

The thermal decomposition of zirconium sulphate hydrate

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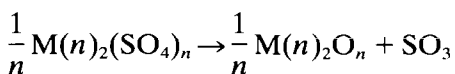
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Abstract

$\text{Zr}(\text{SO}_4)_2 \cdot 5.5\text{H}_2\text{O}$ decomposes in five steps to tetragonal ZrO_2 at 800°C . Dehydration occurs with the loss of 0.5, then 3, then 1 and, in the last dehydration step, 1 molecule of water of hydration. Using a heating rate of 5°C min^{-1} , $\text{Zr}(\text{SO}_4)_2$ decomposes to zirconia from 540°C . This decomposition step consists of at least three intermediate steps that can be derived from the determination of the activation energy values at different transformation degrees (α). Between 800 and 900°C tetragonal zirconia is transformed slowly into monoclinic zirconia which, on cooling to room temperature, remains in the monoclinic structural phase. DTA and DSC measurements showed that 2505 J per g $\text{Zr}(\text{SO}_4)_2 \cdot 5.5\text{H}_2\text{O}$ is needed to obtain ZrO_2 in the monoclinic structure at 900°C . To obtain tetragonal zirconia at 800°C , 2306 J per g of the initial compound is needed.

INTRODUCTION

The thermal decomposition of metal sulphates is represented by the general formula



where M is the metal of oxidation state n . The sulphur trioxide evolved is autocatalytically decomposed on the oxide formed [1]



Tagawa found that the enthalpy change for the decomposition of zirconium sulphate to its oxide and SO_3 at 298 K is $\Delta H_{298}^\ominus = 162.55 \text{ kJ per half mol}$ $\text{Zr}(\text{SO}_4)_2$, and that of the decomposition of SO_3 to SO_2 $\Delta H_{298}^\ominus = 98.89 \text{ kJ per mol}$ SO_3 [1].

Spasibenko found that $\text{Zr}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 5.5, 4.5, 4, 3.5$) undergoes dehydration in two steps to the monohydrate [2]. He also detected the

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formation of the zirconium sulphate hemihydrate and suggested that decomposition of the 0.5 hemihydrate occurs together with the decomposition of the sulphate to the oxide. Bear detected the formation of the monohydrate upon thermal decomposition of the tetrahydrate of zirconium sulphate [3].

Bear [3] reported the formation of cubic ZrO_2 above $650^\circ C$ and monoclinic ZrO_2 above $800^\circ C$. Murase et al. [4] reported that zirconium compounds decompose into three different types of zirconia: the monoclinic form, the monoclinic plus tetragonal form, and the tetragonal plus amorphous form. Wu and Yu [5] reported that cubic or tetragonal, or both, phases of zirconia formed upon calcination of $Zr(SO_4)_2$ at $800^\circ C$.

It is the purpose of this investigation to determine the decomposition products of zirconium sulphate hydrate, to investigate the phases of ZrO_2 that formed, to determine the energy required to decompose the compound and to start a kinetic investigation of the decomposition reactions.

Before starting the kinetic analysis of any process, it is essential to make sure that the process under investigation occurs in a single step. Nearly all the analysis methods for solid-state decomposition reactions described in the literature were developed for single-step processes [6]. Owing to the complexity of the mathematics when complex reactions are involved, the usual methods of fitting decomposition data to a number of mechanism-related equations cannot be used.

As a criterion for a single process, the method described by Vyazovkin and Lesnikovich was used [7]. Activation energy values at different conversion values are determined from dynamic thermogravimetric data using different heating rates. The transformation-degree dependence of the activation energy is determined by this isoconversion method.

