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DERIVATOGRAPHIC STUDIES ON DEHYDRATION OF SALT HYDRATES AND THEIR DEUTERIUM OXIDE ANALOGUES. II

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ABSTRACT

Non-isothermal thermal studies of the dehydration of double salt hydrates of the type $M(I)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their deuterium oxide analogues were carried out, where $M(I) = K(I)$ and $M(II) = Mg(II)$, Co(II), Ni(II), Cu(II) and Zn(II). Thermal parameters like activation energy, order of reaction, enthalpy change, etc. were evaluated from the analysis of TG, DTA and DTG curves. Activation energy required for dehydration of the salt hydrates and their deuterium oxide analogues did not differ much except the Mg(II) salt. Thermal stabilities of the salt hydrates and their deuterium oxide analogues were discussed. The order of reaction was always found unity. The values of ΔH were within 12–14 kcal mol^{-1}.

INTRODUCTION

The thermal analyses of similar type of salts were carried out by a few workers[1,2]. These works were mostly carried out under isothermal conditions. Very recently non-isothermal kinetics of dehydration of single salt hydrates and some similar double salt hydrates were carried out by several groups of workers[3–10]. But none compared the thermal properties of the double salt hydrates and their deuterium oxide analogues, though recently a few workers[11,12] carried out the work on the relative thermal stability of some single salt hydrates and their D_2O analogues. Moreover, none compared the thermal parameters like activation energy, order of reaction, enthalpy change, etc. from the simultaneous analysis of TG, DTA and DTG curves. In continuation to our previous work[13] the present paper deals with the dehydration of $K_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ where $M(II) = Mg(II)$, Co(II), Ni(II), Cu(II), Zn(II) and their deuterium oxide analogues. The evaluation of activation energy of dehydration of the above salt hydrates was made from the simultaneous analyses of TG, DTA and DTG curves. In addition to the evaluation of activation energy, enthalpy change and order of reaction were determined for each step of dehydration. It also shows the influence of deuteration and of the change of cation on the thermal properties of the salt hydrates.

EXPERIMENTAL

Double salt hydrates are prepared following the standard procedure and their deuterium oxide analogues were prepared by dissolving an equimolecular mixture of the anhydrous single salt in D_2O and subsequent crystallisation. A Paulik Paulik Erdey MOM derivatograph has been used for thermal analysis. A platinum crucible was used and the heating rate was 1.5 °C min^{-1}. The particle size of the samples was within 150–200 mesh. The volume of the sample in each case was the same.

RESULTS

The double sulphate hydrates of Co(II) and Zn(II) and their deuterium oxide analogues lose water molecules in two steps, i.e.,

$$K_2M(SO_4)_2 \cdot 6H_2O \rightarrow K_2M(SO_4)_2 \cdot 2H_2O \rightarrow K_2M(SO_4)_2,$$

observed from the respective derivatograms (Fig. 1). For Ni(II) salt, in the first step, five and half molecules of water are eliminated and the rest in the second step (Fig. 1).

