnSO₄ to ZnO involves the formation of ZnO·2ZnSO₄ as an intermediate. The decomposition of the product of the reaction of NH₄HSO₄ is only qualitatively similar to the decompositions of ZnSO₄ and ZnO·2ZnSO₄ and the nature of this product is unclear.

Introduction

Recently attention has been focused on the thermal decomposition of ZnSO₄ because it has been chosen as a viable candidate for solar energy storage [1]. This reaction is also the high temperature reaction step in the ZnSe thermochemical water splitting cycle [2] and can be substituted for the high temperature step of H₂SO₄ decomposition in several other thermochemical water splitting cycles [3-7]. Our interest in the decomposition of ZnSO₄ involves the use of ZnO to separate NH₃ and H₂O from SO₃ or SO₂/O₂ in the ammonium hydrogen sulfate (AHS) cycle for storage of solar energy [8-10], as described in our previous paper [11].

Two different phases of ZnSO₄ exist. The low temperature α phase, has a close-packed orthorhombic structure [12]. Upon heating, the solid undergoes a considerable volume increase and transforms into the high-temperature β phase, which has a cubic high-cristobalite-type structure. The thermal decomposition of either phase into ZnO and SO₃ (or SO₂ + 1/2O₂), involves an intermediate oxide-sulfate (basic zinc sulfate, also called zinc oxyulfate), whose existence is frequently reported in the literature. The formula for this oxyulfate has stirred some discussion and the following have been proposed : 2ZnO·3ZnSO₄[13-15], ZnO·2ZnSO₄[2, 3, 16-31], 3ZnO·ZnSO₄[32, 38] and ZnO·ZnSO₄ [34].

Different aspects of the thermodynamics and kinetics of the decomposition of the zinc sulfates have been studied by several investigators. Ingraham and Kellogg [21] report the decomposition pressures of both the zinc sulfate and the oxyulfate in a static system and show that higher temperatures are required to decompose the oxyulfate
than the sulfate. Skeaff and Espelund [20] used an EMF method for the investigation of
the sulfate-oxide equilibria. Kelley [35], Kellogg [36] and Stern and Weise [15] have
summarized the thermodynamic data on zinc sulfate. However, Kelley’s data has been
questioned by Hosmer and Krikorian [12], who have recently studied the high tempera-
ture enthalpies of zinc sulfate and zinc oxytsulfate. In addition, the data summarized by
Stern and Weise [15] contain values for the activation energies which differ markedly
from each other. Eriksson et al. [24] studied the equilibrium for the decomposition of
the oxytsulfate into ZnO, SO₂ and O₂, by equilibrating the phases ZnO and ZnO:2ZnSO₄
with a continuously flowing SO₂/Ar gas mixture of known concentration. The equili-
brium oxygen partial pressures thus generated were determined by measuring the EMF’s
of an oxygen concentration cell.

Ingram and Marier [31] studied the kinetics of the thermal decomposition of ZnSO₄
and ZnO:2ZnSO₄ with a recording thermogravimetric balance, using sample pellets and a
stream of nitrogen. They report the decomposition of both as topochemical and with
linear kinetics. The effect of partial pressures of SO₂ on the rate of decomposition of the
oxytsulfate suggests that SO₃ is strongly adsorbed on the ZnO reaction product. The tran-
sition from the α-β phase is reported at about 755°C. From the TGA data, the α form
does not have to undergo this transformation to release SO₃ because the process starts
below the transition temperature. A drastic decrease in the rate of decomposition of the
sulfate was observed at a point where about 33 % of the sample had decomposed. This
was attributed to the formation of the oxytsulfate. However, these experiments were
done on the low side of the temperature region required for thermochemical cycles
(750-950°C). Pechkovskii [37, 38] studied the kinetics of the decomposition of the zin-
carbonate and oxytsulfate, but the activation energies obtained are 10-15 % higher than those
obtained by Ingram [31] and four times higher than those obtained by Kolta and
Askari [39]. These data are summarized in Table I.

