

KINETICS OF THE THERMAL DECOMPOSITION OF $\text{Pr}_2(\text{SO}_4)_3$ TO $\text{Pr}_2\text{O}_2\text{SO}_4$

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ABSTRACT

The thermal decomposition kinetics of $\text{Pr}_2(\text{SO}_4)_3$ to $\text{Pr}_2\text{O}_2\text{SO}_4$ have been studied by isothermal weight change determination. The reaction was found to obey a linear law up to $\alpha = 0.5$; beyond $\alpha = 0.5$ it could be described as a phase-boundary controlled process. A dependence of the activation energy upon the sample weight was observed. The changes in surface area and density which occur during the decomposition are also given.

INTRODUCTION

The thermal decomposition of the sulphates of rare earths was first studied by Nathans and Wendlandt [1]. They showed the sequence of the decomposition reactions to be: metal sulphate hydrate \rightarrow metal sulphate \rightarrow metal oxosulphate \rightarrow metal oxide. Preliminary information on the kinetics of the decomposition reactions was obtained.

Kinetics of the thermal decomposition of $\text{Ln}_2(\text{SO}_4)_3$ to $\text{Ln}_2\text{O}_2\text{SO}_4$ were studied isothermally at 950 and 1050°C [2]. The reaction was described by the contracting sphere mechanism. By plotting the equation

$$1 - (1 - \alpha)^{1/3} = kt$$

a line was obtained whose slope changed at one point from k_1 to k_2 . The kinetic parameters were not calculated.

This work is part of our investigations on the structure and thermal decomposition of rare earth sulphates and double sulphates [3].

EXPERIMENTAL

Praseodymium sulphate hydrate was prepared by dissolving praseodymium oxide in 1 M sulphuric acid and evaporating the solution at room temperature. The crystals were dried in a vacuum desiccator and homogenized in a mortar prior to use.

The isothermal weight changes were determined by means of a Mettler TA1 thermoanalyzer. Experimental conditions: TG-Ma sample holder, platinum flat crucibles 8 mm in diameter for 10-mg sample masses, and 12

mm in diameter for 100-mg sample weights, atmosphere of dry air with 5 l h⁻¹ flow rate.

The density of the samples was obtained by displacement of xylene at 20°C. The samples were evacuated and then the xylene was poured into the bottle whilst the sample was still under vacuum.

The surface areas were obtained by the B.E.T. method on a Perkin-Elmer sorptometer. The samples were degassed at 100°C in a flow of pure helium. Measurements were carried out at the boiling point of nitrogen at atmospheric pressure. A cross-sectional area of 16.24 Å² was taken for the nitrogen molecule.

Electron micrographs were taken on a JSM-U2 JEOL electron raster microscope.

RESULTS AND DISCUSSION

The α - t curves for the decomposition $\text{Pr}_2(\text{SO}_4)_3 \rightarrow \text{Pr}_2\text{O}_2\text{SO}_4$ are shown in Figs. 1 and 2. Contrary to Ivakin's results [2], the reduced time plots [4] show poor agreement with the mechanisms describing phase-boundary controlled reactions. On the other hand, there is a close resemblance to the decomposition of MnSO_4 studied by Dollimore and Tonge [5]. All the curves exhibit a constant rate of weight loss up to at least $\alpha = 0.5$. The first part of the isothermal runs ($0.05 < \alpha < 0.5$) is found to obey the Avrami-Erofejev equation $1 - \alpha' = \exp(-kt^n)$, the linear law $\alpha' = kt$, which is a special case of the Avrami-Erofejev expression [5], and the power law $\alpha' = kt^n$. The values of n (Table 1) in the Avrami-Erofejev equation were obtained by plotting $\log|-\log(1 - \alpha')|$ against $\log t$ and those in the power