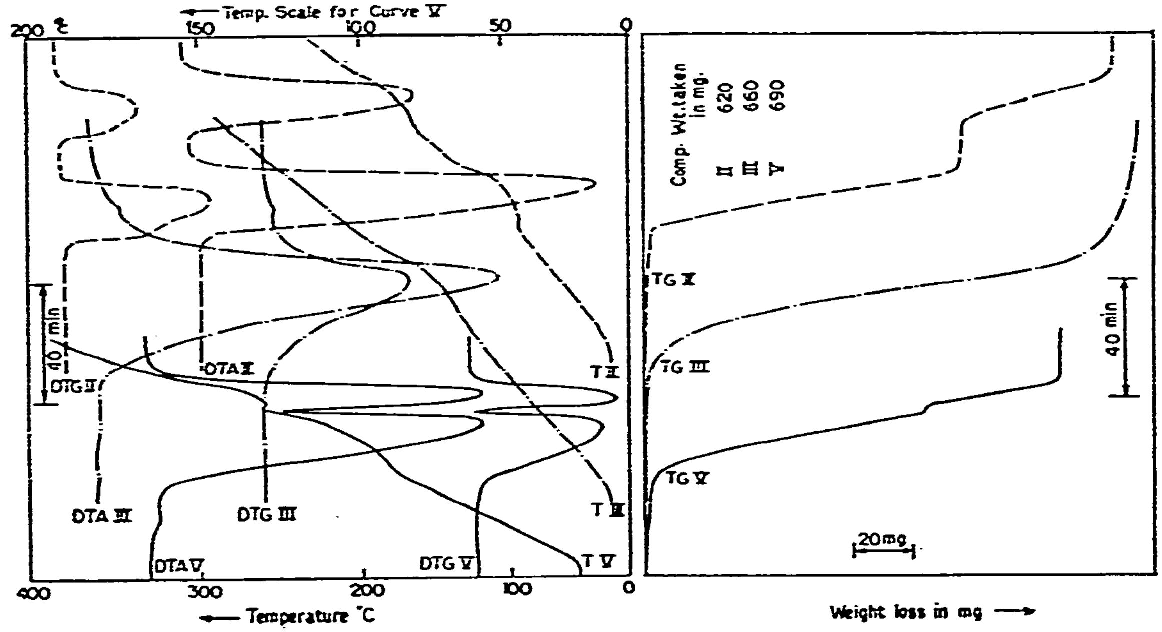

Fig. 1. Derivatograms for the dehydration of $K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$(II), $K_2SO_4 \cdot NiSO_4 \cdot 6H_2O$(III) and $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$(V).

A similar phenomenon is observed in the case of dehydration of its deuterium oxide analogue. The double salt hydrate of Mg(II) loses water in three steps (Fig. 2), i.e.,

$$K_2Mg(SO_4)_2 \cdot 6H_2O \rightarrow K_2Mg(SO_4)_2 \cdot 4H_2O \rightarrow$$

$$\rightarrow K_2Mg(SO_4)_2 \cdot 2H_2O \rightarrow K_2Mg(SO_4)_2$$

But its deuterium oxide analogue loses all six molecules of D_2O in a single step (Fig. 2). The double salt hydrate of Cu(II) loses water in two steps as is evident from the TG curve, i.e.,

$$K_2Cu(SO_4)_2 \cdot 6H_2O \rightarrow K_2Cu(SO_4)_2 \cdot 2H_2O \rightarrow K_2Cu(SO_4)_2$$

but its DTG and DTA curves show multiple steps of dehydration (Fig. 3). On

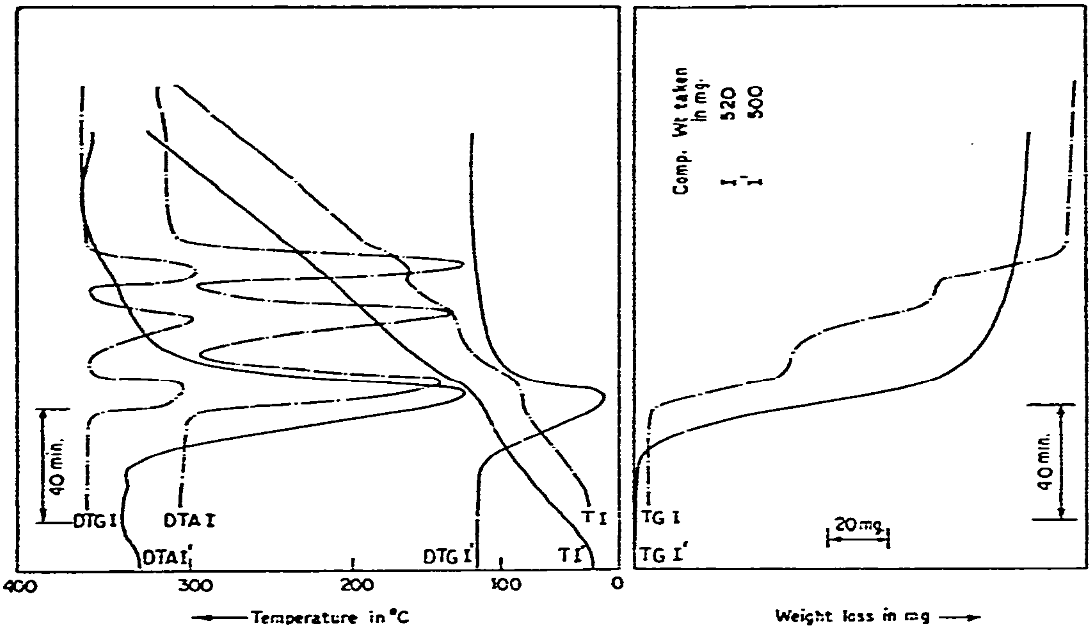

Fig. 2. Derivatograms for the dehydration of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (I) and $K_2SO_4 \cdot MgSO_4 \cdot 6D_2O$ (I′

