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KINETICS OF THE DEHYDRATION OF $CsNd(SO_4)_2 \cdot 4\ H_2O$

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ABSTRACT

The kinetics of the dehydration of $CsNd(SO_4)_2 \cdot 4\ H_2O$ to $CsNd(SO_4)_2 \cdot H_2O$ and then to $CsNd(SO_4)_2$ are studied by isothermal weight change. The reactions are phase-boundary-controlled. Reaction mechanism and activation energy depend on sample weight.

INTRODUCTION

Dehydration of $CsLn(SO_4)_2 \cdot 4\ H_2O$ (Ln = La—Lu and Y) has previously been studied by thermogravimetry and differential thermogravimetry [1]. Two DTG peaks were observed for all compounds except $CsLu(SO_4)_2 \cdot 4\ H_2O$, where only a single DTG effect appeared. By isothermal measurements, stable monohydrates were isolated for Pr, Nd, Sm, Eu and Gd. A two-stage dehydration fitted the crystal structure of the compounds which are all isomorphous and contain two different types of water molecule [3]. Three water molecules are coordinated to a neodymium atom and the fourth is held in the lattice. The compound was formulated as $Cs[Nd(SO_4)_2(H_2O)_3]H_2O$.

This paper examines the dehydration kinetics of $CsNd(SO_4)_2 \cdot 4\ H_2O$ under isothermal conditions.

EXPERIMENTAL

The compound was prepared as described elsewhere [2]. The isothermal runs were produced on a Mettler thermoanalyser TA1 in dry air at a flow rate of $5\ l\ h^{-1}$. A flat crucible of 12 mm diameter was used for 100-mg samples, and of 8 mm diameter for 10-mg sample masses. An optical Metalloplan—Leitz Wetzlar microscope with a magnification of 100 was used to photograph a monocrystal of $CsNd(SO_4)_2 \cdot 4\ H_2O$ at 80°C.

RESULTS

Preliminary isothermal measurements have shown [1] that the monohydrate can be obtained in a stoichiometrically and crystallographically defined