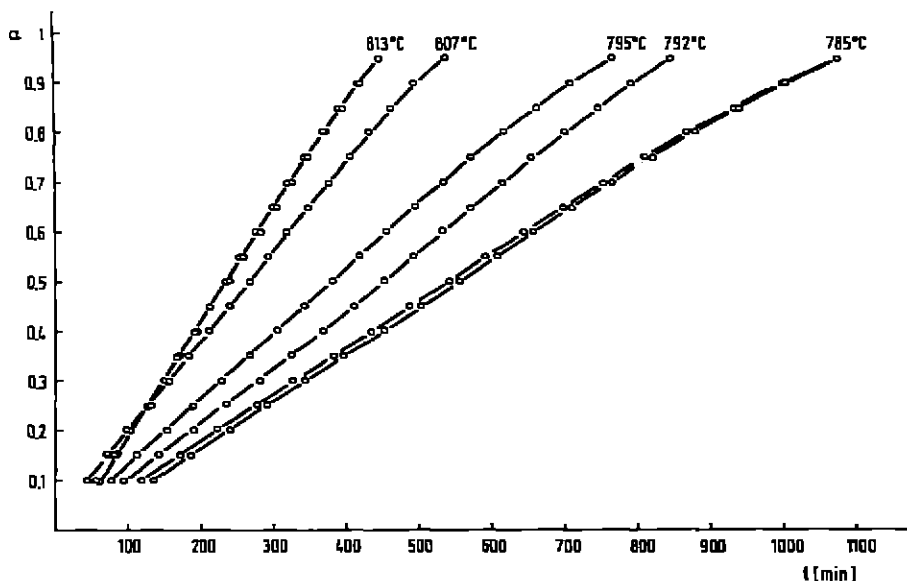


Fig. 1. Isothermal decomposition of $\text{Pr}_2(\text{SO}_4)_3$ to $\text{Pr}_2\text{O}_2\text{SO}_4$ in flowing dry air; sample weight, 100 mg.

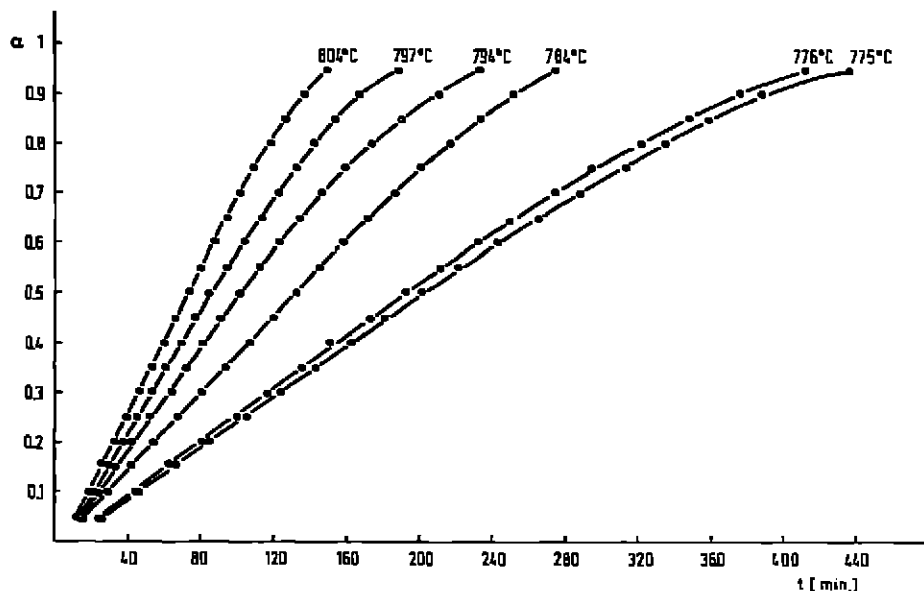


Fig. 2. Isothermal decomposition of $\text{Pr}_2(\text{SO}_4)_3$ to $\text{Pr}_2\text{O}_2\text{SO}_4$ in flowing dry air; sample weight, 10 mg.

law from $\log \alpha'$ vs. $\log t$ ($\alpha' = 1$ at $\alpha = 0.5$). The values of n also bear a close resemblance to those obtained for the decomposition of MnSO_4 [5], where n lies in the range 1.1–1.5. The kinetic parameters for the decomposition of anhydrous praseodymium sulphate were calculated from the linear law (Table 2, Fig. 3).