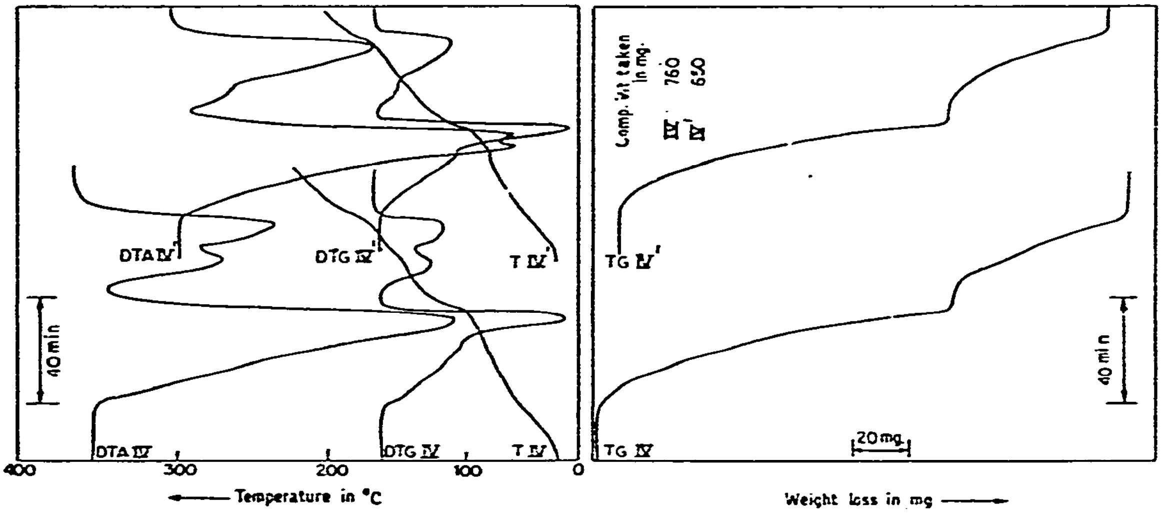

Fig. 3. Derivatograms for the dehydration of $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ (IV) and $K_2SO_4 \cdot CuSO_4 \cdot 6D_2O$ (IV′).

TABLE 1

THERMAL PARAMETERS OF DEHYDRATION OF SALT HYDRATES AND THEIR DEUTERIUM OXIDE ANALOGUES

	Decomposition reactions	*Temp. ranges (°C)*	*DTG peak temp. (°C)*	*Activation energies (kcal mol⁻¹)*			*Enthalpy changes (kcal mol⁻¹)*
				TG	*DTG*	*DTA*	
(Ia)	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	80–105	86	69.0	69.0	69.0	13.3
(Ib)	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$	120–155	132	103.5	103.5	103.5	13.4
(Ic)	$K_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot MgSO_4$	163–190	166	168.0	168.0	168.0	13.5
(I′)	$K_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot MgSO_4$	85–195	117	25.5	30.6	30.6	13.8
(IIa)	$K_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2H_2O$	87–120	102	30.7	35.2	35.2	14.5
(IIb)	$K_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CoSO_4$	164–210	177	56.2	56.2	56.2	13.5
(II′a)	$K_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2D_2O$	90–120	102	30.6	36.8	36.8	13.4
(II′b)	$K_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CoSO_4$	168–210	178	46.0	46.0	46.0	13.9
(III)	$K_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5H_2O$	95–270	150	23.0	23.0	25.1	12.4
(III′)	$K_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5D_2O$	95–270	153	23.0	23.0	26.2	13.2
(IVa)	$K_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot CuSO_4 \cdot 2H_2O$	45–105	95	23.0	—	—	14.8[a]
(IVb)	$K_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CuSO_4$	125–180	171	33.2	—	—	—
(IV′a)	$K_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot CuSO_4 \cdot 2D_2O$	45–105	95	24.8	—	—	13.8[a]
(IV′b)	$K_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot CuSO_4$	130–185	165	39.0	—	—	—
(Va)	$K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot ZnSO_4 \cdot 2H_2O$	56–111	107	34.5	34.5	—	12.6[a]
(Vb)	$K_2SO_4 \cdot ZnSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot ZnSO_4$	112–162	131	57.2	—	—	—
(V′a)	$K_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot ZnSO_4 \cdot 2D_2O$	86–120	106	33.8	33.8	—	14.2[a]
(V′b)	$K_2SO_4 \cdot ZnSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot ZnSO_4$	130–165	128	64.5	—	—	—

