Thermochimica Acta, 13 (1975) 207–221
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

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

N. RAY CHAUDHURI AND G. K. PATHAK

Indian Association for the Cultivation of Science, Calcutta-700032 (India)

(Received 21 April 1975)

ABSTRACT

Non-isothermal studies of the dehydration of double salt hydrates of the type $K_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$ where $AB_4 = BeF_4^{2-}$ or SeO_4^{2-} and M(II) = Mg(II), Co(II), Ni(II), Cu(II) or Zn(II) and their D_2O analogues were carried out. Thermal parameters like activation energy, order of reaction, enthalpy change, etc., for each step of dehydration were evaluated from the analysis of TG, DTA and DTG curves. These parameters were compared with the corresponding double sulphate, i.e., $K_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues. The role of divalent cation on the thermal properties of dehydration of the salt hydrates and also the effect on the thermal properties due to deuteration were discussed. The order of reaction was always found unity. The values of ΔH were within ~ 11–~ 19 kcal mol^{-1}.

INTRODUCTION

Recently, we reported the derivatographic studies on dehydration of double salt hydrates of the type $M(I)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ where $M(I) = NH_4(I)$[1], K(I)[2], Rb(I)[3], Cs(I)[4] or Tl(I)[5] and M(II) = Mg(II), Co(II), Ni(II), Cu(II) or Zn(II) and their D_2O analogues. These studies state that the thermal properties are effected with change of monovalent cation of the double salt hydrates. In continuation to these works the present paper deals with the dehydration of double salt hydrates of the type $K(I)_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$ where $AB_4 = SeO_4^{2-}$ or BeF_4^{2-} and M(II) = Mg(II), Co(II), Ni(II), Cu(II) or Zn(II) and their D_2O analogues to observe the effect in thermal properties with change of anion. The present paper reports the values of activation energy of dehydration processes evaluated from TG, DTA and DTG curves simultaneously, order of reaction from TG, enthalpy change from DTA peak area and thermal stability from first DTG peak temperature. It also reports the effect of deuteration on the thermal properties and a comparison on the thermal properties between the two types of salt hydrates, i.e., $K_2BeF_4 \cdot MSO_4 \cdot 6H_2O$ and $K_2SeO_4 \cdot MSO_4 \cdot 6H_2O$ studied in the present paper and a general comparison with $K_2SO_4 \cdot MSO_4 \cdot 6H_2O$. It reports also the role of divalent cation of each type of salt hydrate on the thermal properties of dehydration.

EXPERIMENTAL

Preparation of potassium fluoberyllato sulphate hexahydrates of Mg(II), Co(II), Ni(II), Cu(II) and Zn(II) (These salt hydrates are abbreviated as 'A'):

The salt hydrates were prepared by mixing equimolecular mixtures of potassium fluoberyllate and metal sulphates, following the method of Ray and Sarkar[6,7]. The salt hydrates were crystallised from the above mixture by slow evaporation. The D_2O analogues of the salt hydrates were prepared by dissolving equimolecular mixtures of anhydrous single salts in D_2O and subsequent crystallisation.

The reagent potassium fluoberyllate was prepared in the laboratory in the following way: For the preparation of potassium fluoberyllate, ammonium fluoberyllate was prepared following the method of Ray et al.[8]. This ammonium fluoberyllate was converted into its acid form, i.e., H_2BeF_4 by passing the molar solution of ammonium fluoberyllate through a cation exchanger. The free acid thus obtained was concentrated by keeping it in a lime desiccator. The strength of the resultant acid was measured by simple acid–base titration and a requisite amount of K_2CO_3 was mixed to obtain the desired salt after evaporation. The beryllium and fluorine content of the salt was analysed following the standard methods before use.

Preparation of potassium selenato sulphate hexahydrates of Mg(II), Co(II), Ni(II), Cu(II) and Zn(II) (these salt hydrates are abbreviated as 'B'):

The salt hydrates were prepared by the procedure adopted by Gerichten[9] and the corresponding D_2O analogues were isolated following the method adopted earlier.

The salt potassium selenate was prepared in the laboratory by adding a requisite amount of K_2CO_3 to the reagent grade of selenic acid solution and followed by crystallisation. The salt potassium selenate was analysed before use.