**TABLE I. - Summary of results related to the thermal decomposition of zinc sulfates.**

<table>
<thead>
<tr>
<th>Property (kcal/mole)</th>
<th>ΔH</th>
<th>Ea</th>
</tr>
</thead>
<tbody>
<tr>
<td>References</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) ZnSO₄ (s) → ZnSO₄ (g)</td>
<td>4.820</td>
<td>6.300</td>
</tr>
<tr>
<td>2) ZnO:2ZnSO₄ (s) → ZnO:2ZnSO₄ (g)</td>
<td>53.73</td>
<td>56.54</td>
</tr>
<tr>
<td>3) ZnSO₄ (s) → ZnO:2ZnSO₄ (g)</td>
<td>29.28</td>
<td>1.40</td>
</tr>
<tr>
<td>4) ZnO:2ZnSO₄ (s) → ZnO:2ZnSO₄ (g)</td>
<td>-1.40</td>
<td>-2.8</td>
</tr>
<tr>
<td>5) (ZnO + 2SO₂(g)) → ZnO + SO₃(g)</td>
<td>92.05</td>
<td></td>
</tr>
<tr>
<td>(from 2) or 3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6) ZnO:2ZnSO₄ (s) → ZnO + SO₂(g)</td>
<td>56.205</td>
<td>76.83</td>
</tr>
<tr>
<td>(prepared stoichiometrically)</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>7) ZnSO₄ (s) → ZnO + SO₂(g)</td>
<td>78.50</td>
<td>79.78</td>
</tr>
</tbody>
</table>

**Notes:**

a. The values are given per mole of SO₂, unless otherwise specified.
b. Values given per mole of SO₂ (SO₂ = SO₂ + 1/2 O₂ assumed).
c. Unspecified form (assumed to be α).
d. Coexistence of products or stoichiometry not specified.

The objectives of the present work were to study the thermal decomposition kinetics
of zinc sulfate, zinc oxytsulfate, and the reaction product from the reaction between
AHS and ZnO and to establish a correct formula for the zinc oxytsulfate. The composi-
tion of the product gas mixtures produced by the thermal decomposition of zinc sulfate,
zinc oxytsulfate, and the AHS/ZnO reaction product are currently being determined, but
our results are not conclusive yet.
Experimental

ZnSO₄·7H₂O (Fisher, A.C.S. Certified) was ground in a mortar and dehydrated at 400°C for several hours. Zinc oxysulfate was prepared by reacting dehydrated ZnSO₄ with ZnO (Alfa, 99.9 %) at 600°C for 12-24 hours, as suggested by Ingraham and Kellogg [21]. The residue from the reaction between AHS (Cerac/Purac) and 1.5 ZnO (Alfa, 99.9 %) was prepared reacting the stoichiometric ratio at 400°C [9].

For kinetic studies the rates of weight loss by these three substances were measured as a function of decomposition temperature with a Mettler H54-AR balance (nominal accuracy, ± 0.01 mg) with under-the-balance weighing capability (fig. I). The balance was mounted above a cylindrical 3-zone vertical furnace (Applied Test Systems, 3110). The furnace temperature could be held to ± 2°C of the selected set point (Eurotherm Temperature Control Model 3395) and was limited to a maximum of 1200°C. The measuring thermocouple (Omega type K, Ni-Cr vs. Ni-Al) was connected to a Digitec (Model 590 K C) digital thermometer, and placed at the center of the oven next to the reaction sample mixture. The controller thermocouple, fixed at the oven’s surface in the middle zone, was an Omega type S (Pt vs. Pt, 10 % Rh). A quartz vial containing the sample was suspended from the balance by means of a quartz fiber. The diameter of these fibers was 0.2-0.6 mm. Typical samples contained 5-10 milligrams of zinc sulfate or oxysulfate.

![Figure 1](image.png)

**Fig. 1.** - Apparatus used for measuring weight losses at function of time and temperature.

A quartz tube with a side arm attached to its upper section was permanently centered in the cylindrical furnace. The side arm was connected to a pump. This tube served: 1) to direct the corrosive sulfur oxides out of the oven and away from the balance, 2) to minimize the effect of convection currents inside the oven, 3) to separate the sample from the heating elements, thus providing a more homogeneous sample temperature and 4) as a reference for positioning the vial.