[a] These indicate the overall enthalpy changes where DTA curves are too much overlapped.

deuteration of the Cu(II) salt hydrate, the first endotherm splits into two and the resolution of the second endotherm is decreased (Fig. 3). The DTG peak temperature and temperature range of dehydration for the double salt hydrates and their deuterium oxide analogues are given in Table 1. Enthalpy changes for each step of dehydration of the double salt hydrates and their deuterium oxide analogues were evaluated by the method of Sano[14] using copper sulphate pentahydrate as the standard and the values are given in the Table 1. ΔH values were evaluated from the overall area of the DTA curves where the DTA curves are too much overlapped. Activation energies for each step of dehydration of the salt hydrates and their deuterium oxide analogues were evaluated from the analysis of TG curves using Freeman and Carroll's equation[15]. The results are tabulated in Table 1 and the curves are shown in Figs. 4 and 5. The activation energies for each step of dehydration (wherever possible) were also evaluated from the analysis of the DTG curve using the method of Dave and Chopra[16] and the method described in our earlier work[13] and also from the analysis of DTA curves using Brochardt's[17] equation for first order reaction. All these values are tabulated in Table 1 and the corresponding curves are shown in Figs. 6 and 7. The order of reaction was found to be unity for the dehydration of all the mentioned

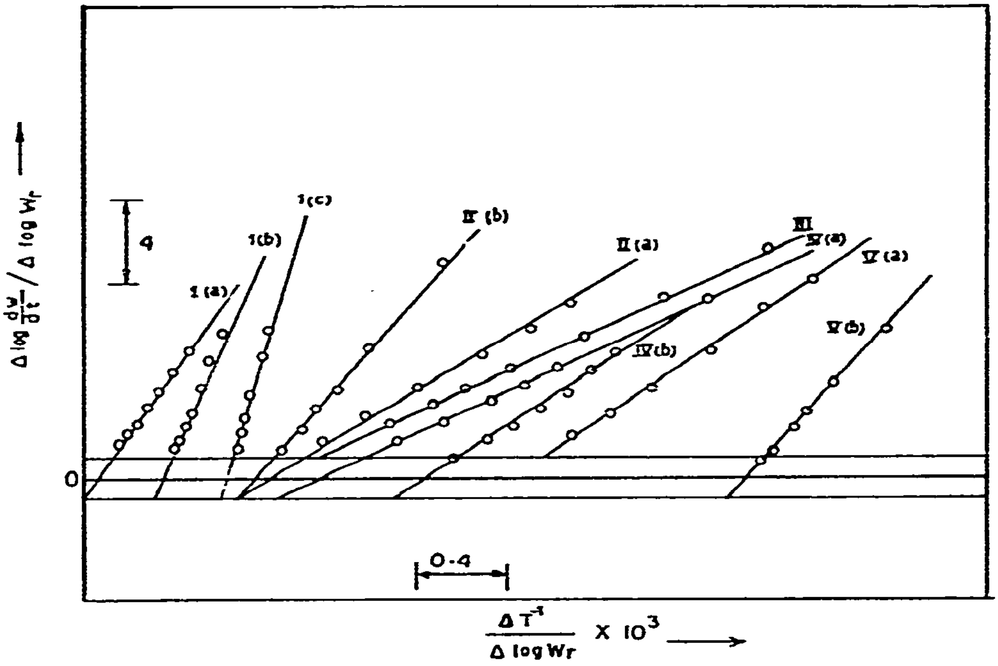

Fig. 4. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ vs. $\frac{\Delta T^{-1}}{\Delta \log W_r} \times 10^3$ [from the TG curves] for dehydration of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Ia), $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ (Ib), $K_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot MgSO_4$ (Ic), $K_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2H_2O$ (IIa), $K_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CoSO_4$ (IIb), $K_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5H_2O$ (III), $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot CuSO_4 \cdot 2H_2O$ (IVa), $K_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CuSO_4$ (IVb), $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot ZnSO_4 \cdot 2H_2O$ (Va) and $K_2SO_4 \cdot ZnSO_4 \cdot ZnSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot ZnSO_4$ (Vb).