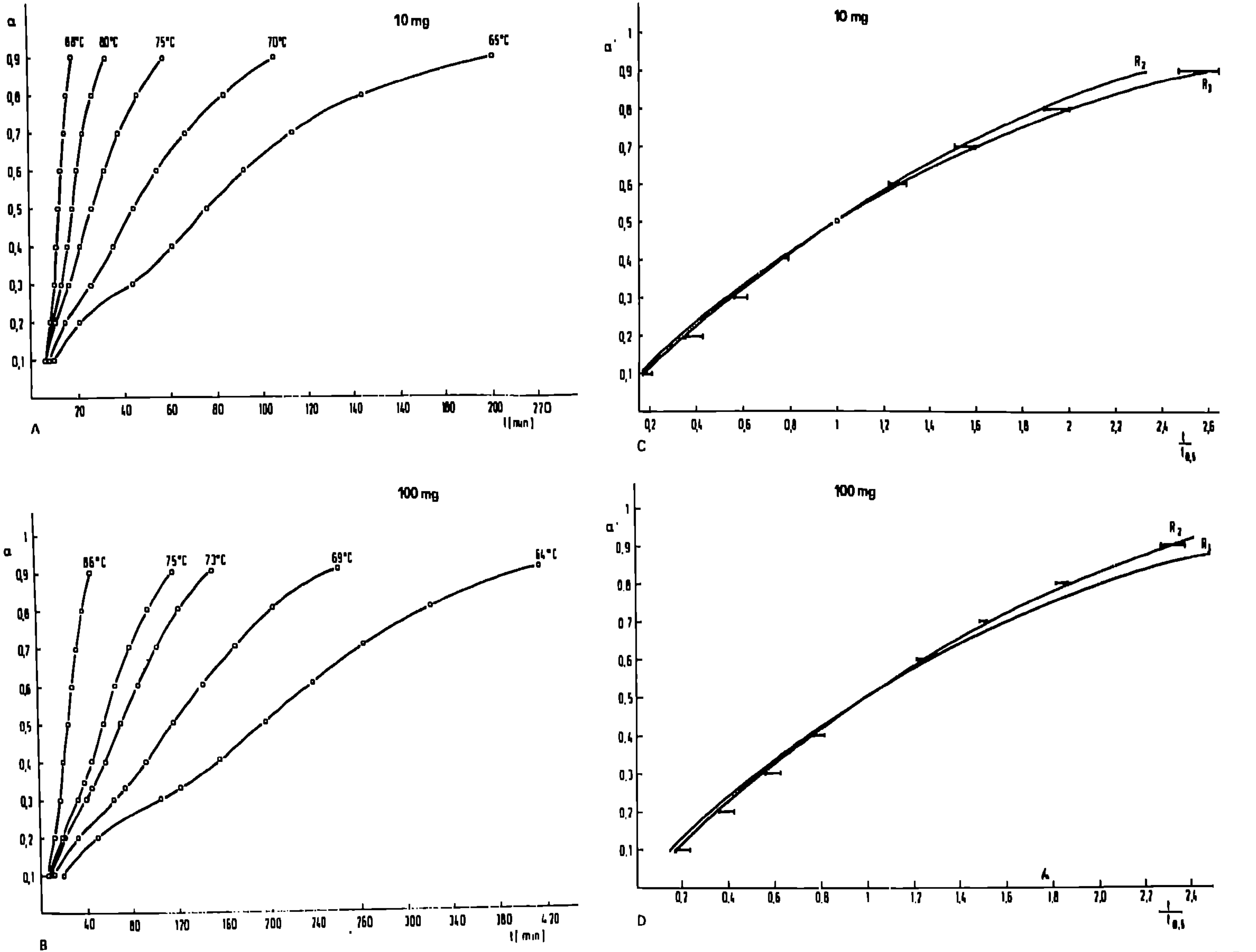

Fig. 1. Isothermal decomposition of $CsNd(SO_4) \cdot 4\,H_2O$ to $CsNd(SO_4)_2 \cdot H_2O$. A, B: Isothermal decomposition curves; C, D: reduced time plots.