The reduced time plots for α'' ($\alpha'' = 0$ at $\alpha = 0.5$ and $\alpha'' = 1$ at $\alpha = 1$) cor-

TABLE 1

Experimental values for n

Sample weight	T ($^{\circ}\text{C}$)	Power law		Avramij—Erofeev eqn.	
		n	Correlation coeff.	n	Correlation coeff.
10 mg	804	1.21	0.9996	1.41	0.9998
	797	1.18	0.9992	1.37	0.9999
	794	1.11	0.9993	1.29	0.9996
	784	0.81	0.9981	1.21	0.9997
	776	1.10	0.9996	1.28	0.9998
	775	1.09	0.9998	1.27	0.9996
100 mg	813	1.11	0.9999	1.34	0.9955
	813	1.11	0.9999	1.37	0.9931
	807	0.93	0.9998	1.08	0.9981
	795	0.99	0.9999	1.17	0.9992
	792	1.02	0.9997	1.17	0.9971
	785	1.12	0.9995	1.32	0.9997
	785	1.05	0.9999	1.23	0.9995

TABLE 2

Activation energies from the Arrhenius equation (A) and using Wiedemann's method (W)

	α	E_a (kcal mole ⁻¹)	
		Sample wt: 10 mg	Sample wt: 100 mg
A		82.3 ± 3.7	68.9 ± 2.2
W	0.2	81.7 ± 3.2	62.6 ± 3.9
	0.3	81.5 ± 5.8	69.1 ± 3.5
	0.5	78.3 ± 5.2	73.8 ± 2.8
	0.6	77.9 ± 2.7	69.5 ± 6.4
	0.7	79.5 ± 4.2	70.7 ± 6.6
	0.8	80.6 ± 5.0	71.9 ± 1.8

respond roughly to the phase-boundary controlled reaction for a disc, $1 - (1 - \alpha'')^{1/2} = kt$. As the agreement is rather coarse, we did not analyse the second part of the curve using the equation mentioned above.

For the sake of comparison, the whole α range was analysed according to

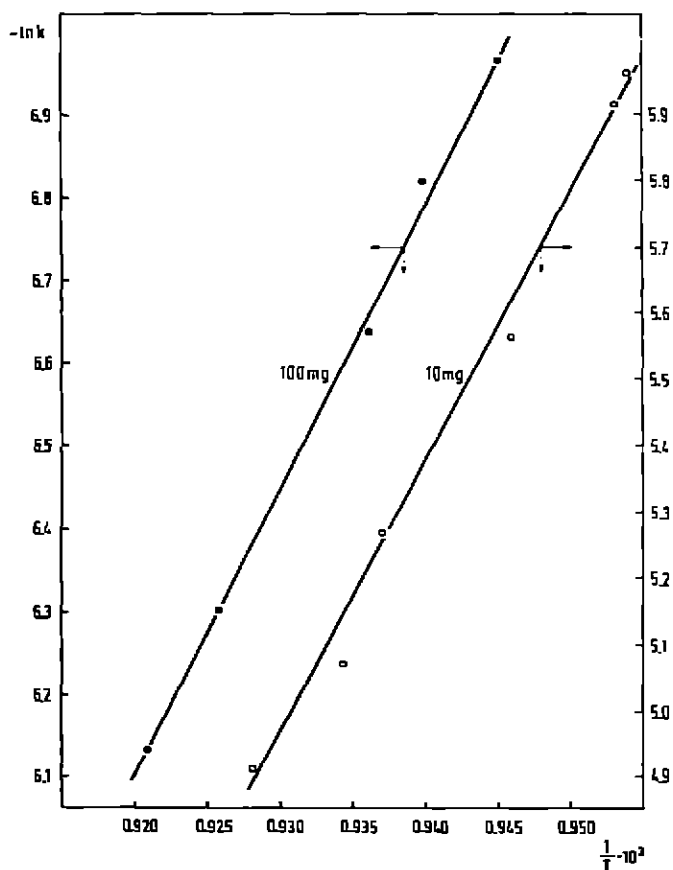


Fig. 3. Arrhenius plots for $\text{Pr}_2(\text{SO}_4)_3$ decomposition up to $\alpha = 0.5$; sample weight: ●, 100 mg; ○, 10 mg.