The isoconversion method represents the results of several non-isothermal runs as

$$\ln[(d\alpha/dt)\beta] = \ln Af(\alpha) - (E/RT)$$

where β is the heating rate and T the temperature at the degree of decomposition α [8, 9]. This can be used to determine the activation energy E without identification of the reaction model or $f(\alpha)$, by plotting $\ln \beta$ against $1/T$ at constant α . The activation energy values are then calculated from the slopes of the curves. The existence of any dependence indicates that the process is complex. If the activation energy does not change with transformation-degree, the decomposition occurs in a single step. A concave decreasing transformation-degree dependence of the activation energy indicates that the process proceeds through an intermediate reversible stage. If the α - E dependence has a decreasing convex form, the process occurs with a change in the limiting stage of the reaction. An increasing α - E dependence indicates that parallel reactions are involved in the decomposition step [7].

EXPERIMENTAL

Sample preparation

Acid zirconium sulphate tetrahydrate grade 4 (>99% pure) was obtained from Palabora Mining Company, South Africa. Y_2O_3 (>99% pure) was obtained from Sankoh Corporation, Nagoya, Japan. $MgSO_4 \cdot 7H_2O$ AR was bought from Saarchem and $Y_2(SO_4)_2$ was prepared by the reaction of Y_2O_3 with H_2SO_4 .

Thermogravimetric analysis

A Stanton–Redcroft STA 780 simultaneous thermal analyser was used to collect the thermogravimetric data. Nitrogen was used as a dynamic atmosphere (flow rate approx. $20 \text{ cm}^3 \text{ min}^{-1}$). Platinum sample pans were used and temperature calibration was achieved using the ICTA-recommended DTA standards.

DTA and DSC analysis

Differential scanning calorimetric analysis was performed on a Du Pont 910 calorimeter, controlled by a 1090 thermal analyser system. Peak integration and enthalpy calculations were done using the Du Pont partial area integration data analysis program. The analysis was performed in air, using aluminum sample pans. This instrument can only accurately reach temperatures of 700°C ; analysis to temperatures of 1200°C was performed on a Perkin-Elmer DTA 1700 with a System 7/4 controller. Platinum sample pans were used in the Perkin-Elmer DTA and argon was employed as a slow flowing atmosphere ($<40 \text{ cm}^3 \text{ min}^{-1}$). The temperature and enthalpy calibration of both instruments was achieved using the ICTA-recommended DTA standards.

Infrared spectroscopic analysis

Infrared spectroscopic analyses were recorded on a Bruker IFS 113V spectrometer, between 4000 and 400 cm^{-1} . Samples were prepared in the form of KBr discs.

X-ray powder diffraction

X-ray powder diffraction patterns were recorded on a Siemens D501 instrument with two monochromators attached to it. $\text{Cu K}\alpha$ radiation at 25 mA and 30 kV was used.

RESULTS AND DISCUSSION

Thermogravimetric decomposition data

Although the reactant bought was labelled as tetrahydrate, zirconium sulphate seems to be rather hygroscopic and from mass losses (reactant to

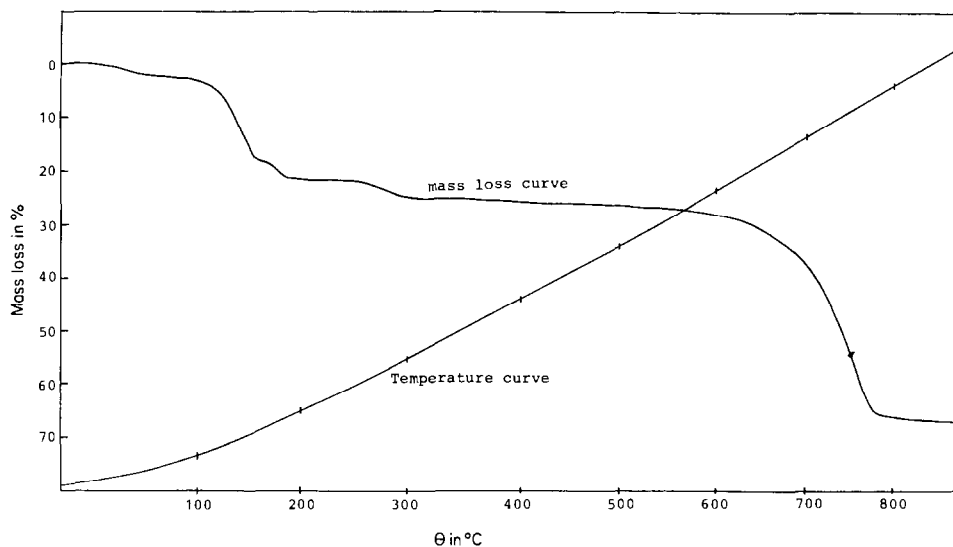
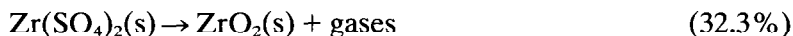
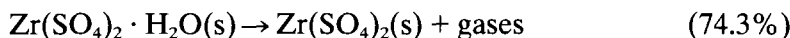
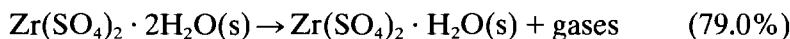
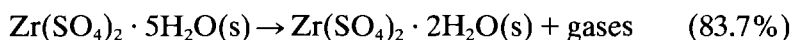
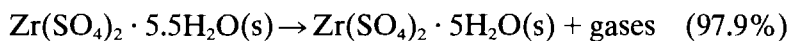