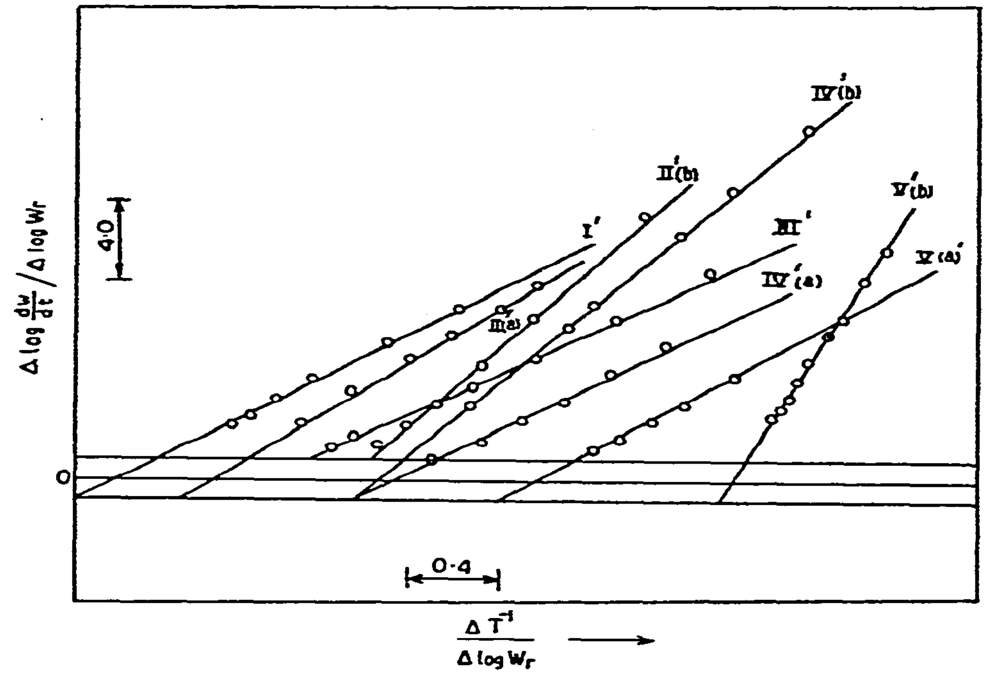

Fig. 5. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ vs. $\frac{\Delta T^{-1}}{\Delta \log W_r} \times 10^3$ for the dehydration (from TG curves) of $K_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot MgSO_4$(I'), $K_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2D_2O$(II'a), $K_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot CoSO_4$(II'b), $K_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5D_2O$(III'), $K_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot CuSO_4 \cdot 2D_2O$(IV'a), $K_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot CuSO_4$(IV'b), $K_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot ZnSO_4 \cdot 2D_2O$(V'a) and $K_2SO_4 \cdot ZnSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot ZnSO_4$(V'b).

double salt hydrates and their deuterium oxide analogues. X-ray analyses of the salt hydrates and their corresponding deuterium oxide analogues show that they are isomorphuos to each other.