To start a kinetic run, the furnace was heated to a set-point temperature. Then, the quartz fiber and the sample were lowered into the quartz tube and hung from the balance. This procedure typically required two minutes during which weight loss data could not be recorded. Then, the readings were taken at specified time intervals. Since the original weight under these conditions was lost we calculated it by taking the weight of the sample in another balance (Mettler H 40) before and after the reaction occurred, thus getting the total weight lost and adding this amount to the weight of the sample taken after the reaction went to completion. This gives an excellent approximation to the first reading, which was originally lost. The temperature inside the furnace never changed more than 1°C during the whole experimental procedure.
Results and discussion

ZnSO₄ decomposition

The results of experiments in the temperature range 900-980°C are shown in figure 2. The fraction decomposed (α) was calculated by taking the weight loss up to a given time and dividing it by the total theoretical weight loss. As can be seen two regions were obtained in each plot (except at the highest T), one extending up to α ~ 0.33 and the other one from α ~ 0.33 to α ~ 1.00. This is in accord with the literature summarized above, where the first region is interpreted as the decomposition of ZnSO₄ whereas the second region corresponds to the decomposition of the zinc oxyxulfate. At the highest temperature, the reactions are so fast that it is difficult to find the turning point between these two mechanisms. Also note that all the final alphas were within 1% of the theoretical weight losses, as calculated from the formula ZnSO₄. These results can aid in the elucidation of the true formula for the zinc oxyxulfate, known to be an intermediate in the ZnSO₄ decomposition.

As mentioned above, the formulas that have been proposed in the literature are: 2ZnO·3ZnSO₄ [13-15], ZnO·2ZnSO₄ [2, 3, 16-31], 3ZnO·ZnSO₄ [32,33] and ZnO·ZnSO₄ [34]. The last formula is very likely a misprint [see ref. 19]. For the other 3 formulas, the decomposition reactions would be (assuming SO₃ production in all cases, for the sake of argument):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>TPWLI</th>
<th>TPWLI</th>
<th>R</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>3ZnSO₄</td>
<td>→</td>
<td>ZnO·2ZnSO₄ + SO₃</td>
<td>16.53</td>
<td>(\frac{1}{2}) (\frac{2}{3}) (\frac{3}{4}) (\frac{3}{1}) (\frac{3}{2}) (\frac{3}{5})</td>
</tr>
<tr>
<td>ZnO·2ZnSO₄</td>
<td>→</td>
<td>3ZnO + 2SO₃</td>
<td>39.61</td>
<td>(1b)</td>
</tr>
<tr>
<td>4ZnSO₄</td>
<td>→</td>
<td>3ZnO·ZnSO₄ + 3 SO₃</td>
<td>37.19</td>
<td>(2a)</td>
</tr>
<tr>
<td>3ZnO·ZnSO₄</td>
<td>→</td>
<td>4ZnO + SO₃</td>
<td>19.74</td>
<td>(2b)</td>
</tr>
<tr>
<td>5ZnSO₄</td>
<td>→</td>
<td>2ZnO·3ZnSO₄ + 2SO₃</td>
<td>19.84</td>
<td>(3a)</td>
</tr>
<tr>
<td>2ZnO·3ZnSO₄</td>
<td>→</td>
<td>5ZnO + 3SO₃</td>
<td>37.12</td>
<td>(3b)</td>
</tr>
</tbody>
</table>

where TPWLI and TPWLI² are the Theoretical Percent Weight Losses that would be expected from the first reaction (1a, 2a, 3a) and the second reaction (1b, 2b, 3b) respectively; R is the ratio of the theoretical weight loss in reactions (1a, 2a, 3a) to the weight lost in reactions (1b, 2b, 3b); α is the fraction decomposed at which the first reaction in the sequence is theoretically complete and the second reaction about to begin.