Fig. 1. The mass loss curve of $\text{Zr}(\text{SO}_4)_2 \cdot 5.5\text{H}_2\text{O}$ in nitrogen using a heating rate of 5°C min^{-1} .

$\text{Zr}(\text{SO}_4)_2$ of between 24% and 26%, it was concluded that the starting reactant is zirconium sulphate with 5.5 moles of hydrated water attached to it, $\text{Zr}(\text{SO}_4)_2 \cdot 5.5\text{H}_2\text{O}$. The mass loss curve of this compound using a heating rate of 5°C min^{-1} is given in Fig. 1. From the figure, it seems that products are formed at remaining masses of 98% ($\approx 70^\circ\text{C}$), 83% (163°C), 79% (196°C), 75% (330°C) and 32% (890°C). These values compare very well to the calculated values (in parentheses next to reactions) for the reactions

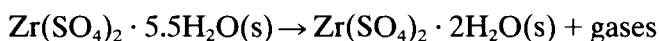


Some variation in the percentage decomposition was observed for some samples which came into contact with the atmosphere (moisture) for different periods of time. This could be correlated very well to the absorption of fewer water molecules from the air. All further analyses were done on samples which had been in contact with air for at least 30 min, to yield the product with 5.5 molecules of hydrated water.

Infrared spectroscopic and X-ray powder diffraction data indicated that the proposed decomposition products were obtained, although the number of hydrated water molecules was not calculated using these two methods.

DTA and DSC analysis

The DSC curve recorded between 40 and 360°C using a heating rate of 5°C min⁻¹ of a sample of zirconium sulphate hydrate is given in Fig. 2. As smaller sample masses (<40 mg) were used and because of the increased sensitivity of the DSC instrument, three completely separated peaks were observed. The first peak occurs between approximately 95 and 165°C and an average endothermic enthalpy change of 476 J per g or 182 kJ per mol Zr(SO₄)₂ · 5.5H₂O was calculated. A shoulder at the start of the peak indicates that a reaction with a small enthalpy change occurs just before the major change. The first peak seems to represent the total reaction:



The second smaller peak between 175 and 190°C represents the loss of one molecule of hydrated water from the zirconium sulphate dihydrate compound. The endothermic enthalpy change of this reaction amounts to an average value of 24 J per g of the initial reactant (the 5.5 hydrated species) or 8 kJ per mol Zr(SO₄)₂ · 2H₂O. The third peak which represents the loss of one molecule of hydrated water from the monohydrate, yielding the dehydrated sulphate, is observed between 250 and 305°C. An average