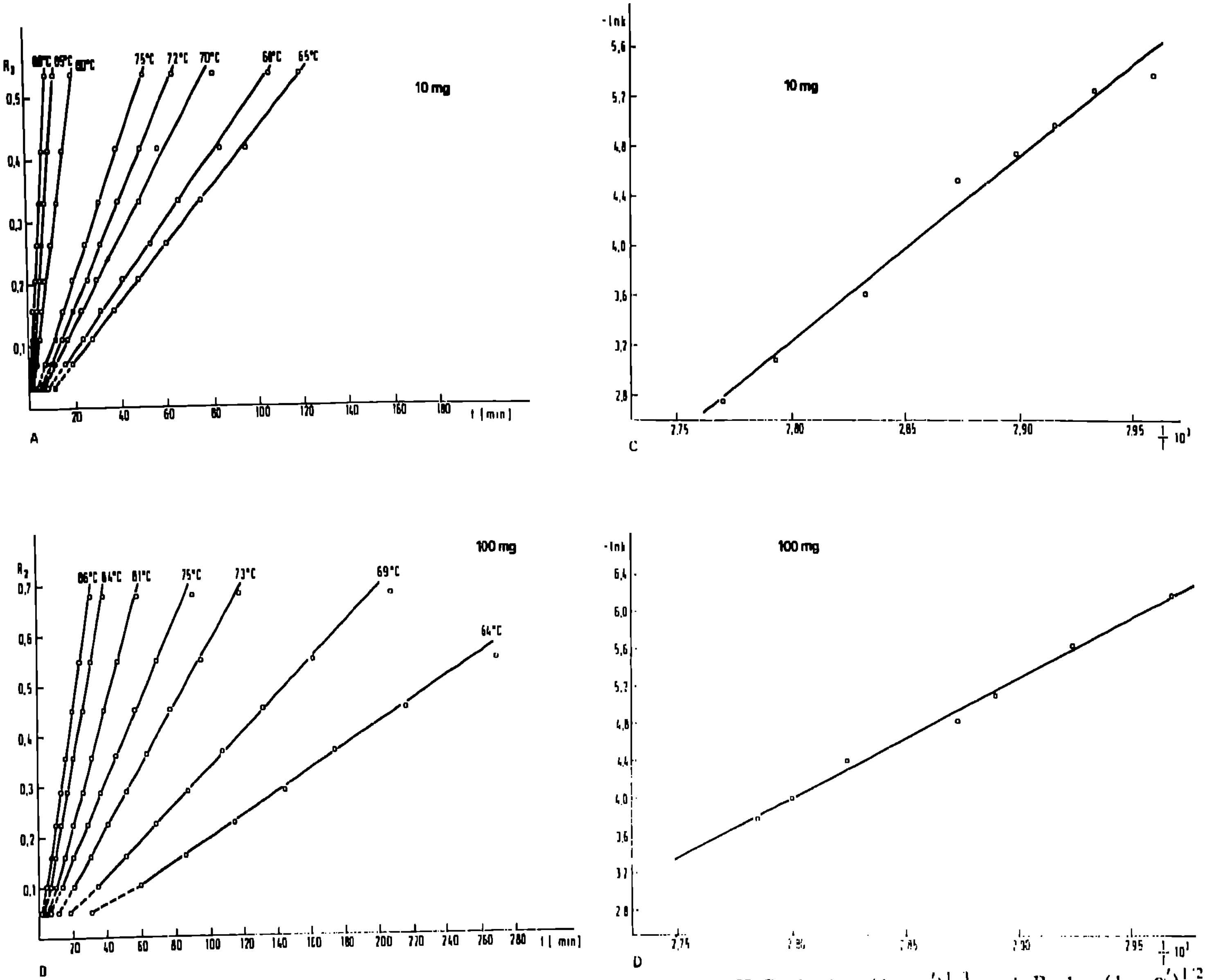

Fig. 2. Isothermal decomposition of $CsNd(SO_4)_2 \cdot 4\ H_2O$ to $CsNd(SO_4)_2 \cdot H_2O$. A: $1-(1-\alpha')^{1/3}$ vs. t; B: $1-(1-\alpha')^{1/2}$ vs. t; C, D: Arrhenius plots.

