

THE ISOTHERMAL DECOMPOSITION OF METAL SULPHATE POWDERS IN HIGH VACUUM

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ABSTRACT

The isothermal decomposition of MSO_4 powder ($M = Cu^{2+}, Ni^{2+}, Zn^{2+}$) in a high vacuum was studied by following the mass of 40 mg samples in a small platinum cup. The respective rate equations are $dw/dt = k_1$, $dw/dt = k_2$, $dw/dt = k_3w^{-1}$, where w is weight loss and t is time, and the activation enthalpies are 262 ± 10 kJ mole⁻¹, 260 ± 21 kJ mole⁻¹, and 238 ± 14 kJ mole⁻¹. The morphologies of the decompositions were observed and their correlation with the physical measurements is discussed.

INTRODUCTION

Most kinetic studies of decomposition reactions [i.e. $A(s) \rightarrow B(s) + C(g)$] have involved conditions in which each particle of the reactant mass decomposes independently. Under such conditions the kinetics have been successfully explained in terms of the formation, growth and interaction of product nuclei [1]. While work on packed powders has produced less well-defined data, a common observation is that the reaction proceeds at a single macroscopic interface [2,3], as if the powder were a continuous porous solid. The present study is of the isothermal decomposition of packed powders of $CuSO_4$, $NiSO_4$, and $ZnSO_4$, in a high vacuum, using small samples and low reaction rates. These conditions ensure that neither diffusion of product gas from the exterior surface of the sample, nor heat flow to maintain the reaction, is rate limiting. The results are accordingly more easily interpreted than when flowing inert atmospheres are involved. Visual examination and scanning electron microscopy provide evidence of the morphological course of these reactions.

SAMPLE PREPARATION

Fisons analytical reagent salts were dehydrated in a muffle furnace for 48 h and desiccated under vacuum for a further 48 h. The anhydrous cake was then ground to a fine powder in an agate mortar and a single source was drawn upon for all experiments with a particular salt. Scanning electron microscopy (SEM) showed the resulting $CuSO_4$ and $NiSO_4$ particles to be crystalline, while the $ZnSO_4$ particles were highly porous.

EXPERIMENTAL

A 40 mg sample of the powder was packed by gentle tapping in a cylindrical platinum cup 7 mm in diameter and 7 mm high. This was suspended in the hot zone of an evacuated furnace by a fine platinum thread from one arm of a C.I. Electronics Ltd. microbalance. The vertically mounted cylindrical furnace and the balance arrangement were as described previously [4], but platinum thread replaced molybdenum for the present application to avoid attack by the acid gas. A calibrated chromel—alumel thermocouple, situated 2 mm from the cup, measured the sample temperature and the vacuum was created by a rotary pump and an oil diffusion pump. To avoid disturbing the microbalance during measurements the diffusion pump alone maintained the vacuum, which was always better than 2×10^{-5} torr, as measured by a Penning gauge.

Our procedure was to take the temperature up to 350°C while simultaneously creating the vacuum, following which a period of 5 h was allowed for thermal equilibration. The temperature was next raised to near the desired value at $10^\circ\text{C min}^{-1}$ and then, upon switching off the temperature programmer, there was a further rise and fall of about 7°C before the temperature stabilized at better than $\pm 2^\circ\text{C}$ for the remainder of the experiment. Weight loss readings were started when the temperature became steady, which was about 10 min after switching off the programmer.

Typically decomposition was taken to the extent of 15% of the reactant mass, after which the residue was made into a nujol mull and its IR spectrum recorded at slow scan speed in the region $800\text{--}1300\text{ cm}^{-1}$. The spectra of all possible decomposition products have been recorded in this region by Pechkovskii and Gaisinovitch [5] and our identifications are based on these.

RESULTS

Morphological evidence

CuSO_4 and NiSO_4 decomposed at a clearly visible, single macroscopic interface of constant area, which formed on the exposed surface of the sample and advanced in a direction parallel to the axis of the cup. The product layer in both cases was a powder of loosely packed oxide particles which SEM showed to be crystalline. There was no evidence of $\text{CuO} \cdot \text{CuSO}_4$, although it may be a transient intermediate. The remaining reactant showed only slight nucleation with oxide in both cases. ZnSO_4 decomposed similarly but with one important difference. The product powder, identified as $\text{ZnO} \cdot 2\text{ZnSO}_4$, sintered partially and created a gap between itself and the wall of the cup. This sintering process was confirmed by SEM, which showed the joining of porous particles of $\text{ZnO} \cdot 2\text{ZnSO}_4$.