In reference to reactions 1a, 1b and 3a, 3b Ingraham and Kellogg [21] suggested that most likely all investigators have studied the same compound, but reported different formulas as a result of the difficulty in distinguishing the small difference in composition between the alleged oxyxulfates ZnO·2ZnSO₄ and 2ZnO·3ZnSO₄ (see summary above). This view is supported with a thermodynamic phase diagram for the Zn-S-O system in which it is unlikely that more than one basic zinc sulfate exists. Also it was noted that
Hoscheck [13] reports an X-ray powder pattern for this alleged 2ZnO·3ZnSO₄ which agrees with their pattern for ZnO·2ZnSO₄ within experimental error. Eriksson et al. [24] obtained later (1979) a more careful X-ray pattern for the basic zinc sulfate, indexing the powder pattern lines, which again agrees with the two published earlier. The weight loss after the decomposition of some basic sulfate was also checked (although with only one experiment) and was in agreement within 0.03 % of reaction 1a, thus supporting ZnO·2ZnSO₄. [21] Furthermore, the Zn content was checked by Atomic Absorption analysis and EDTA titration and again, agreed with the theoretical Zn content of ZnO·2ZnSO₄ within 1 and 1.3 %, respectively.

From our results for the ZnSO₄ decomposition equations 1a and 1b apparently explain the process, since the turning point observed corresponds to $\alpha \approx 1/3$. This supports the formula ZnO·2ZnSO₄ for the intermediate oxy-sulfate.

**Zinc oxy-sulfate decomposition**

The results of experiments in the temperature range 900-980 °C are plotted in figure 3, as the fraction decomposed ($\alpha$) vs. time ($t$). Here, only one region was observed in each plot except for the initial period of desorption of gases and induction which is common to most thermal decomposition reactions [40-42]. This seems to indicate that the oxy-sulfate decomposes in a single step, as reported previously in the literature [12, 17, 21, 30, 31, 37].

It is important to note that, out of a total of 6 experiments performed, all but one showed a weight loss within 0.25 % of the theoretical calculated for the formula.
ZnO·2ZnSO₄. With this evidence, together with that presented in the previous section and from the literature discussed above, the thermal processes that occur with the zinc sulfates can be summarized as follows:

\[
\text{ZnSO}_4 \ (\alpha) \rightarrow \text{ZnSO}_4 \ (\beta) \quad T = 734^\circ C
\]  
(4)

\[
3\text{ZnSO}_4 \ (\alpha) \rightarrow \text{ZnO}·2\text{ZnSO}_4 + x\text{SO}_3 + (1 - x)\text{SO}_2 + \frac{1 - x}{2} \text{O}_2 \quad T < 734^\circ C
\]  
(5)

\[
3\text{ZnSO}_4 \ (\beta) \rightarrow \text{ZnO}·2\text{ZnSO}_4 + x\text{SO}_3 + (1 - x)\text{SO}_2 + \frac{1 - x}{2} \text{O}_2 \quad T > 734^\circ C
\]  
(6)

\[
\text{ZnO}·2\text{ZnSO}_4 \rightarrow 3\text{ZnO} + 2x\text{SO}_3 + 2(1 - x)\text{SO}_2 + (1 - x)\text{O}_2 \quad T \geq 800^\circ C
\]  
(1b)

And if the system is at equilibrium,

\[
\text{SO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2
\]  
(7)

Decomposition of the residue from the reaction between AHS and 1.5 ZnO.

The results of experiments in the temperature range 860-980°C are plotted in figure 4, as the fraction decomposed (a) vs. time (t). It can be seen that there is a very steep region at the beginning of the decomposition, and that all the weight losses were between 100.0 and 103.0 % of the SO₃ content, calculated on the basis of the yields from the reaction between AHS and 1.5 ZnO. The yields above 100 % can be attributed to resi-
dual NH₃ from the first reaction or H₂O absorbed from the dissiccant in a desiccator (some samples were stored for long periods of time before carrying out the decomposition of the residue).