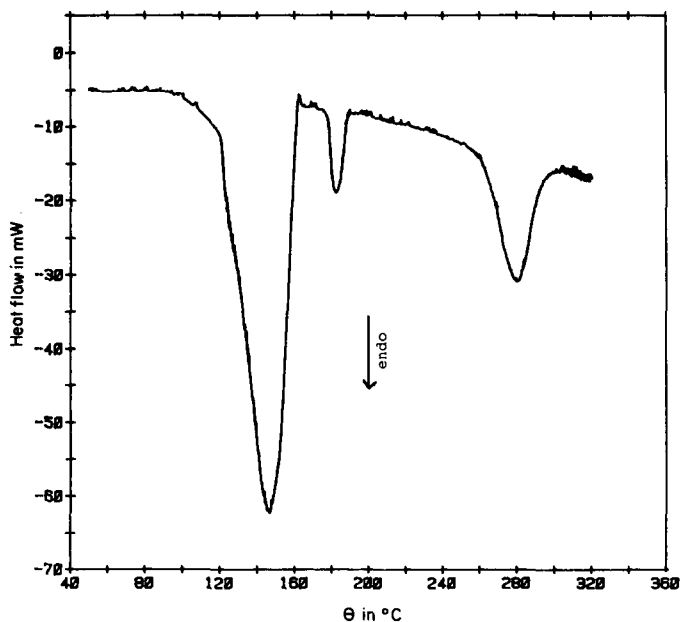


Fig. 2. The DSC curve of the dehydration of Zr(SO₄)₂ · 5.5H₂O using a heating rate of 5°C min⁻¹.

value of 132 J per g of the initial compound or 40 kJ per mol $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ was calculated for the enthalpy change of this reaction.

It must be emphasised that the enthalpy changes above are calculated for the total reactions that occur between the mentioned temperatures. The total reactions could include some phase transition or other non-mass-loss reactions.

The DTA curve between 400 and 1000°C (heating rate 5°C min^{-1}) is given in Fig. 3; two peaks are apparent. The first peak between 540 and 800°C gives an average endothermic enthalpy change of 1647 J per g of the initial hydrated compound, or 2233 J per g $\text{Zr}(\text{SO}_4)_2$ or 633 kJ per mol $\text{Zr}(\text{SO}_4)_2$. Assuming that ΔH is constant between 25 and 800°C, this value is approximately 20% higher than the value of 523 kJ per mol $\text{Zr}(\text{SO}_4)_2$ published by Tagawa [1] for the decomposition of $\text{Zr}(\text{SO}_4)_2$ to ZrO_2 , SO_2 and O_2 . X-ray powder diffraction data of the product at 800°C showed that ZrO_2 in the tetragonal structural phase is formed at this temperature. The average enthalpy change of the second peak (810 to 900°C) is 199 J per g of the initial hydrated compound, 265 J per g $\text{Zr}(\text{SO}_4)_2$ or 75 kJ per mol $\text{Zr}(\text{SO}_4)_2$. X-ray powder diffraction data showed that the ZrO_2 found at 900°C has the monoclinic structure. Whether this peak is due to the phase transition of ZrO_2 in the tetragonal to monoclinic state only, or whether it also includes the last part of the decomposition of $\text{Zr}(\text{SO}_4)_2$ remains under investigation.

