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STUDY OF THE THERMAL DECOMPOSITION OF MSO_4 (M = Zn(II), Cd(II), Hg(II)) IN A SODIUM NITRATE–POTASSIUM NITRATE MELT

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ABSTRACT

MSO_4 ($M = Zn^{2+}$, Cd^{2+}, Hg^{2+}) dissolves in the molten $NaNO_3$–KNO_3 eutectic and is decomposed on further heating. The kinetics of decomposition have been studied at different temperatures. The decomposition of $CdSO_4$ and $HgSO_4$ in the eutectic melt obey first-order kinetics whereas the decomposition of $ZnSO_4$ at 420–460°C obeys second-order kinetics. However, at 480°C the decomposition of $ZnSO_4$ obeys first-order kinetics. The mechanism of decomposition has been given as

$$M^{2+} + SO_4^{2-} + Na^+ + K^+ + 2NO_3^- \rightleftharpoons (Na,K)SO_4 + M^{2+} + 2NO_3^-$$

$$M^{2+} + NO_3^- \rightarrow MO + NO_2^+$$

$$NO_3^- + NO_2^+ \rightarrow NO_2 + \tfrac{1}{2}O_2$$

Some of the end products have been analysed by X-ray diffraction.

INTRODUCTION

Molten nitrates and nitrites have recently been used as non-aqueous solvents for studying a number of reactions [1–3]. Recently, Singh and co-workers [4,5] found that metal salts decompose at much lower temperatures in molten nitrate eutectics. This paper describes the decomposition of $ZnSO_4$, $CdSO_4$ and $HgSO_4$ in an $NaNO_3$–KNO_3 eutectic melt.

EXPERIMENTAL

Materials

$NaNO_3$, KNO_3, $ZnSO_4 \cdot 7H_2O$, $3CdSO_4 \cdot 8H_2O$, and $HgSO_4$, all AR (BDH), were used during the reaction. The sodium nitrate–potassium nitrate

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eutectic was prepared [6] in 45 : 55% ratio. $ZnSO_4$ and $CdSO_4$ were obtained by dehydrating them at 300 and 400°C, respectively.

PROCEDURE

Thermal studies

Thermogravimetric studies of metal sulphates ($ZnSO_4$, $CdSO_4$, $HgSO_4$) in $NaNO_3$, KNO_3 and $NaNO_3/KNO_3$ eutectic were carried out with a thermogravimetric analyzer (supplied by P & D Division, Sindri, Dhanbad) in atmospheric air at a heating rate of 4°C min^{-1}. A Corning glass crucible was used during the experiment. DTA studies of metal sulphates in the eutectic melt were carried out with a recording thermal analyzer (Paulik–Paulik–Erdey MOM derivatograph, Hungary) in atmospheric air at a heating rate of 5°C min^{-1}. Kinetics of the thermal decomposition of metal sulphates in the eutectic melt have also been studied using a Corning glass crucible in atmospheric air. The weight losses were noted at different time intervals at constant temperatures. Known weights of the eutectic and metal sulphates were taken during the experiment.

Powder X-ray diffraction studies

The powder X-ray diffraction patterns of the residues left after TG were obtained with an X-ray diffractograph (XRD-5 General Electric, U.S.A.) using CuK_α radiation.

Gravimetric estimations

The reaction products left at the end of TG were washed several times with water to obtain insoluble metal oxides. Zinc, cadmium and mercury were estimated gravimetrically [7] in the oxides.

Qualitative analysis of evolved gases

The evolved gases were tested in the usual way and found to be NO_2 and O_2.

RESULTS AND DISCUSSION

TG studies (Fig. 1, Table 1) indicate that the metal sulphates decompose at a much lower temperature in nitrate melts than when heated alone. DTA studies (Fig. 2, Table 2) indicate a number of endothermic peaks below