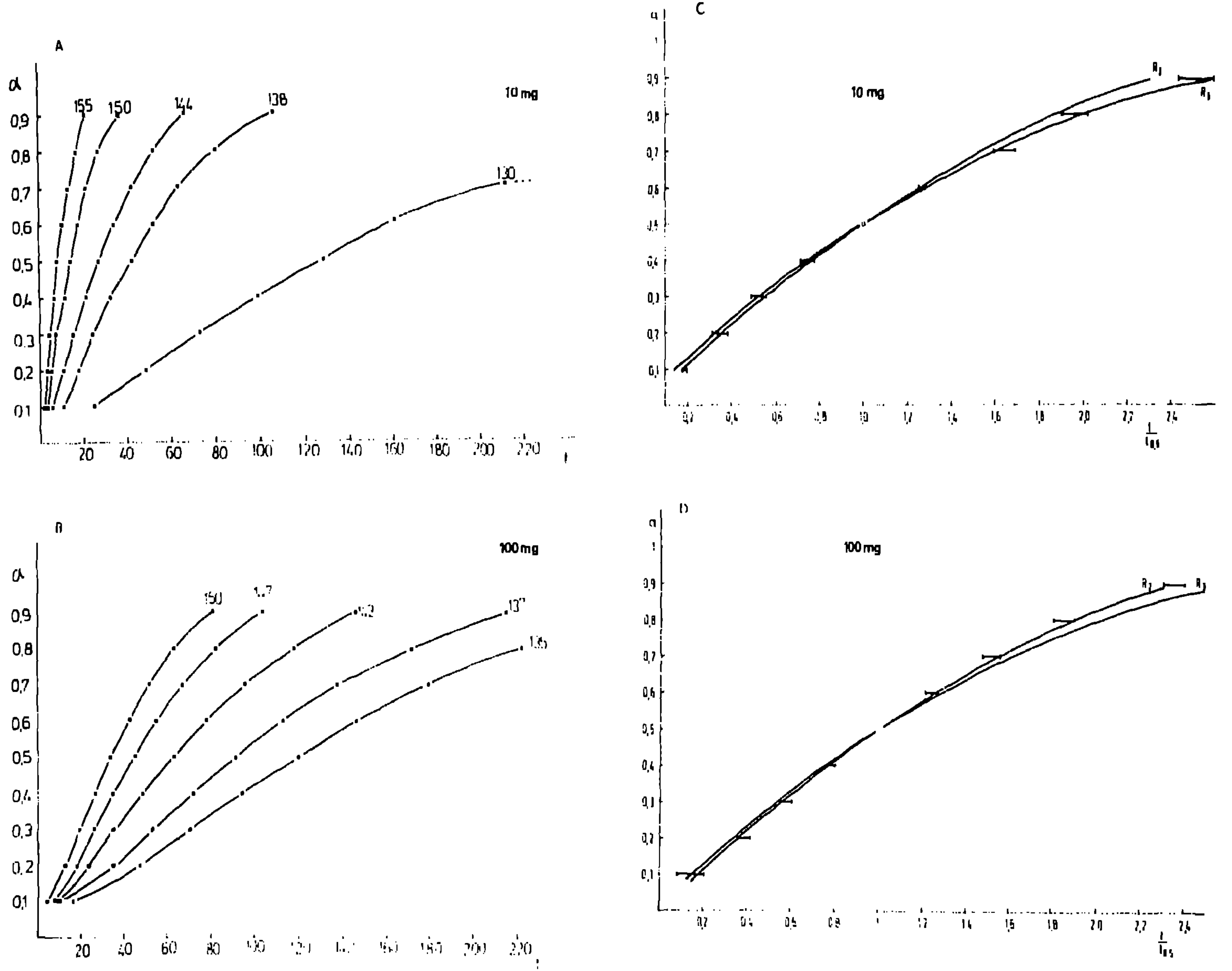

Fig. 3. Isothermal decomposition of $CsNd(SO_4)_2 \cdot H_2O$ to $CsNd(SO_4)_2$. A, B: Isothermal decomposition curves; C, D: reduced time plots.