A Paulik–Paulik–Erdey MOM derivatograph had 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 nearly the same.

RESULTS

Figure 1 shows the derivatograms of $K_2AB_4 \cdot MgSO_4 \cdot 6H_2O$. The fluoberyllate loses water molecules in a single step, whereas, the selenate loses water molecules in two steps. The first step corresponds to four molecules of water and the rest is eliminated in the second step. The similar fluoberyllate and selenate of Co(II) loses water molecules like the salt hydrate, $K_2SeO_4 \cdot MgSO_4 \cdot 6H_2O$, which is indicated from their TG curves but the DTG curve for the first step of dehydration of the selenate indicates the existence of thermally unstable salt hydrates (Fig. 2). The salt hydrate $K_2BeF_4 \cdot NiSO_4 \cdot 6H_2O$ loses water molecules like that of Mg(II) (Fig. 3). Similarly, the selenate loses water molecules upon heating like that of Mg(II) (Fig. 3). Whereas, its D_2O analogue (Fig. 3) loses D_2O molecules as follows: $K_2SeO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O \rightarrow K_2SeO_4 \cdot NiSO_4$. Figure 4 shows the derivatograms of $K_2AB_4 \cdot CuSO_4 \cdot 6H_2O$ and its D_2O analogues. The fluoberyllate loses its H_2O molecule on heating like that of Co(II) indicated from its TG curve. But its DTA and DTG curves for dehydration of the first four molecules of water indicate the existence of another thermally unstable intermediate salt hydrate. On deuteration the nature of dehydration seems unaltered from its TG curve. But the corresponding

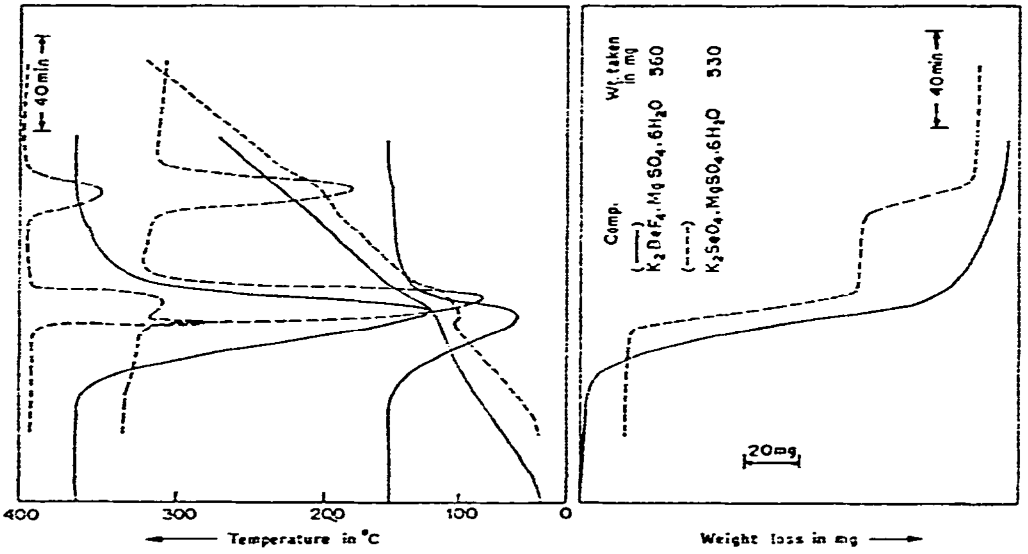

Fig. 1. Derivatograms for the dehydration of $K_2BeF_4 \cdot MgSO_4 \cdot 6H_2O$ (———) and $K_2SeO_4 \cdot MgSO_4 \cdot 6H_2O$ (— — —).