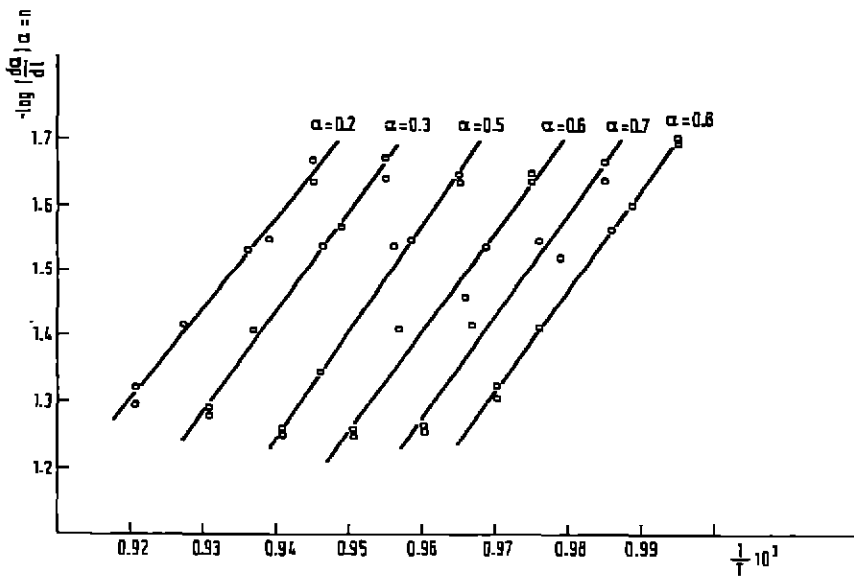


Fig. 4. Plots obtained by Wiedemann's method for various α values; sample weight, 100 mg.

the method of Wiedemann et al. [6]. In Figs. 4 and 5 the function $-\log(d\alpha/dt)$ is plotted vs. $1/T$, while the activation energies are given in Table 2. The activation energies for various α values are practically constant within the same sample mass. Only the E_a at $m_0 = 100$ mg and $\alpha = 0.2$ gave a somewhat lower value than the others. There is also good agreement between the E_a values obtained by Wiedemann's method and those deduced from the linear law.

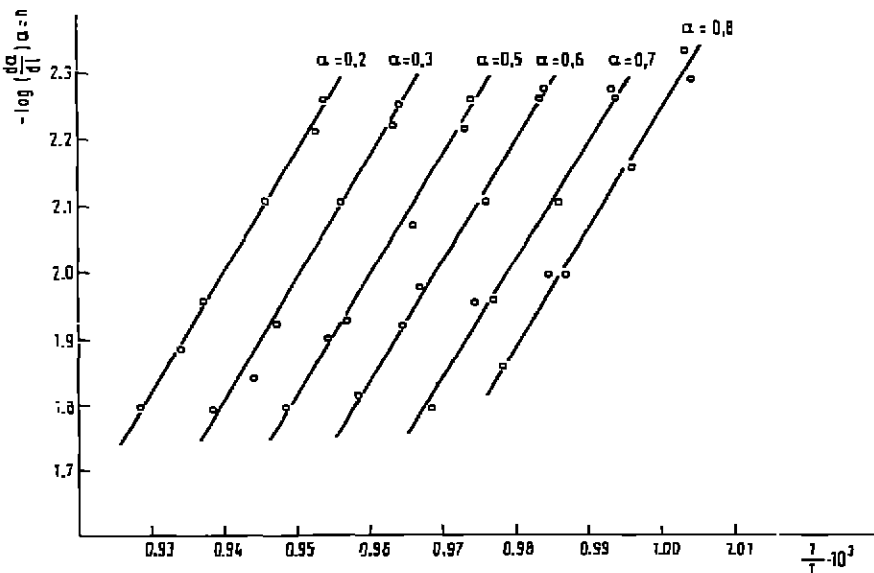


Fig. 5. Plots obtained by Wiedemann's method for various α values; sample weight, 10 mg.