DISCUSSION

The nature of decomposition of double salt hydrates of the potassium series differs from the corresponding ammonium series. In the ammonium series[13] complete dehydration takes place in two steps in the case of Mg(II) salt whereas, the corresponding salt hydrate of the potassium series loses water molecules in three distinct steps. On complete deuteration of this salt hydrate of the K(I) series dehydration takes place in a single step whereas, the corresponding D_2O analogue of the ammonium series follows the same pattern of dehydration as the aquated salt. Though the enthalpy changes of the Mg(II) salts of both NH_4(I) and K(I) are nearly equal, the activation energy of the dehydration of the Mg(II) salt of the K(I) series is too high with respect to the corresponding NH_4(I) series. The activation energy of dehydration of the Mg(II) salt hydrate of the K(I) series decreases considerably on deuteration (Table 1). This is probably due to the complete change in the nature of dehydration of the corresponding D_2O-analogue. The thermal stability of the same salt hydrate of the K(I) series is less than the corresponding NH_4(I) series. In the case of the K(I) series of the same salt hydrate, it is observed that the thermal stability increases noticeably on deuteration of the hydrate, whereas, in the NH_4(I) series a very slight increase of thermal stability is observed on deuteration. In the case of the Co(II) salt of the present series, the dehydration takes place in two distinct steps whereas, the corresponding salt hydrate of the NH_4(I) series shows a single step of dehydration. The thermal stability and the enthalpy change of the Co(II) salt of the K(I) series are less than those of the NH_4(I) series, whereas, the activation energy of dehydration of the same salt hydrate is higher than that of the corresponding NH_4(I) series. In this case, like in the NH_4(I) series there is practically no effect on the thermal properties of the corresponding deuterated salt hydrate. On dehydration of the Ni(II) salt thermal properties like DTG peak temperature and activation energy do not change significantly with respect to the NH_4(I) salt although the nature of dehydration is different from that of the NH_4(I) salt. For the corresponding salt hydrate of the NH_4(I) series, the ΔH value is higher than that of the K(I) salt. Here, there is also

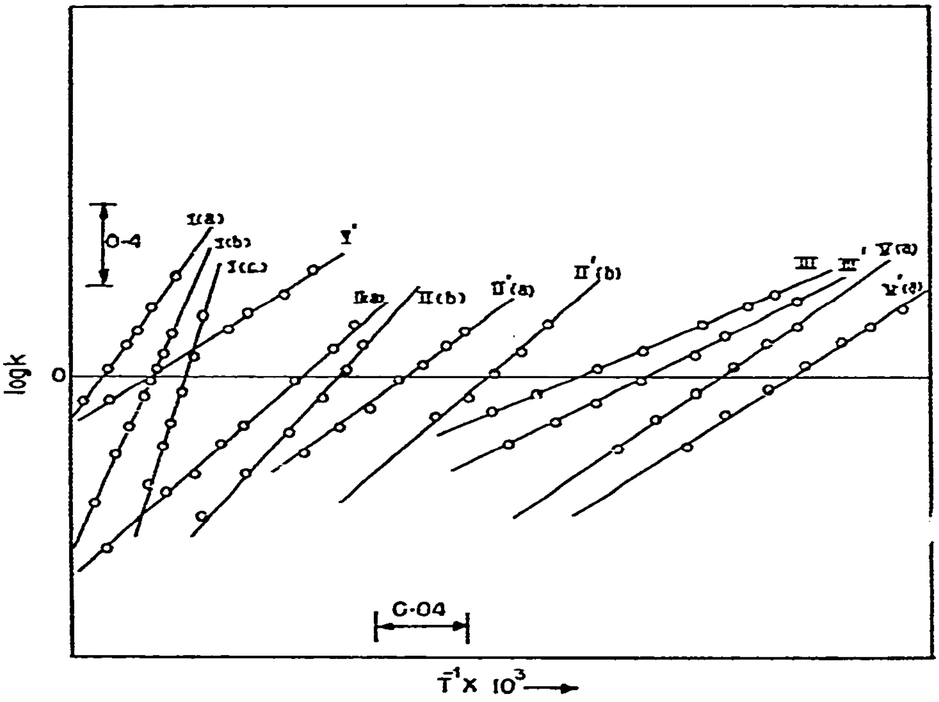

Fig. 6. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTG curves for the dehydration of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Ia), $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ (Ib), $K_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot MgSO_4$ (Ic), $K_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot MgSO_4$ (I'), $K_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2H_2O$ (IIa), $K_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CoSO_4$ (IIb) $K_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2D_2O$ (II'a), $K_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot CoSO_4$ (II'b), $K_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5H_2O$ (III), $K_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5D_2O$ (III'), $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot ZnSO_4 \cdot 2H_2O$ (Va) and $K_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot ZnSO_4 \cdot 2D_2O$ (V'a).