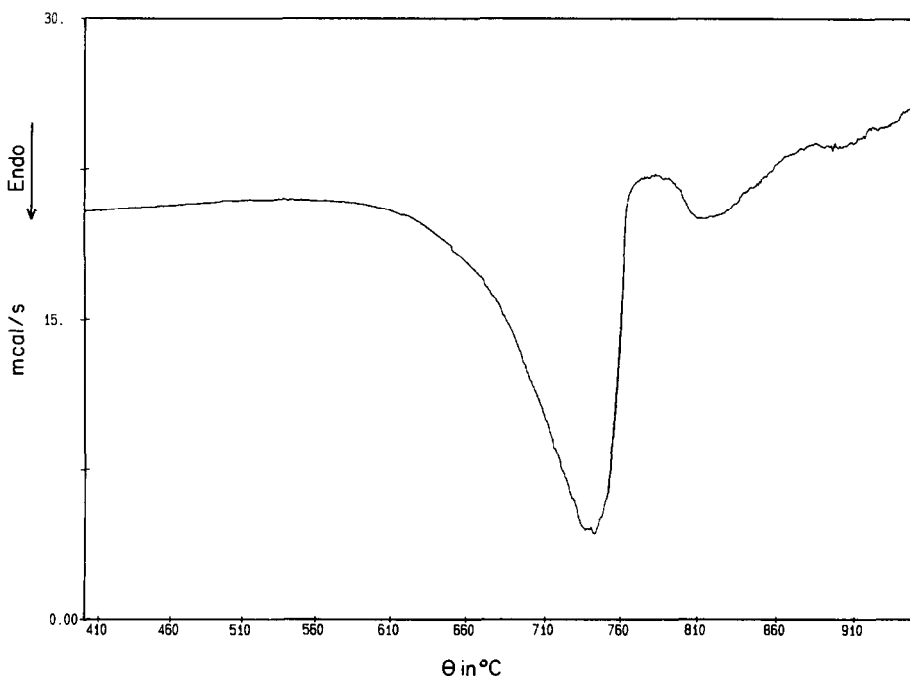


Fig. 3. The DTA curve of the decomposition of $\text{Zr}(\text{SO}_4)_2$ using a heating rate of 5°C min^{-1} .

Infrared spectroscopic and X-ray diffraction analysis

The literature indicates that Y_2O_3 (5.5 wt.%) stabilises ZrO_2 in the tetragonal phase at room temperature [10]. Stabilisation occurs after heating to temperatures between 950 and 1200°C [11]. Gradual decomposition of a saturated solution of $\text{Zr}(\text{SO}_4)_2$ and $\text{Y}_2(\text{SO}_4)_3$ at 800°C resulted in the formation of ZrO_2 which is fully stabilised in the tetragonal structure at room temperature [12]. Heating this product to 1100°C and then cooling it to room temperature, resulted in the same diffractogram, which indicates that no changes took place and that the compound is still in the tetragonal structural phase. Part of the X-ray powder diffraction pattern of this product ($\text{Y}_2\text{O}_3\text{-ZrO}_2$) is given in Fig. 4. The X-ray diffractogram at room temperature of the decomposition product of $\text{Zr}(\text{SO}_4)_2$ (Fig. 4, ZrO_2)