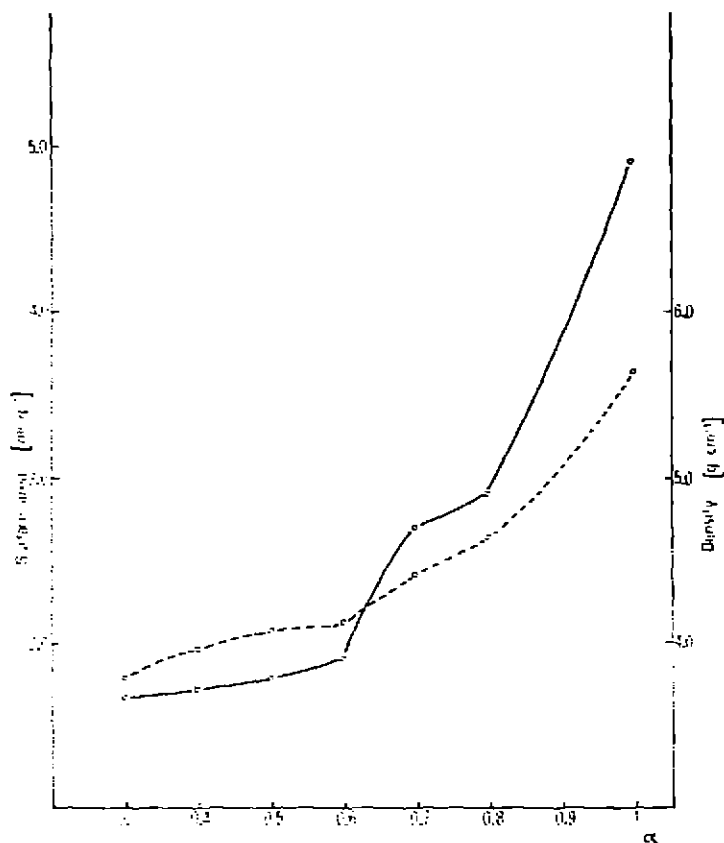


Fig. 6. Plots of surface area (solid lines) and density (dashed lines) as a function of fraction decomposed.

Inspection of Table 2 also shows that activation energies at 10-mg sample weights are roughly $10 \text{ kcal mole}^{-1}$ higher than those at 100 mg. The dependence of kinetic parameters on the experimental conditions was analysed thoroughly by Gallagher and Johnson [7]. They also found that E_a increased with decreasing sample sizes and concluded that thermal transport was rate determining.

The plots of surface area and density as a function of fraction decomposed are given in Fig. 6, while the corresponding electron micrographs are given in Fig. 7. Electron micrographs at $\alpha = 0.1$ – 0.75 show that the surface becomes more furrowy toward the end of the reaction. The cracks formed by breaking up the particles are quite visible in the micrograph which represents the crystallized $\text{Pr}_2\text{O}_2\text{SO}_4$.

There is a small change in the surface area up to $\alpha = 0.6$. This is in accordance with the linear law which describes the first part of decomposition. As already stated with reference to MnSO_4 decomposition, the rate of weight loss must be linear if the diffusion is fast enough to enable the surface area to remain constant. Later, the rate of the reaction slowly diminishes due to a limited supply of the reagent. This process is accompanied by the breaking up of the particles and an increase in the surface area.