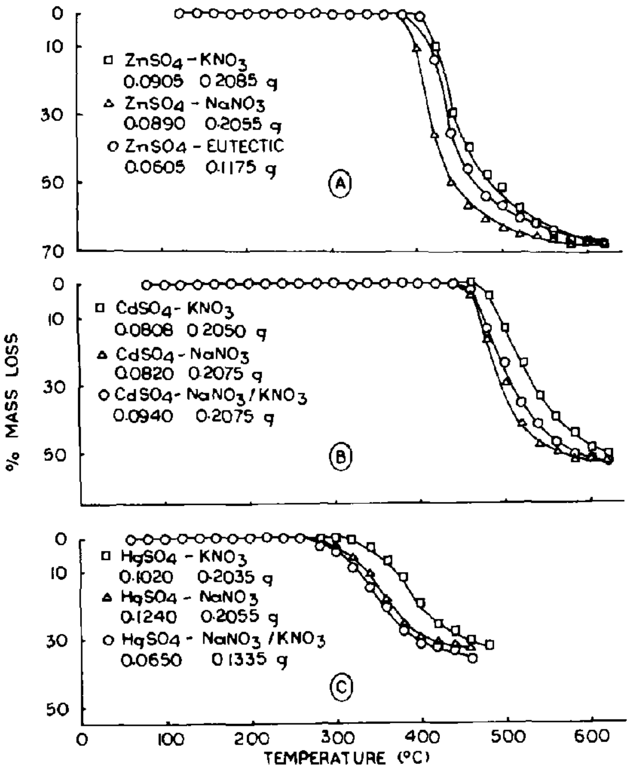

Fig. 1. TG curves.

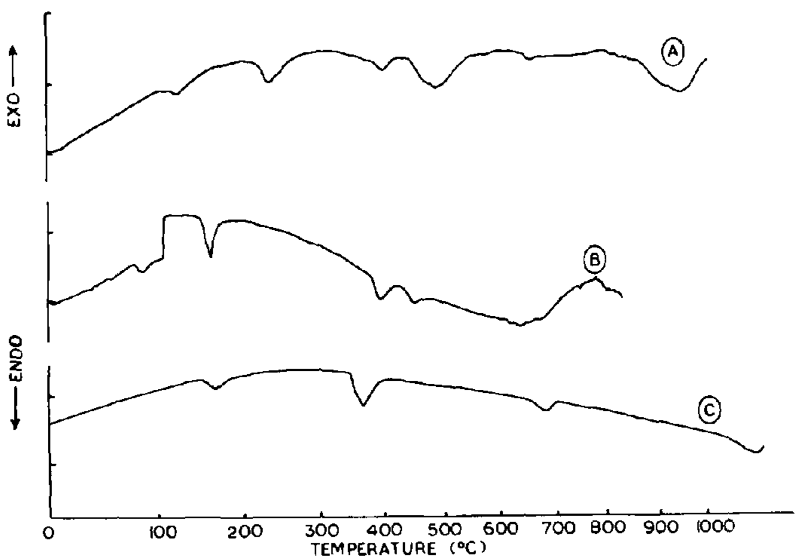

Fig. 2. DTA curves in the $NaNO_3$–KNO_3 eutectic of (A) $ZnSO_4$; (B) $CdSO_4$, (C) $HgSO_4$.

600°C. An endothermic peak at around 120°C is indicative of a phase transformation in KNO_3, whereas an endotherm at around 220°C is due to the melting of the $NaNO_3$-KNO_3 eutectic. In each curve, there are two closely associated endothermic peaks in the region 400–500°C ($ZnSO_4$), 500–600°C ($CdSO_4$), 300–400°C ($HgSO_4$). These endotherms, when compared with the corresponding TG experiments, show that these peaks appear in the temperature range where decomposition takes place. Since there are two endotherms, it suggests that there are two stages of decomposition, although this is not indicated by TG. It may be inferred that two decomposi-

TABLE 1

Decomposition temperatures

System	Decomp temp. (°C)
$ZnSO_4$	930
$ZnSO_4$-KNO_3	420
$ZnSO_4$-$NaNO_3$	400
$ZnSO_4$-$NaNO_3$/KNO_3 eutectic	420
$CdSO_4$	> 700
$CdSO_4$-KNO_3	480
$CdSO_4$-$NaNO_3$	460
$CdSO_4$-$NaNO_3$/KNO_3 eutectic	460
$HgSO_4$	> 600
$HgSO_4$-KNO_3	340
$HgSO_4$-$NaNO_3$	320
$HgSO_4$-$NaNO_3$/KNO_3 eutectic	320

TABLE 2

DTA peak temperatures

System	Peak temp. (°C)	Process
$ZnSO_4$-$NaNO_3$/KNO_3	120	Phase transformation in KNO_3
eutectic	220	Melting of eutectic
	400, 480	Decomposition of metal sulphate
$CdSO_4$-$NaNO_3$/KNO_3	120	Phase transformation in KNO_3
eutectic	220	Melting of eutectic
	520, 580	Decomposition of metal sulphate
$HgSO_4$-$NaNO_3$/KNO_3	120	Phase transformation in KNO_3
eutectic	230	Melting of eutectic
	300, 380	Decomposition of metal sulphate

tion stages are taking place simultaneously, probably with no mass loss in one decomposition, but with a mass loss in the other.