Since it is suspected that the residues from the AHS + 1.5 ZnO reaction contained ZnSO₄, ZnO-2ZnSO₄ or a mixture of both, these decomposition plots are compared with those of the sulfates. The very fast decomposition rates of the residues of the AHS/ZnO reaction at the beginning of the reactions (up to ~ 8%) resembles the fast rates observed during the first part of the ZnSO₄ decomposition. However, most of the decomposition of the residues of the AHS/ZnO reaction show what appears to be only one mechanism after the initial desorption and induction period which resembles the decomposition of the oxy sulfate. Since the presence of ZnSO₄ and/or ZnO-2ZnSO₄ in this residue was suspected, an X-ray powder diffraction pattern was obtained and compared with standard diffraction patterns (A.S.M.E.) of ZnO, ZnSO₄, ZnSO₄·ZnSO₄·7H₂O and ZnO-2ZnSO₄ (this last one from reference [21]). Our AHS/1.5 ZnO residue showed the main line of pure ZnO, suggesting an excess of ZnO in the sample. It did not show any of the ZnSO₄ lines, had only one or two lines in common with the ZnO-2ZnSO₄, and was missing practically all the other lines of the oxy sulfates. The diffraction pattern was also significantly different than that of the hydrates mentioned above. From these data, neither of those two species (ZnSO₄ and ZnO-2ZnSO₄) seem to be present in the residue of AHS/1.5 ZnO.

In addition, if ZnSO₄ or ZnO-2ZnSO₄ were present in the AHS/ZnO residues, a kinetic analysis of the second region in the decomposition plots should yield an activa-
tion energy equal to that found for the ZnO-2ZnSO₄. This point is analyzed in the next section.

**Kinetic Evaluation**

In order to analyze the kinetics of these decompositions, the different equations for thermal decomposition mechanisms (see Table II) were plotted for each experiment for selected samples of ZnSO₄, ZnO-2ZnSO₄ and the residue from the reaction between AHS/ZnO. These equations should show a linear plot, depending on which mechanism best represents the true process [43]. None of them was found to give a more significantly linear plot than the α vs. time curves themselves. Consequently, the slope of the best straight line drawn along each curve was taken as the rate constant $k_0$, as suggested in reference [43], according to

$$k_0 = at + a$$  \hspace{1cm} (8)

<table>
<thead>
<tr>
<th>Name of the mechanism</th>
<th>Alpha function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power law</td>
<td>$\alpha^n (n = 1, 2, 1/2, 1/3, 1/4)$</td>
</tr>
<tr>
<td>Contracting geometry</td>
<td>$1 - (1 - \alpha)^{1/n} (n = 2, 3)$</td>
</tr>
<tr>
<td>Erdeven</td>
<td>$[\ln (1 - \alpha)]^{1/m} (n = 1, 3/2, 2, 3, 4)$</td>
</tr>
<tr>
<td>2 D Diffusion controlled</td>
<td>$(1 - \alpha) \ln (1 - \alpha) + a$</td>
</tr>
<tr>
<td>3 D Diffusion controlled</td>
<td>$(1 - a/(1 - a) - 1)$</td>
</tr>
<tr>
<td>Jander</td>
<td>$1 - (1 - \alpha)^{1/3}$</td>
</tr>
<tr>
<td>Prout - Tompkins</td>
<td>$\ln [\alpha/(1 - \alpha)]$</td>
</tr>
<tr>
<td>Second order</td>
<td>$1/(1 - \alpha) - 1$</td>
</tr>
<tr>
<td>Exponential</td>
<td>$\ln \alpha$</td>
</tr>
</tbody>
</table>

**TABLE II.** — *Alpha functions used in analysis of reaction data v.s. time*

It is generally agreed [40-43] that the phenomenological aspects (i.e., induction, acceleration and decay) of the thermal decomposition of solids can be explained in terms of the concepts of the formation and growth of nuclei. If the rates of these two processes (formation, $k_f$, and growth, $k_g$, of nuclei) are compared [41], either single step (where $k_f \ll k_g$) or multiple step (in which there is no clear distinction between nucleation and growth) nucleation mechanisms are encountered. For the first case (single step) it has been shown [40, 41] that if there are $N_0$ potential nucleus-forming sites and the number of these formed in time $t$ is $n$, then

$$dn/dt = k_f (N_0 - n)$$ \hspace{1cm} (9)

where $k_f$ is the rate constant for the single step nucleation mechanism. Integrating:

$$n = N_0 \left[1 - \exp\left(-k_f t\right)\right]$$ \hspace{1cm} (10)