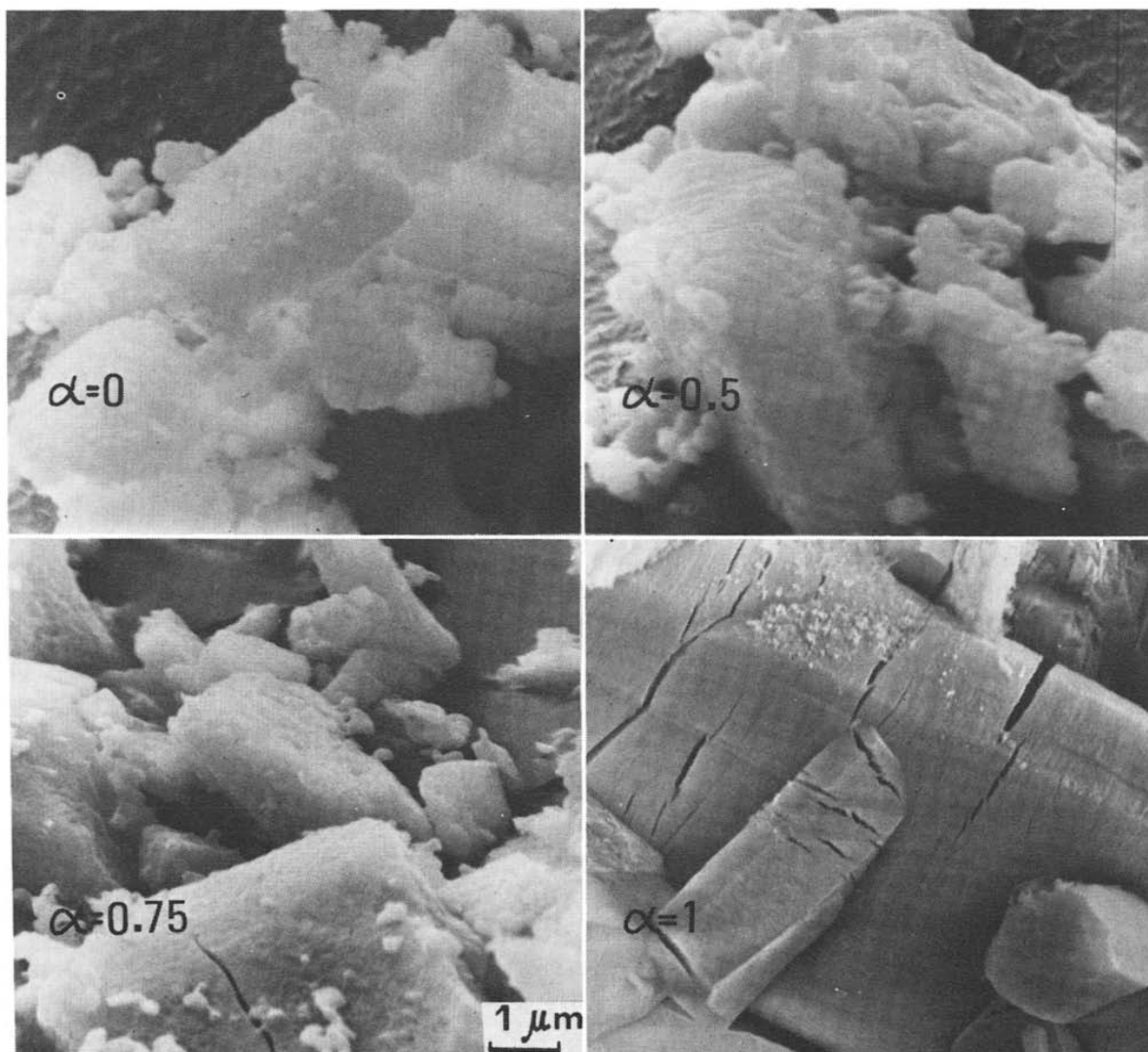


Fig. 7. Electron micrographs (magnification $\times 10\,000$).

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REFERENCES

- 1 N.W. Nathans and W.W. Wendlandt, *J. Inorg. Nucl. Chem.*, **24** (1962) 869.
- 2 A.A. Ivakin, *Izv. Sib. Otd. Akad. Nauk S.S.S.R.*, **1** (1962) 49.
- 3 N. Bukovec, P. Bukovec, L. Golič and J. Šiftar, *Monatsh. Chem.*, **108** (1977) 997.
- 4 J.H. Sharp, G.W. Brindley and B.N. Narahaki Achar, *J. Am. Ceram. Soc.*, **49** (1966) 379.
- 5 D. Dollimore and K.H. Tonge, in G.M. Schwab (Ed.), *5th Int. Symp. Reactivity Solids*, Elsevier, Amsterdam, 1965, p. 497.
- 6 H.G. Wiedemann, A.V. Tets and H.P. Vaughan, Presented at the Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, 21 February, 1966.
- 7 P.K. Gallagher and D.W. Johnson, Jr., *Thermochim. Acta*, **6** (1973) 67.