The end products, when examined by powder X-ray diffraction, were

TABLE 3

X-ray diffraction studies (*d* values of three lines in order of decreasing intensity are given)

System	*d* (Å) (rep)	*d* (Å) (obs)
$ZnSO_4$–NaNO/KNO_3 eutectic		
ZnO	2.48	2.46
	2.81	2.80
	2.60	2.60
Na_2SO_4	4.66	4.60
	2.64	2.63
	2.32	2.32
K_2SO_4	3.00	3.01
	3.74	3.75
	4.17	4.10
$CdSO_4$–$NaNO_3$/KNO_3 eutectic		
CdO	2.71	2.71
	2.35	2.34
	1.66	1.66
Na_2SO_4	2.78	2.78
	4.66	4.65
	2.64	2.64
K_2SO_4	3.00	3.02
	3.74	3.75
	2.08	2.05
$HgSO_4$–$NaNO_3$/KNO_3 eutectic		
HgO	2.92	2.94
	3.10	3.01
	1.77	1.76
Na_2SO_4	2.78	2.75
	2.64	2.63
	2.32	2.30
K_2SO_4	2.90	2.90
	3.74	3.73
	2.42	2.40

TABLE 4

Gravimetric estimation of metals in different oxides

Metal oxide	% of metal	
	obs.	calc.
ZnO	80.56	80.33
CdO	86.20	87.53
HgO	92.68	92.61

found to be ZnO, Na_2SO_4, K_2SO_4; CdO, Na_2SO_4, K_2SO_4; and HgO, Na_2SO_4, K_2SO_4 (Table 3). The presence of oxides was also confirmed by gravimetric estimations (Table 4). The evolved gases were identified as NO_2 and O_2.

On the basis of the above results, the following stoichiometric reaction may be proposed

$$2MSO_4 + 2NaNO_3 + 2KNO_3 \rightarrow 2MO + Na_2SO_4 + K_2SO_4 + 4NO_2 + O_2$$

where M = Zn(II), Cd(II), Hg(II).

The decomposition of $CdSO_4$ and $HgSO_4$ obeys a first-order rate law (Fig. 3) and the rate equation is

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

The decomposition of $ZnSO_4$ at 480°C also obeys a first-order rate law (Fig. 4). However, between 420 and 460°C, the decomposition of $ZnSO_4$ obeys a second-order rate law (Fig. 4). The second-order rate equation is