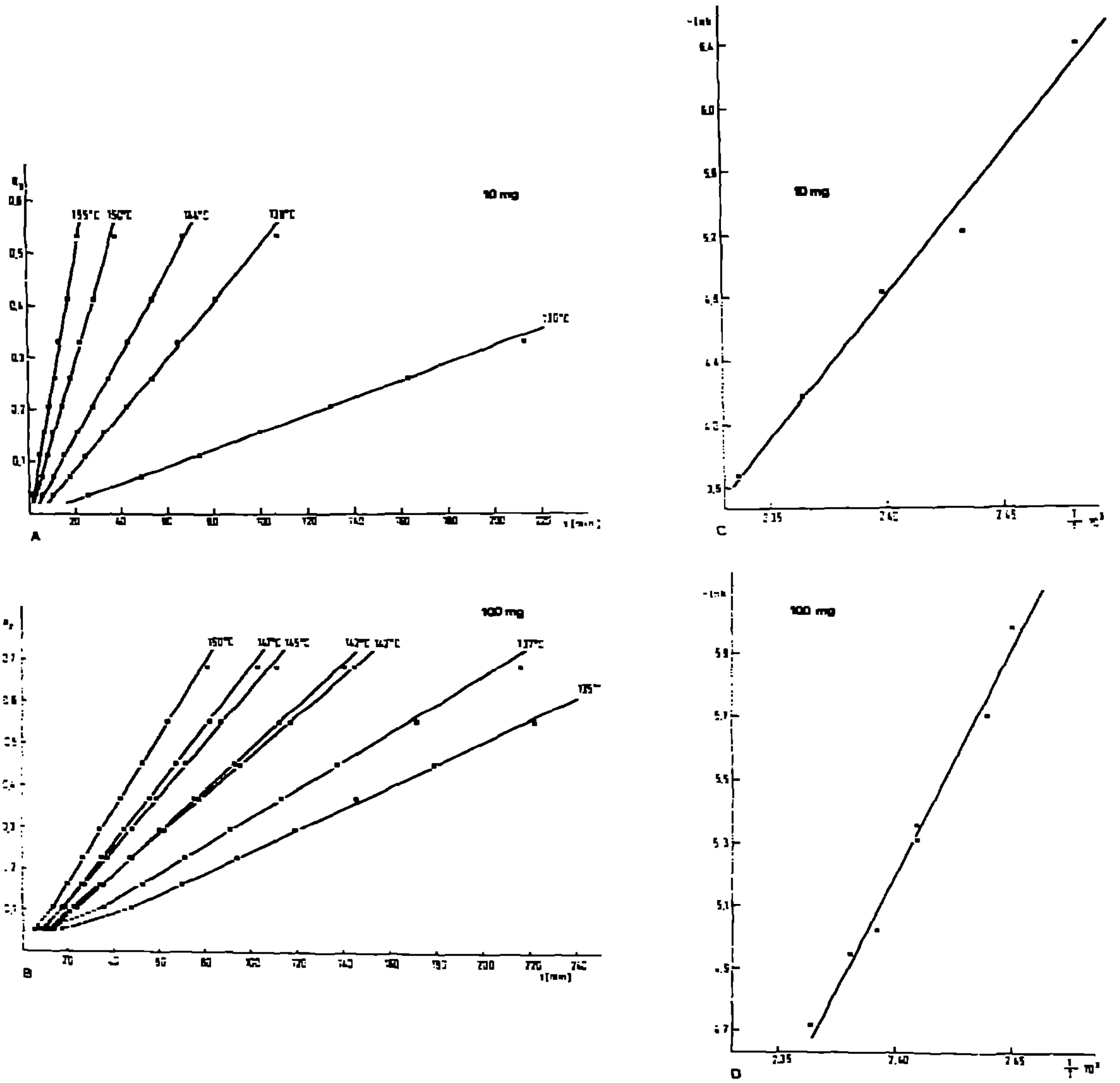

Fig. 4. Isothermal decomposition of $CsNd(SO_4)_2 \cdot H_2O$ to $CsNd(SO_4)_2$. A: $1 - (1 - \alpha)^{1/3}$ vs. t; B: $1 - (1 - \alpha)^{1/2}$ vs. t; C, D: Arrhenius plots.

TABLE 1

Activation energies from Wiedemann's method

Reaction	α	E_a (kJ mole^{-1})	
		Sample weight 10 mg	Sample weight 100 mg
1	0.2	131 ± 9	106 ± 6
	0.5	124 ± 7	105 ± 4
	0.6	128 ± 7	105 ± 5
	0.7	136 ± 9	103 ± 5
	0.8	136 ± 9	113 ± 7
2	0.5	158 ± 3	114 ± 5