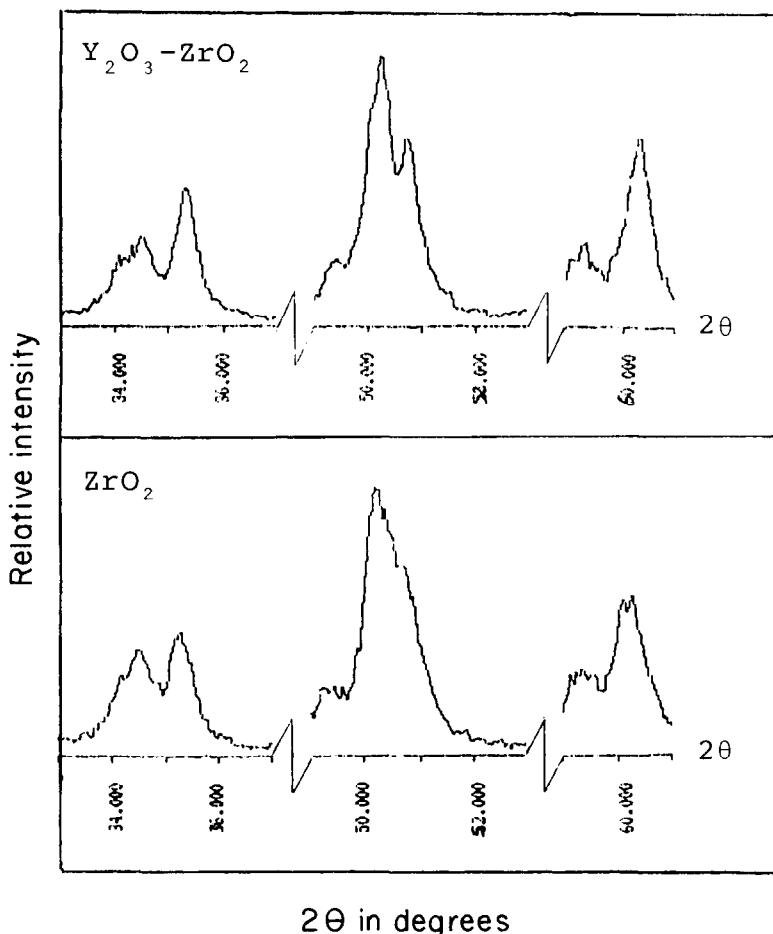


Fig. 4. X-ray powder diffraction patterns at room temperature of ZrO_2 with $\text{Y}_2(\text{SO}_4)_3$ (after heating to 800°C) and of ZrO_2 (obtained from the decomposition of the sulphate at 800°C).

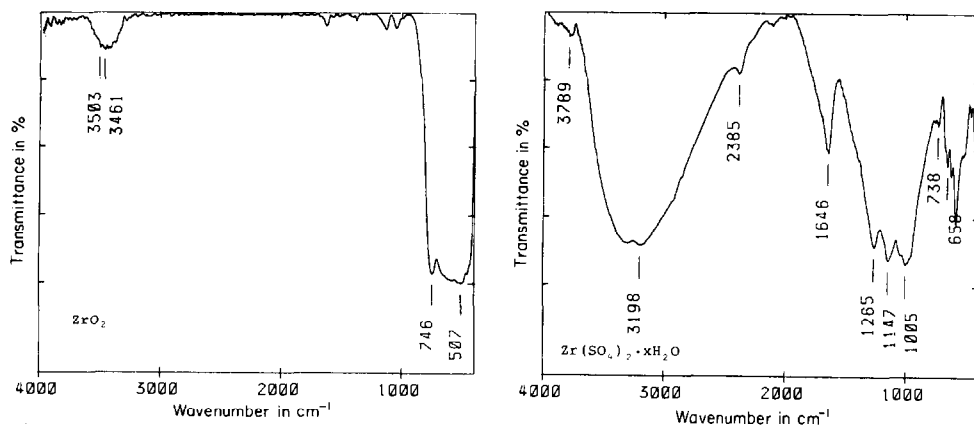


Fig. 5. Infrared spectra of ZrO_2 and $\text{Zr}(\text{SO}_4)_2$.

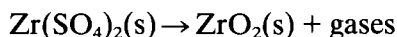
indicates that the product is also in the tetragonal phase below 800°C . Both tetragonal and cubic X-ray diffraction patterns have $I/I = 100$ peaks at $d = 2.96$, but in the 2θ regions of $34\text{--}36^\circ$, $50\text{--}51^\circ$ and $59\text{--}60^\circ$, tetragonal ZrO_2 has two peaks in each region, while cubic zirconia only has one peak in each region [13].

At 800°C , no $\text{Zr}(\text{SO}_4)_2$ could be observed in ZrO_2 , as indicated on the infrared spectra (Fig. 5). This proves that the zirconium sulphate does not act as a stabilising agent to keep zirconia in the tetragonal phase.

It seems that the phase transformation between the tetragonal and monoclinic phases of zirconia (no stabilising agents) above 800°C is a slow reaction: mixtures of these two phases are observed between 800 and 900°C .