$$k_2 = \frac{1}{t} \frac{x}{a(a-x)}$$

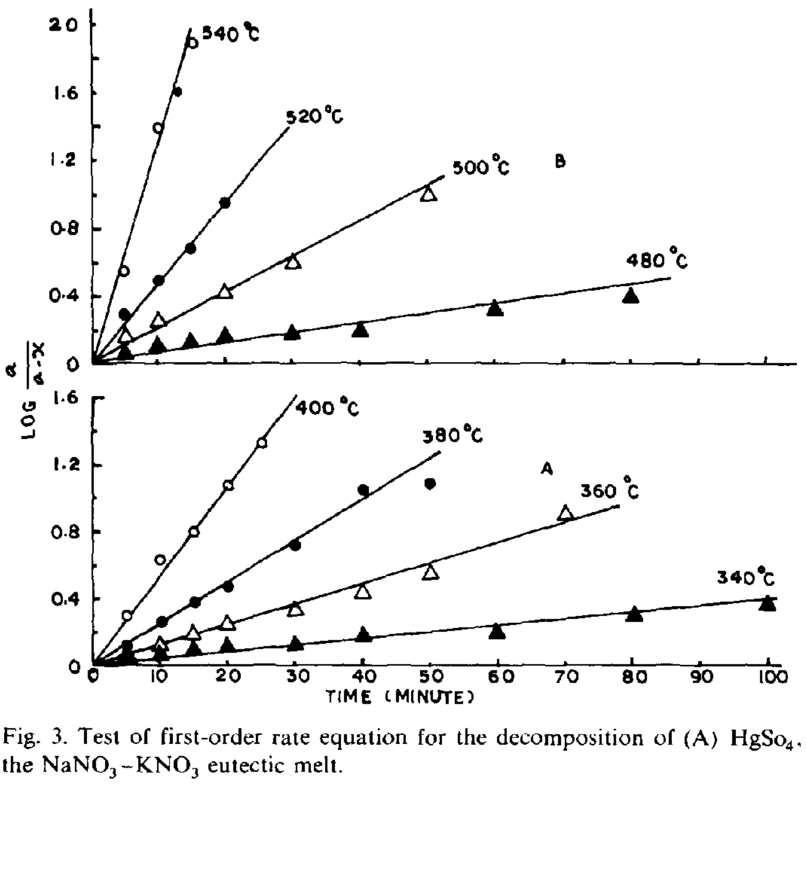

Fig. 3. Test of first-order rate equation for the decomposition of (A) $HgSo_4$, (B) $CdSO_4$ in the $NaNO_3$–KNO_3 eutectic melt.

where k_1 and k_2 are the reaction rates, a is the initial concentration of reactant and x is the amount decomposed, i.e., the amount of NO_2 and O_2 liberated at any time t. It appears that below 480°C the kinetic feature is different and probably at lower temperatures Zn^{2+} forms some complex intermediates and hence the kinetic feature is changed. The formation of complex intermediates in molten electrolytes is well known. For example, the $CdBr^+$ complex ion is formed in a KNO_3–$NaNO_3$ melt [8].

In the present reaction systems, all the reactants are in the molten state and in the ionic form. The overall reactions between ions can be represented by the following steps

$$M^{2+} + SO_4^{2-} + Na^+ + K^+ + 2NO_3^- \overset{I}{\rightleftharpoons} Na_2SO_4 + K_2SO_4 + M^{2+} + 2NO_3^-$$

$$M^{2+} + NO_3^- \overset{II}{\rightarrow} MO + NO_2^+$$

$$NO_3^- + NO_2^+ \overset{III}{\rightarrow} NO_2 + \tfrac{1}{2}O_2$$

where $M = Zn^{2+}$, Cd^{2+}, Hg^{2+}. Step II can be considered as a Lux–Flood acid-base reaction [9]. The metal cation M^{2+} acts as a Lux–Flood acid and NO_3^- acts as a Lux–Flood base. When the NO_3^- ion comes into contact with the M^{2+} ion in the melt, it is decomposed as

$$M^{2+} + O{=}N\genfrac{}{}{0pt}{}{\nearrow O^-}{\searrow O} \rightarrow MO + NO_2^+$$

However, it is difficult to understand how this decomposition occurs.

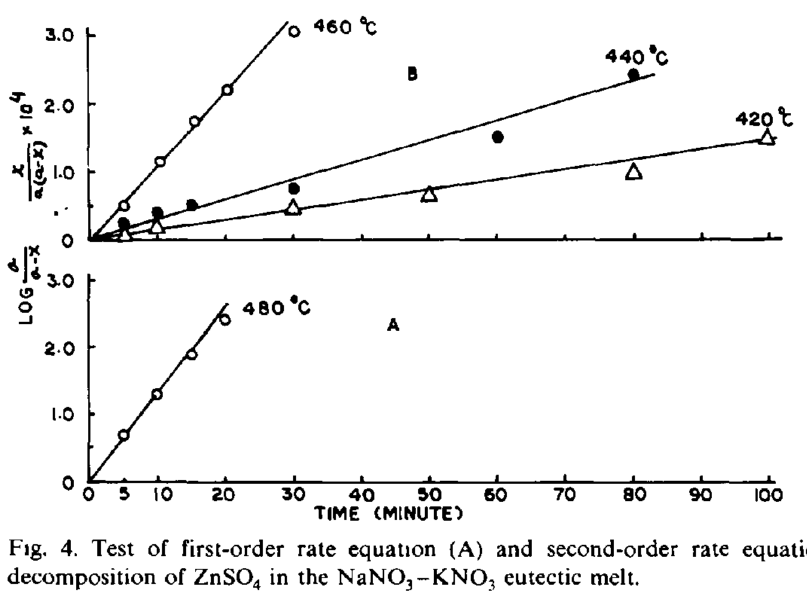

Fig. 4. Test of first-order rate equation (A) and second-order rate equation (B) for the decomposition of $ZnSO_4$ in the $NaNO_3$–KNO_3 eutectic melt.