Physical measurements

Plots of weight loss, w , against time were linear for CuSO_4 and NiSO_4 at all temperatures and up to at least 80% conversion to oxide, indicating rate

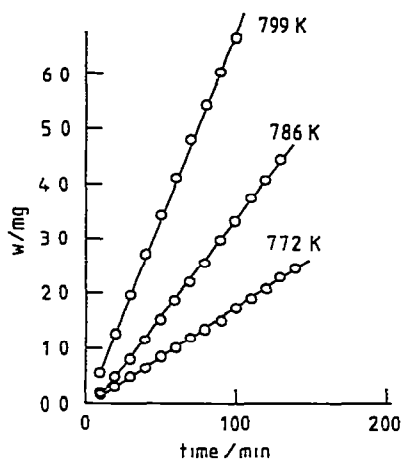


Fig. 1. Representative plots of weight loss against time for CuSO_4 decomposition.

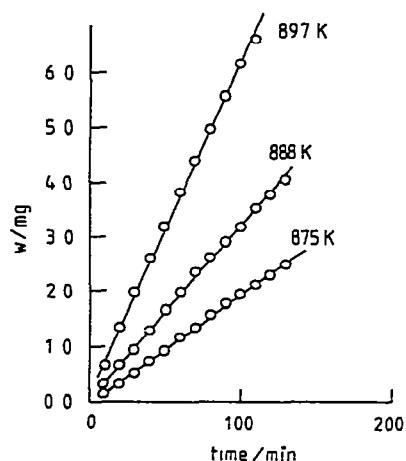


Fig. 2. Representative plots of weight loss against time for NiSO_4 decomposition.

equations $dw/dt = k_1$ and $dw/dt = k_2$ (Figs. 1 and 2). Apart from a short initial period, ZnSO_4 loses weight linearly with the square root of time, indicating the rate equation $dw/dt = k_3 w^{-1}$ of which $w = \sqrt{2 k_3} \sqrt{t}$ is a solution (Fig. 3).

The rate constants varied with temperature, T , according to the following equations

$$\log[k_1/\text{mg min}^{-1}] = -\frac{(1.367 \pm 0.054) \times 10^4 \text{ K}}{T} + 15.94 \pm 0.69$$

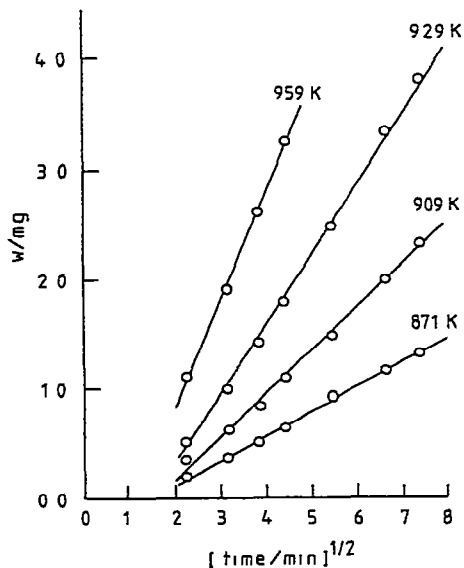


Fig. 3. Representative plots of weight loss against the square root of time for ZnSO_4 decomposition.

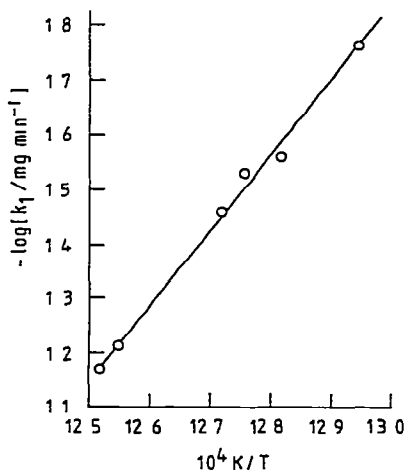


Fig. 4. The temperature dependence of the CuSO_4 decomposition rate constant.

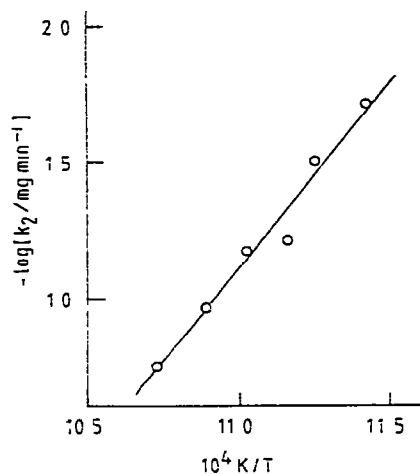


Fig. 5. The temperature dependence of the NiSO_4 decomposition rate constant.