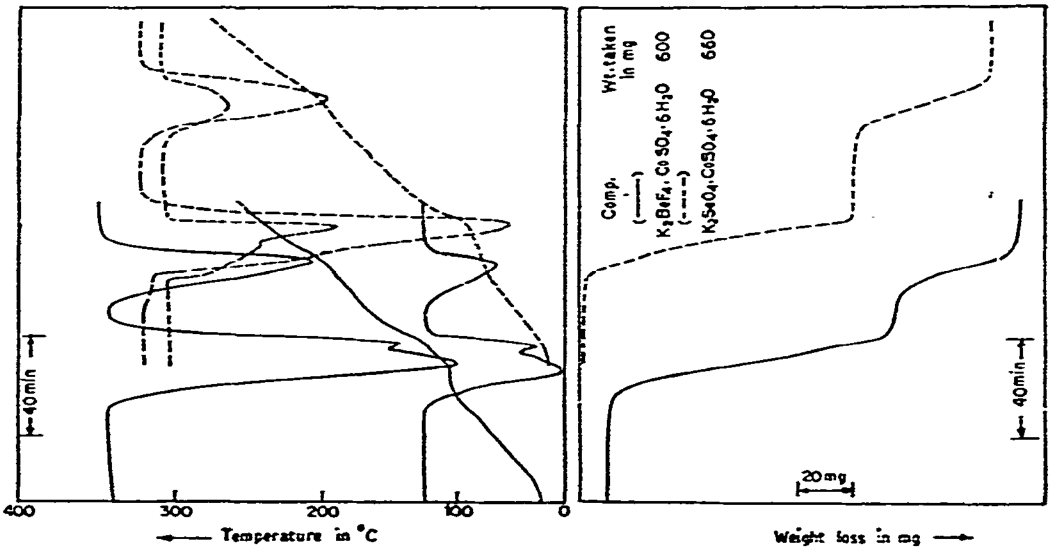

Fig. 2. Derivatograms for the dehydration of $K_2BeF_4 \cdot CoSO_4 \cdot 6H_2O$ (———) and $K_2SeO_4 \cdot CoSO_4 \cdot 6H_2O$ (— — —).

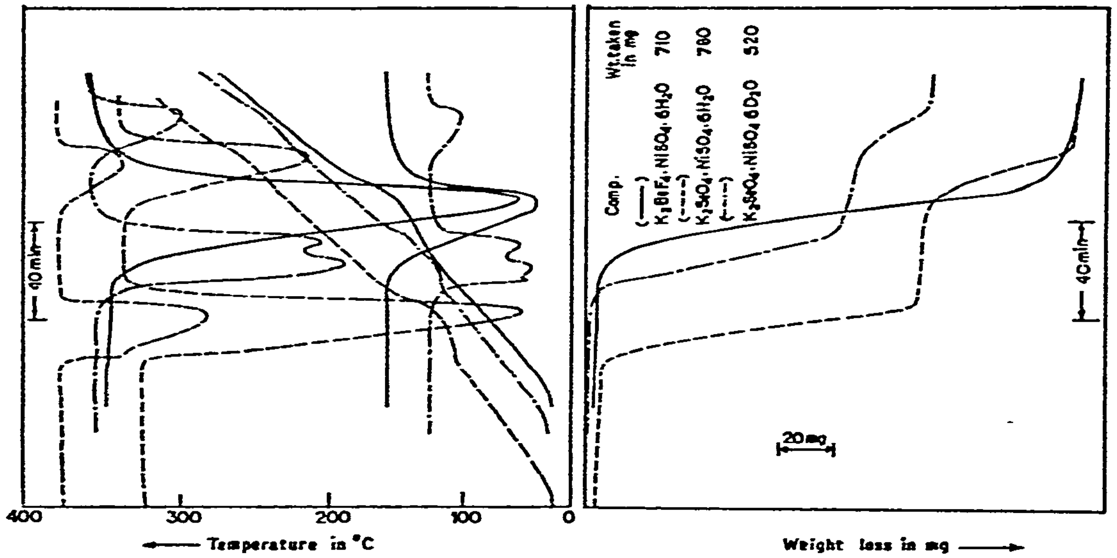

Fig. 3. Derivatograms for the dehydration of $K_2BeF_4 \cdot NiSO_4 \cdot 6H_2O$ (———), $K_2SeO_4 \cdot NiSO_4 \cdot 6H_2O$ (— — —) and $K_2SeO_4 \cdot NiSO_4 \cdot 6D_2O$ (—·—·—).