TABLE 5

Apparent rate constant and activation energy

Reaction system	Decomp. temp. (°C)	Wt. of eutectic (g)	Wt. of metal sulphate (g)	k_1 (min^{-1})	E (kcal mol^{-1})
$CdSO_4$–$NaNO_3$/KNO_3	480	0.2035	0.1100	0.0061	
	500	0.2065	0.1025	0.0213	62
eutectic	520	0.2025	0.1015	0.0480	
	540	0.2045	0.1095	0.1333	
$HgSO_4$–$NaNO_3$/KNO_3	340	0.2080	0.1095	0.0040	
	360	0.2035	0.1590	0.0120	31
eutectic	380	0.2015	0.1230	0.0250	
	400	0.2000	0.1110	0.0533	
$ZnSO_4$–$NaNO_3$/KNO_3 eutectic	480	0.2025	0.1060		

TABLE 6

Apparent rate constant and activation energy

Reaction system	Decomp. temp. (°C)	Wt. of eutectic (g)	Wt. of $ZnSO_4$ (g)	k_2 (min^{-1} mol^{-1})	E (kcal mol^{-1})
$ZnSO_4$–$NaNO_3$/KNO_3	420	0.2065	0.1050	155.0	
	440	0.1965	0.1010	285.7	52
eutectic	460	0.2020	0.1030	1066.0	

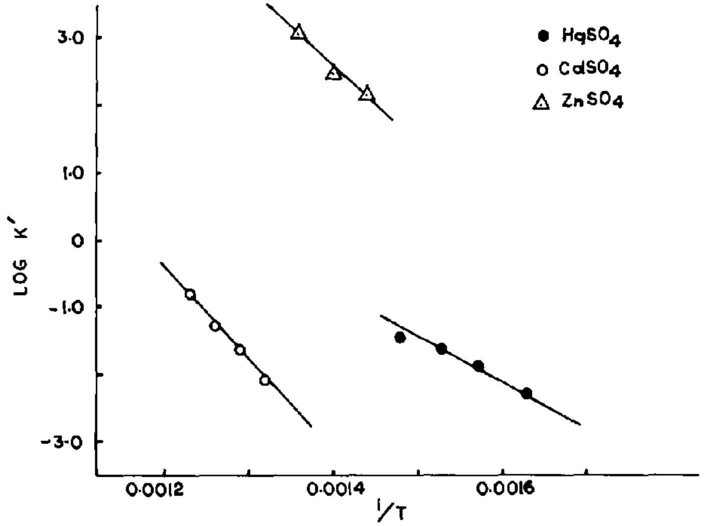

Fig. 5. Arrhenius plot for the $ZnSO_4$–$NaNO_3$/KNO_3, $CdSO_4$–$NaNO_3$/KNO_3, $HgSO_4$–$NaNO_3$/KNO_3 eutectic systems.

It has already been reported that the reaction between NO_3^- is slow and hence is the rate-determining step. The reaction is first order with respect to NO_2^+ or with respect to M^{2+} since both are proportional to each other. The change in NO_3^- ion concentration remains constant since it is part of the solvent and is in excess. Actually, the reactions of $CdSO_4$ and $HgSO_4$ in the nitrate eutectic melt are found to be first order. The reaction of $ZnSO_4$ at 480°C is also found to be first order. However, the reaction of $ZnSO_4$ at 420, 440 and 460°C is found to be second order. In view of the lack of knowledge about the complex ions formed in the $ZnSO_4$–$NaNO_3$/KNO_3 system at lower temperatures, it is difficult to give an explanation.

The values of k_1 and k_2 were determined (Tables 5 and 6) at different temperatures for all the three systems and, from an Arrhenius plot (Fig. 5), the activation energies were calculated and are given in Tables 5 and 6. These values show that there is no definite sequence.

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