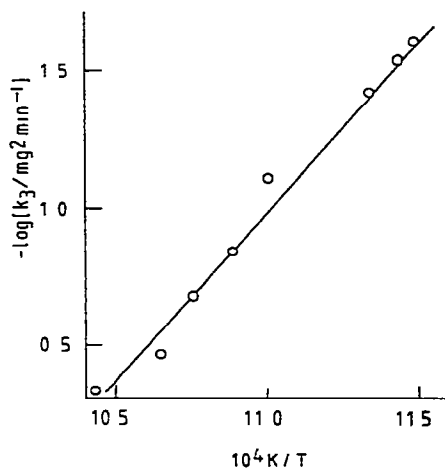


Fig. 6. The temperature dependence of the ZnSO_4 decomposition rate constant.

$$\log[k_2/\text{mg min}^{-1}] = -\frac{(1.360 \pm 0.108) \times 10^4 \text{ K}}{T} + 13.85 \pm 1.20$$

$$\log[k_3/\text{mg}^2 \text{ min}^{-1}] = -\frac{(1.243 \pm 0.073) \times 10^4 \text{ K}}{T} + 12.69 \pm 0.81$$

as shown (Figs. 4–6).

DISCUSSION

Our results associate a constant rate of weight loss with a product layer which is a powder of loosely packed crystalline particles (NiO and CuO), and a diminishing rate with a partially sintered powder of porous particles ($\text{ZnO} \cdot 2 \text{ZnSO}_4$). A simple correlation between the physical and morphological data can be made if one assumes gas is released at a constant rate from the interface and the product layer can “reflect” some of this back to the interface to give a reverse reaction. The mechanism of this “reflection” depends on the nature of the gas flow. For all our experiments the mean free paths of gas molecules at the maximum possible pressures in the product layer (i.e. equilibrium vapour pressures) exceed the dimensions of interparticle spaces measured by SEM, indicating Knudsen flow conditions [6]. Clausing [7] has studied the Knudsen flow of molecules from a source through a tube of length L and radius R to a perfect condenser. The probability that a molecule entering the tube will reach the condenser is

$$P = 1/(1 + 0.4 L/R) \quad (1)$$

We recognise that eqn. (1) is not directly applicable to flow through the spaces of a powder and that the cold traps in our vacuum line are not quite

TABLE 1

Comparison of activation enthalpies with standard enthalpy changes

Reaction	ΔH_a (kJ mole ⁻¹)	ΔH^0 (kJ mole ⁻¹)
$\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_3$	262	217
$\text{NiSO}_4 \rightarrow \text{NiO} + \text{SO}_3$	260	248
$3 \text{ZnSO}_4(\alpha) \rightarrow \text{ZnO} \cdot 2 \text{ZnSO}_4 + \text{SO}_3$	238	225

perfect condensers for the flux of particles emerging from the product layer. However, it is not unreasonable that a similar relationship should apply, for example

$$P = 1/(1 + L/C) \quad (2)$$

Here C is a constant which is proportional to the dimensions of interparticle spaces and one expects C to be greater for the loosely packed NiO and CuO layers than for the partially sintered $\text{ZnO} \cdot 2 \text{ZnSO}_4$.

Two limiting cases of eqn. (2) are $P = 1$ when $L/C \ll 1$, and $P = C/L$ when $L/C \gg 1$. The first implies that there is no "reflection" of molecules back to the interface, no reverse reaction and therefore a constant rate. This corresponds to our results for CuSO_4 and NiSO_4 . The second case implies a reverse reaction which increases proportionally with the thickness, L , of the product layer. If the rate of gas release at the interface is k , the overall rate is $dw/dt = k - (1 - P)k = Pk = kC/L$

Since w is proportional to L , this is equivalent to our empirical equation for ZnSO_4 decomposition. Note that this equation will apply only after L has become sufficiently large, accounting for the anomalous initial period in Fig. 3.

The porosity of the $\text{ZnO} \cdot 2 \text{ZnSO}_4$ is incidental to the argument. Smith and Topley [8] have shown that although decomposition reactions yield a porous product, this may or may not convert rapidly to a crystalline form, depending on local conditions. Our analysis simply postulates the tendency of the observed product layer structure to impede gas flow.

If gas release at the interface is a chemically controlled step, then one would expect the temperature dependences of the rate constants k_1 , k_2 and k_3 to give activation enthalpies greater than the corresponding standard enthalpy values [9] in the same temperature region. This is confirmed by the data in Table 1.

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