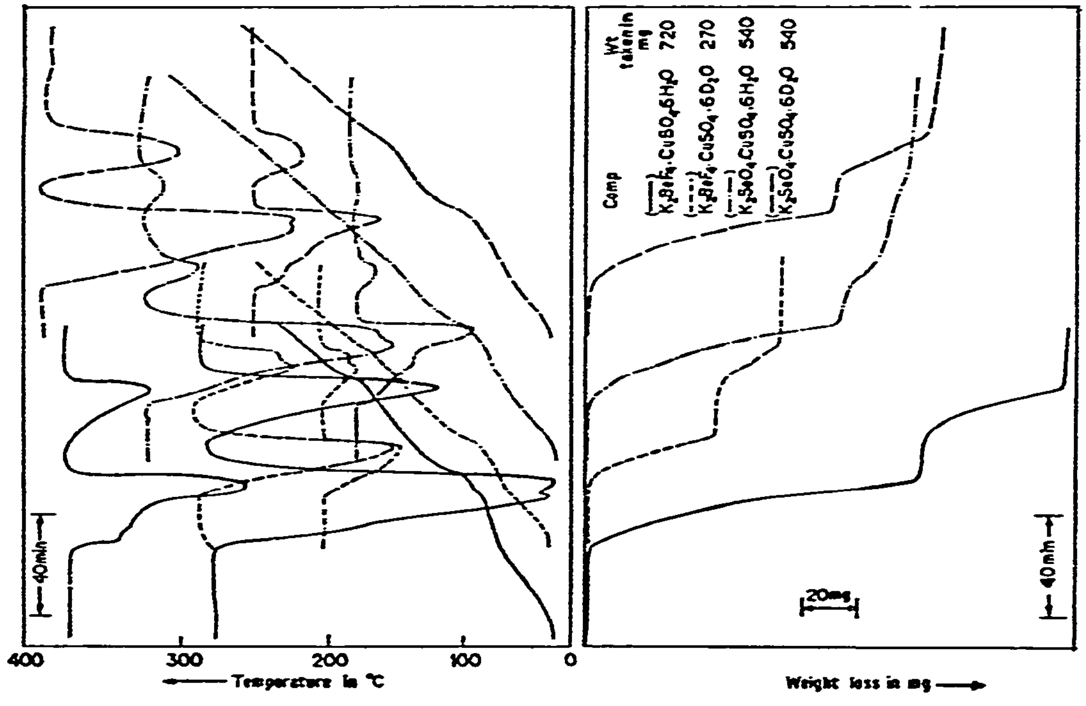

Fig. 4. Derivatograms for the dehydration of $K_2BeF_4 \cdot CuSO_4 \cdot 6H_2O$ (———), $K_2BeF_4 \cdot CuSO_4 \cdot 6D_2O$ (— — —), $K_2SeO_4 \cdot CuSO_4 \cdot 6H_2O$ (—·—·—) and $K_2SeO_4 \cdot CuSO_4 \cdot 6D_2O$ (— — —).

DTA and DTG curves for the elimination of the first four molecules of D_2O do not show any sign of the existence of an intermediate salt hydrate but show an additional intermediate thermally unstable deuterated salt hydrate during the elimination of the last two molecules of D_2O. The selenate loses water molecules as follows: $K_2SeO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 1.5H_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 0.5H_2O \rightarrow K_2SeO_4 \cdot CuSO_4$. The nature of dehydration is effected on deuteration as follows: $K_2SeO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CuSO_4$. Figure 5 shows the derivatograms of $K_2AB_4 \cdot ZnSO_4 \cdot 6H_2O$. The fluoberyllate shows a single step dehydration, whereas, the selenate shows a two-step dehydration like that of Mg(II). The D_2O analogues of the above salt hydrates whose derivatograms are not shown, do not show any noticeable variation in the nature of dehydration. The DTG peak temperatures and the temperature ranges of dehydration of the double salt hydrates of 'A' and 'B' and their corresponding D_2O analogues are tabulated in the Tables 1 and 2, respectively. Enthalpy changes for each step of dehydration are evaluated by the method of Sano[10] using copper sulphate pentahydrate as the standard and the values are tabulated in Tables 1 and 2. ΔH values are evaluated from the overall area of the DTA curves, where the DTA curves overlap too much. The activation energies for each step of dehydration of the salt hydrates and their D_2O analogues are evaluated from the analysis of TG curves using Freeman and Carroll's[11] equation. The results are tabulated in Tables 1 and 2 and the corresponding curves are shown in Figs. 6, 9 and 10. The activation energy for each step of dehydration was also determined from the analysis of DTG curves using the method of Dave and Chopra[12] and the methods used in our earlier work[1] and also from the analysis of DTA curves using Borchardt's[13] equation for first order reactions. All these values are tabulated