It has also been shown [40, 41] that a multistep nucleation follows the equation

$$n = k_m \rho^p$$ \hspace{1cm} (11)

where $\rho$ is a measure of the nucleation propagation efficiency, and $k_m$ is the rate constant for the multistep nucleation process.
This last equation (called Power Law) \[(12)\]
seemed to fit our data for \(p = 1\). However, when we attempted to obtain the experimental activation energies for the \(\text{ZnSO}_4\), \(\text{ZnO} \cdot 2\text{ZnSO}_4\), and the residue of the AHS/\(\text{ZnO}\) reaction, by application of the Arrhenius equation:
\[k_0 = A \exp\left(-\frac{E_a}{RT}\right)\]
or
\[\ln k_0 = \ln A - \frac{E_a}{RT}\]  \[(13)\]

it was noted that the experiments that involved larger amounts of sample gave exceptionally low \(k_0\) values and showed significant negative deviations in the Arrhenius graphs.

Such observations seemed to be explained better by the Linear Law of Nuclei Formation \[(14)\], which applies to those reactions in which the characteristic time for nucleus formation \(\tau = (1/k_2)\) is very large. In such cases \(n\) is very small, and from Eq. 9 (for \(n \ll N_0\))
\[
dn/dt = k_2(N_0 - n) \sim k_2 N_0\]
and dividing both sides by the number of moles of \(\text{SO}_3\) available at the beginning of the reaction, \(M_0\):
\[
\frac{dn/M_0}{dt} = k \frac{dn}{dt} = \frac{k_2}{M_0} \cdot N_0\]  \[(15)\]

### TABLE III. Summary of the kinetics of the thermal decompositions of \(\text{ZnSO}_4\), \(\text{ZnO} \cdot 2\text{ZnSO}_4\) and res. AHS/\(\text{ZnO}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. (°C)</th>
<th>(\text{SO}_3) Content (moles)</th>
<th>(k_0 \times 10^3) (min(^{-1}))</th>
<th>(k_2^2 \times 10^3) (min(^{-1}) mole)</th>
<th>(\frac{E_a}{M_0}) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{ZnSO}_4)</td>
<td>900</td>
<td>4.669</td>
<td>0.985</td>
<td>0.460</td>
<td>73.2 ± 5.8</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>4.680</td>
<td>2.524</td>
<td>1.186</td>
<td>73.2 ± 5.8</td>
</tr>
<tr>
<td></td>
<td>940</td>
<td>4.670</td>
<td>2.745</td>
<td>1.282</td>
<td>73.2 ± 5.8</td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>6.054</td>
<td>3.249</td>
<td>1.967</td>
<td>73.2 ± 5.8</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>5.135</td>
<td>4.110</td>
<td>2.110</td>
<td>73.2 ± 5.8</td>
</tr>
<tr>
<td>(\text{ZnO} \cdot 2\text{ZnSO}_4)</td>
<td>920</td>
<td>4.749</td>
<td>1.728</td>
<td>0.821</td>
<td>76.3 ± 8.3</td>
</tr>
<tr>
<td></td>
<td>940</td>
<td>3.591</td>
<td>3.499</td>
<td>1.256</td>
<td>76.3 ± 8.3</td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>4.935</td>
<td>4.141</td>
<td>2.044</td>
<td>76.3 ± 8.3</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>4.905</td>
<td>4.681</td>
<td>2.296</td>
<td>76.3 ± 8.3</td>
</tr>
<tr>
<td>Res AHS + 1.5 (\text{ZnO})</td>
<td>860</td>
<td>3.672</td>
<td>0.447</td>
<td>0.172</td>
<td>60.3 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>880</td>
<td>3.649</td>
<td>1.140</td>
<td>0.416</td>
<td>60.3 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>3.714</td>
<td>1.273</td>
<td>0.473</td>
<td>60.3 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>3.655</td>
<td>1.933</td>
<td>0.714</td>
<td>60.3 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>940</td>
<td>2.449</td>
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<td>12.766</td>
<td>2.913</td>
<td>60.3 ± 2.7</td>
</tr>
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</table>