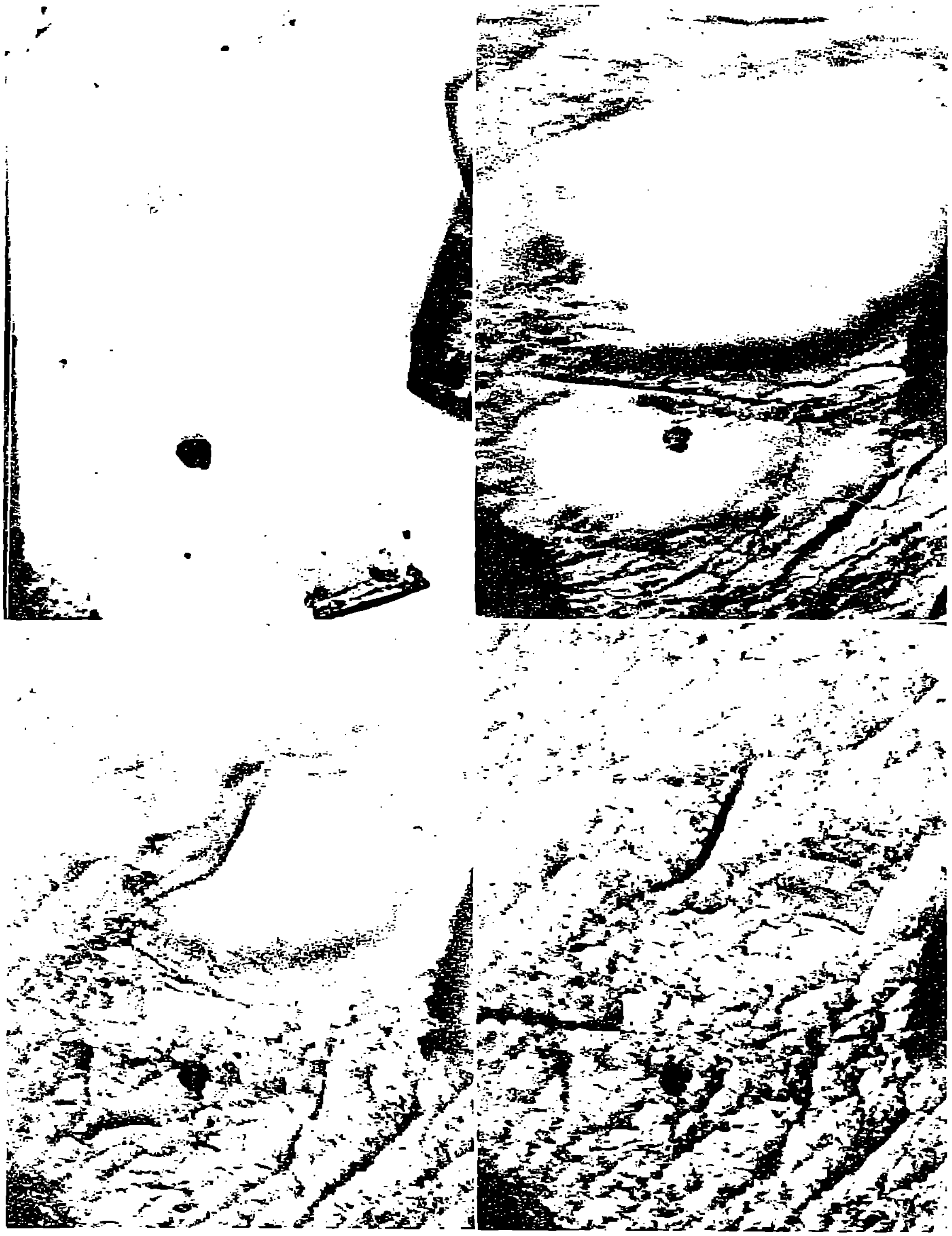

Fig. 5. Micrographs of the dehydration (magnification 100 ×).

form at 80°C which is fairly stable up to 110°C. The dehydration kinetics were therefore studied for

$$CsNd(SO_4)_2 \cdot 4\,H_2O \rightarrow CsNd(SO_4)_2 \cdot H_2O \qquad (1)$$

$$CsNd(SO_4)_2 \cdot H_2O \rightarrow CsNd(SO_4)_2 \qquad (2)$$

in the temperature range 64—88°C for reaction (1) and 130—155°C for reaction (2).

Typical isothermal decomposition curves for reaction (1) are given in Fig. 1. The dehydration starts very fast and when isothermal conditions are reached about 10% of the total water is already lost. Reaction (1) proceeds in two overlapping stages. The beginning of the second stage was determined by extrapolation ($\alpha' = 0.0$ at $\alpha = 0.35$). Both parts of the curves were analysed by reduced time plots [4]. The first period did not give satisfactory results; this is not surprising because both the beginning and end of this stage are ill defined. The second stage of reaction (1) can be described by two phase-boundary-controlled mechanisms (Fig. 1). The contracting sphere model $R_3(\alpha') = 1 - (1 - \alpha')^{1/3}$ can be applied to 10-mg samples, whereas the contracting disc model $R_2(\alpha') = 1 - (1 - \alpha')^{1/2}$ holds for 100-mg sample masses.

Plots of the corresponding $f(\alpha')$ values against time for $\alpha' = 0.1$—0.9 are shown in Fig. 2. The Arrhenius plots (Fig. 2) gave activation energies of 124 ± 6 kJ mole^{-1} for 10-mg samples and 107 ± 4 kJ mole^{-1} for 100-mg samples.

The same approach has been used to follow reaction (2). The decomposition curves are simpler in this case. According to reduced time plots the same decreasing rate mechanisms operate (Fig. 3). Plots of $f(\alpha)$ vs. t and $\ln k$ vs. $1/T$ are given in Fig. 4. The activation energies were 151 ± 3 kJ mole^{-1} for 10-mg sample masses and 119 ± 6 kJ mole^{-1} for 100-mg samples calculated for the region $\alpha = 0.1$—0.9.

As the first part of the curve for reaction (1) could not be described satisfactorily, we also applied Wiedemann's method [5]. Activation energies for reaction (1) were calculated for various α values and for reaction (2) at $\alpha = 0.5$. Table 1 shows that these results are comparable with those obtained for phase-boundary-controlled mechanisms.

The dehydration was also followed with an optical microscope (Fig. 5). On heating crystals of $CsNd(SO_4)_2 \cdot 4\,H_2O$ to 80°C, cracks formed and in a few seconds the surface was covered by a new phase. No further change in the surface then occurred. Microscopic observations at 80°C showed rapid surface nucleation and then advance of the interface towards the crystal. The thickness for 100-mg samples is about 4 times greater than that for 10-mg samples, thus giving different water vapour pressures within the samples. This could be the reason for the difference in kinetic parameters of the 10-mg and 100-mg samples.

ACKNOWLEDGEMENT

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