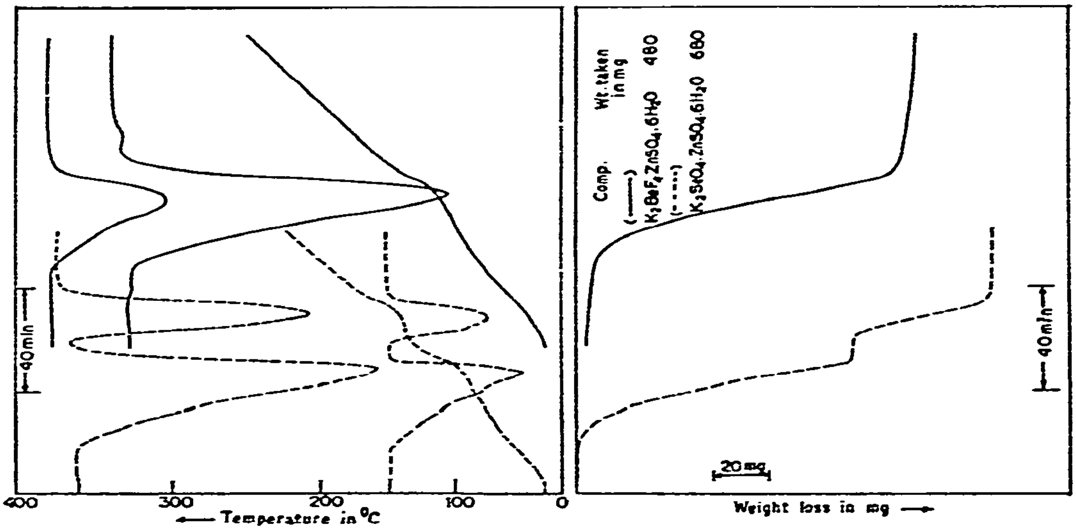

Fig. 5. Derivatograms for the dehydration of $K_2BeF_4 \cdot ZnSO_4 \cdot 6H_2O$ (———) and $K_2SeO_4 \cdot ZnSO_4 \cdot 6H_2O$ (– – –).

TABLE 1

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

Decomposition reaction	*Temp. range (°C)*	*DTG peak temp. (°C)*	*Activation energy (kcal mol⁻¹)*			*Enthalpy change (kcal mol⁻¹)*
			TG	*DTG*	*DTA*	
(I) $K_2BeF_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot MgSO_4$	78–165	120	30.6	30.6	30.6	12.7
(I′) $K_2BeF_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot MgSO_4$	76–164	120	26.0	26.0	26.0	16.4
(IIa) $K_2BeF_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot CoSO_4 \cdot 2H_2O$	85–155	106	46.0	—	—	14.4[a]
(IIb) $K_2BeF_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2BeF_4 \cdot CoSO_4$	170–220	197	61.3	61.3	61.3	12.8
(II′a) $K_2BeF_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot CoSO_4 \cdot 2D_2O$	86–156	107	46.0	—	—	14.8[a]
(II′b) $K_2BeF_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2BeF_4 \cdot CoSO_4$	171–222	198	64.4	64.4	64.4	13.5
(III) $K_2BeF_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot NiSO_4$	105–230	150	34.5	34.5	34.5	12.7
(III′) $K_2BeF_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot NiSO_4$	100–225	150	33.4	35.4	36.8	12.7
(IVa) $K_2BeF_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot CuSO_4 \cdot 2H_2O$	62–110	90	40.2	—	—	11.3[a]
(IVb) $K_2BeF_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow K_2BeF_4 \cdot CuSO_4$	134–195	170	52.0	52.0	52.0	12.6
(IV′a) $K_2BeF_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot CuSO_4 \cdot 2D_2O$	57– 90	85	40.2	41.4	41.4	14.8
(IV′b) $K_2BeF_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2BeF_4 \cdot CuSO_4$	127–195	157	56.2	—	—	16.5[a]
(V) $K_2BeF_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot ZnSO_4$	64–155	110	23.0	26.3	26.3	13.2
(V′) $K_2BeF_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot ZnSO_4$	60–151	112	23.0	30.6	30.6	14.3