Kinetic investigation of the sulphate decomposition step

The decomposition of the dehydrated sulphate to zirconium oxide was investigated kinetically using heating rates of $0.5\text{--}5^\circ\text{C min}^{-1}$ to determine whether it is a single or complex reaction. Samples were heated to constant mass at 350°C to obtain the dehydrated sulphate. The mass loss of $\text{Zr}(\text{SO}_4)_2$ varied between 56.5% and 59.0% . This compares well to the calculated value of 56.5% for the reaction



The dependence of the activation energy on the fraction decomposed (α) is presented in Fig. 6. From this figure it is clear that the reaction is of a complex nature. The reaction can be divided into at least three parts: the first part, between $\alpha = 0.05$ (and probably lower) and 0.4 , seems to represent a reaction in which there is a change in the limiting stage of the reaction, as indicated by the convex decreasing $E\text{--}\alpha$ relationship [2]; the second part, between $\alpha = 0.4$ and 0.9 , seems to have a single-step nature

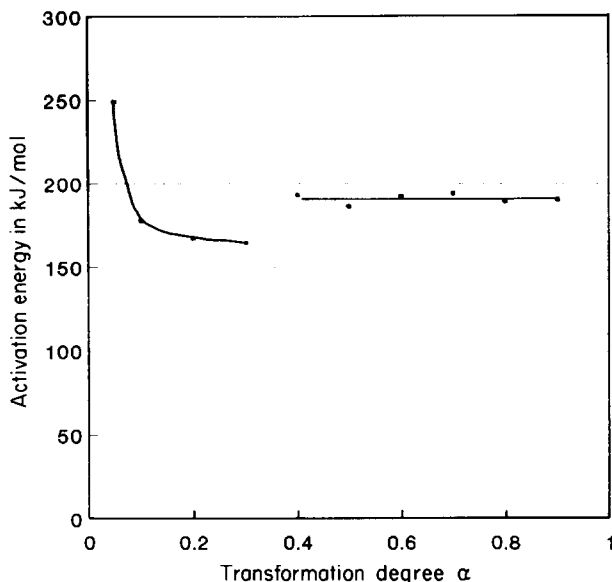


Fig. 6. The dependence of the activation energy on the fraction decomposed (α) for the decomposition reaction of $\text{Zr}(\text{SO}_4)_2$ to ZrO_2 .

and an average activation energy value of 191 kJ mol^{-1} can be calculated for this part; a third part of the reaction seems to occur between the $\alpha = 0.9$ and 1.0, as the reaction has slowed down visibly and the time taken to complete the reaction from an α value of 0.9 is nearly the same as that taken by the reaction from $\alpha = 0.1$ to $\alpha = 0.9$. The kinetics of the decomposition reactions of zirconium sulphate hydrate are under further investigation and will be reported in a future paper.

CONCLUSIONS

Bear [3] reported the formation of zirconium sulphate monohydrate after heating the tetrahydrate for 1 h at $200\text{--}220^\circ\text{C}$. This corresponds very well to the temperature at which the monohydrate is observed in this study, i.e. 196°C , using a heating rate of 5°C min^{-1} . According to Bear this monohydrate is metastable and is only observed during thermal decomposition of the higher hydrates [3]. Dehydration of zirconium sulphate hydrate occurs in 4 steps, i.e. with the loss of 0.5, then 3, then 1 and, in the last reaction, 1 molecule of hydrated water.

Bear [3] further observed that zirconium sulphate decomposes to cubic ZrO_2 above 650°C , which transforms into the monoclinic form above 800°C . The same result was obtained in this study except for the important difference that tetragonal zirconium oxide and not cubic ZrO_2 was observed above 540°C and below 800°C . The tetragonal to monoclinic structural

change of zirconium oxide is a slow process, which takes hours at temperatures just above 800°C. The gradual decomposition of $Zr(OH)_4$ at temperatures below 800°C also resulted in tetragonal zirconia, which is stable on cooling down to room temperature [12]. It thus seems possible that the decomposition of oxo-zirconium and zirconium halide compounds at temperatures less than 800°C will result in the formation of tetragonal zirconia.

DTA and DSC data indicate that a total energy of 2505 J per g $Zr(SO_4)_2 \cdot 5.5H_2O$ is needed to obtain ZrO_2 in the monoclinic structure above 900°C. To obtain tetragonal ZrO_2 , 2306 J per g of the initial compound is needed.

From the kinetic analysis of the decomposition of $Zr(SO_4)_2$ to ZrO_2 , it seems that the decomposition reaction consists of at least three parts, of which the second part is a single-step reaction.

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