Notes: a. Calculated using a standard least squares fit. \(k_2 = k_2 \cdot M_0\).

b. Calculated using the individual Probable Errors for each \(k_1\) (except \(\sigma_{k_0}\) \(\cdot \) \(M_0\), since \(\sigma_{k_0}\) is very small), and a rigorous least squares adjustment procedure [44].
where \( k \) is a proportionality constant. Regrouping all constants, we obtain:

\[
dq/dt = k_1/M_0
\]  

(16)

This equation is consistent with our experimental observations (i.e. larger reaction times for larger sample sizes). New rate constants \( k_1 \) were calculated for all the experiments, and the corresponding Arrhenius plots were constructed (see fig. 5 to 7). A good fit to the Arrhenius equation was obtained. The activation energies thus obtained are listed in table III. They are consistent with the data published for lower temperatures (see table II). It is important to note that the activation energy required for the decomposition of the residue of the reaction between AHS and ZnO is significantly lower than that required for the decomposition of zinc sulfate and oxysulfate. The structure of such residue remains unexplained.

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**FIG. 5.** — Plot of the natural logarithm of the rate constants \( k_1 \) vs. Reciprocal temperature for the decomposition of ZnSO₄.

**FIG. 6.** — Plot of the natural logarithm of the rate constants \( k_1 \) vs. Reciprocal temperature for the decomposition of ZnO · 2ZnSO₄.

**FIG. 7.** — Evolution of \( k_1 \) (constante de vitesse) en fonction de \( 1/T \) lors de la décomposition du résidu AHS + 1.5 ZnO.
Conclusions
Several conclusions can be drawn from these experimental results.

a) The thermal decomposition of ZnSO₄ proceeds in two steps, the first one up to α ≈ 33% and the second one from α = 0.33 to α = 1. This is consistent with the reaction sequence in which ZnSO₄ decomposes first to an oxysulfate of the formula ZnO·2ZnSO₄.

b) The decompositions of the zinc sulfate and oxysulfate go essentially to completion at the temperatures used in this study (900-980°C).

c) The weight losses of the oxysulfate samples were within 0.25% of the theoretical for the ZnO·2ZnSO₄ formula, thus supporting this composition over the other formulas under discussion (2ZnO·3ZnSO₄, 3ZnSO₄, and ZnO·ZnSO₄).

d) No zinc oxide decomposition or vaporization was found up to 980°C, in agreement with references [17, 20, 29, 31 and 45], and in disagreement with ref. [39 and 46].

e) The behavior and activation energy of the ZnSO₄ samples (in the second region of the decomposition plots) are consistent with those found for the ZnO·2ZnSO₄, thus supporting the oxysulfate as the product formed during the ZnSO₄ decomposition.

f) The decompositions of the three solids included in this section are best explained by the equation $dα/dt = k_1M_0^{1/2}$ ($M_0$ is the no. of moles of SO₃ available at the beginning of the reaction), derived from the linear Law of Nuclei Formation [40].

g) The nature of the residue of the reaction between AHS + 1.5 ZnO is not clear, but its decomposition goes essentially to completion (at temperatures above 900°C), which enhances the possibilities of the AHS cycle [9-11, 47, 48] as a viable candidate for Solar Energy Storage.

h) We have studied the amounts of total SO₂, (SO₃ and SO₂) produced in the steps discussed above. However, the relative amounts of SO₂ and SO₃ produced are under investigation.

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References


[42] Peckovskii (V.V.). — Factors influencing the activity of solids. *Hid., Chap. 2."