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

TABLE 2

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

	Decomposition reaction	*Temp. range (°C)*	*DTG peak temp. (°C)*	*Activation energy (kcal mol⁻¹)*			*Enthalpy change (kcal mol⁻¹)*
				TG	*DTG*	*DTA*	
(Ia)	$K_2SeO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot MgSO_4 \cdot 2H_2O$	87–144	100	69.0	—	69.0	15.8
(Ib)	$K_2SeO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot MgSO_4$	175–235	200	80.5	80.5	80.5	15.8
(I'a)	$K_2SeO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O$	78–135	100	60.0	—	61.3	17.6
(I'b)	$K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot MgSO_4$	178–230	210	73.0	73.0	73.0	17.6
(IIa)	$K_2SeO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot CoSO_4 \cdot 2H_2O$	70–100	95	55.2	—	53.6	14.7
(IIb)	$K_2SeO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot CoSO_4$	170–220	200	59.1	59.1	59.1	14.7
(II'a)	$K_2SeO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O$	60–100	98	30.6	—	30.6	14.2
(II'b)	$K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CoSO_4$	165–235	200	51.1	51.1	51.1	14.5
(IIIa)	$K_2SeO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot NiSO_4 \cdot 2H_2O$	100–140	120	35.2	36.8	39.4	12.8
(IIIb)	$K_2SeO_4 \cdot NiSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot NiSO_4$	214–300	258	59.2	59.2	59.2	13.2
(III'a)	$K_2SeO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O$	98–175	123	30.6	—	—	13.9[a]
(III'b)	$K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O \rightarrow K_2SeO_4 \cdot NiSO_4$	202–265	243	69.0	69.0	69.0	17.4
(IVa)	$K_2SeO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 1.5H_2O$	42–102	95	23.0	—	—	14.6[a]
(IVb)	$K_2SeO_4 \cdot CuSO_4 \cdot 1.5H_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 0.5H_2O$	102–190	150	—	—	46.0	—
(IVc)	$K_2SeO_4 \cdot CuSO_4 \cdot 0.5H_2O \rightarrow K_2SeO_4 \cdot CuSO_4$	190–237	220	—	—	—	—[b]
(IV'a)	$K_2SeO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O$	42–110	93	23.0	—	—	18.2[a]
(IV'b)	$K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CuSO_4$	131–240	148	76.6	76.6	76.6	18.2
(Va)	$K_2SeO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2H_2O$	40–108	94	23.0	23.0	23.0	14.1
(Vb)	$K_2SeO_4 \cdot ZnSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$	130–175	142	107.0	107.0	107.0	14.1
(V'a)	$K_2SeO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O$	45–110	96	20.0	23.0	23.0	18.4
(V'b)	$K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$	120–180	145	103.5	103.5	103.5	14.5

[a] These indicate the overall enthalpy changes where DTA curves overlap too much. [b] The calculation of thermal parameters is not done due to very poor resolution of the curves.