practically no effect on deuteration of the Ni(II) salt of the K(I) series. In the Cu(II) salt, the nature of dehydration is completely different from that of the corresponding ammonium salt hydrate. On deuteration of the K(I) salt hydrate the first endotherm splits into two, and the resolution of the second endotherm is decreased (Fig. 2). Thermal stability, activation energy, and enthalpy change are higher for the ammonium salt than for the corresponding salt of the potassium series. In our previous work[13] it is observed that the double salt hydrate of the Zn(II) salt of the ammonium series loses water molecules in a single step whereas, the corresponding salt hydrate of K(I) series eliminates water molecules in two steps. The thermal stability and enthalpy change of the Zn(II) salt of the NH_4(I) series are higher than that of the corresponding K(I) salt whereas, the reverse applies for the activation energy. Here also there is practically no effect on the thermal properties due to deuteration of the same salts.

In the ammonium series[13] the highest value of ΔH was ~ 18 kcal mol^{-1} whereas in the present series it is only 14.8 kcal mol^{-1}. With respect to the first DTG peak temperature the increasing order of thermal stability is as follows Mg(II) < Cu(II) < Co(II) < Zn(II) < Ni(II). This order is maintained also in the NH_4(I) series except Mg(II) where the order is reversed. The activation energy for the first step of dehydration decreases in the order Mg(II) > Zn(II) > Co(II) > Ni(II). The activation energy value of the Cu(II) salt of the K(I) series is equal to the Ni(II) salt of the same

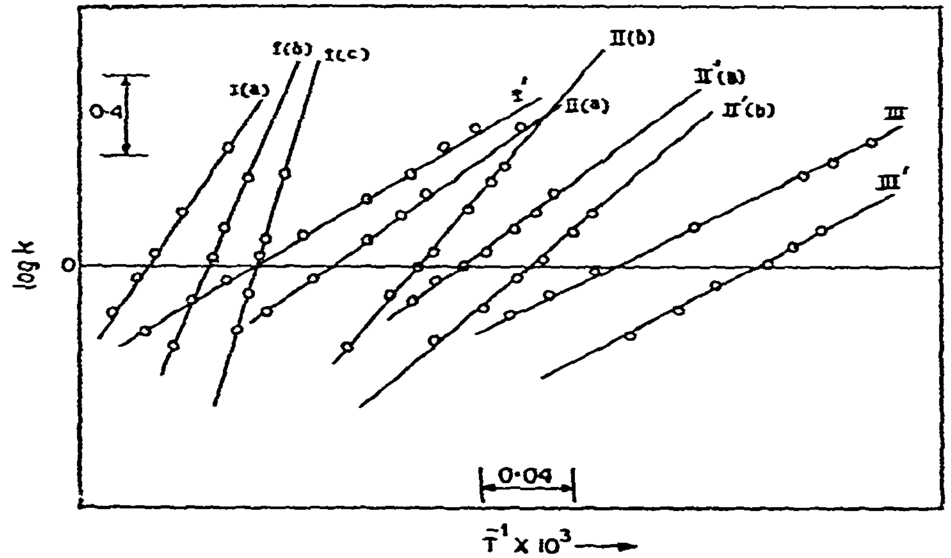

Fig. 7. Arrhenius plots of log *k* vs. $T^{-1} \times 10^3$ from DTA curves for the dehydration of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Ia), $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ (Ib), $K_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot MgSO_4$ (Ic), $K_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot MgSO_4$ (I'), $K_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2H_2O$ (IIa), $K_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CoSO_4$ (IIb), $K_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot CoSO_4 \cdot 2D_2O$ (II'a), $K_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SO_4 \cdot CoSO_4$ (II'b), $K_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5H_2O$ (III) and $K_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SO_4 \cdot NiSO_4 \cdot 0.5D_2O$ (III').

series. In the ammonium series these values had an order with increase of atomic weight of the central metal which is absent in this case.

The difference in thermal properties of dehydration between the NH_4(I) and K(I) salts is due to natural cause, i.e., slight difference in ionic size of NH_4^+ (1.43) and K^+ (1.33). We attempted to isolate the Cd(II) and Mn(II) double salt hydrate but could not succeed. The same attempt was made by Tutton[18] the father of these salt hydrates. He observed that these two salt hydrates crystallised in unequal proportions. Moreover, the salt hydrates lose water as soon as the crystals are removed from their mother liquor.

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