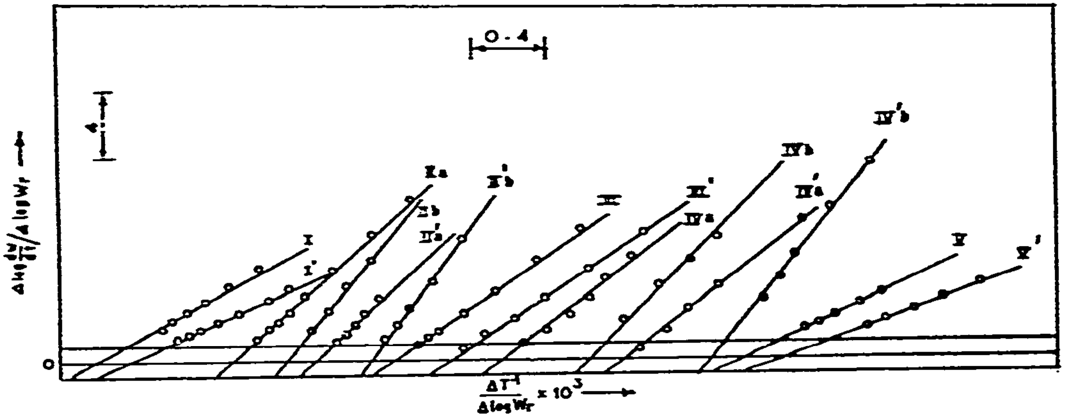

Fig. 6. Plots of $\Delta \log (d\alpha/dt)/\Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from the TG curves for the dehydration of $K_2BeF_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot MgSO_4$(I), $K_2BeF_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot MgSO_4$(I'), $K_2BeF_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot CoSO_4 \cdot 2H_2O$(IIa), $K_2BeF_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2BeF_4 \cdot CoSO_4$(IIb), $K_2BeF_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot CoSO_4 \cdot 2D_2O$(II'a), $K_2BeF_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2BeF_4 \cdot CoSO_4$(II'b), $K_2BeF_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot NiSO_4$(III), $K_2BeF_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot NiSO_4$(III'), $K_2BeF_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot CuSO_4 \cdot 2H_2O$(IVa), $K_2BeF_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow K_2BeF_4 \cdot CuSO_4$(IVb), $K_2BeF_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot CuSO_4 \cdot 2D_2O$(IV'a), $K_2BeF_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2BeF_4 \cdot CuSO_4$(IV'b), $K_2BeF_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot ZnSO_4$(V) and $K_2BeF_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot ZnSO_4$(V').

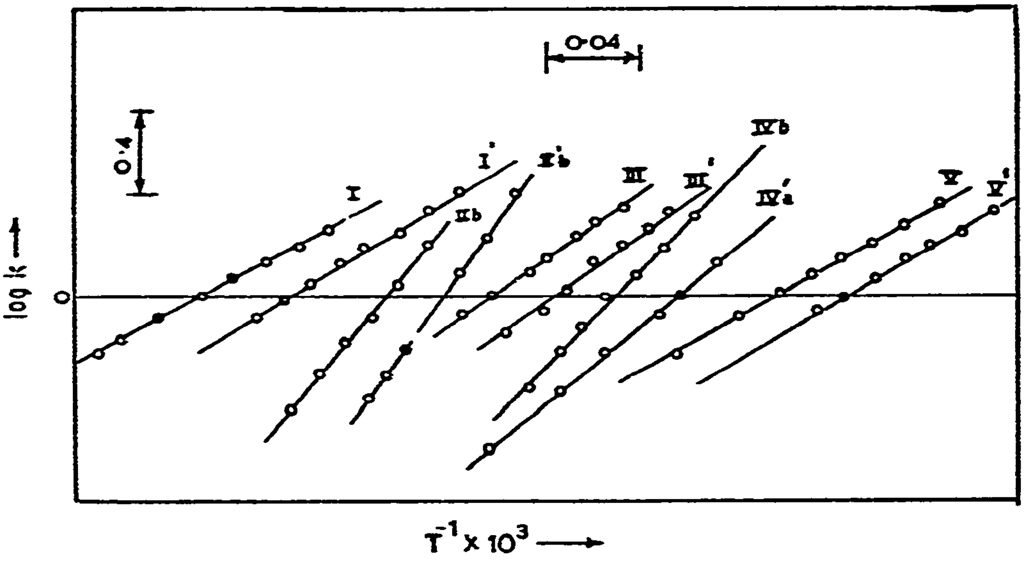

Fig. 7. Arrhenius plots of log k vs. $T^{-1} \times 10^3$, from the DTG curves for the dehydration of $K_2BeF_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot MgSO_4$(I), $K_2BeF_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot MgSO_4$(I'), $K_2BeF_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2BeF_4 \cdot CoSO_4$(IIb), $K_2BeF_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2BeF_4 \cdot CoSO_4$(II'b), $K_2BeF_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot NiSO_4$(III), $K_2BeF_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot NiSO_4$(III'), $K_2BeF_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow K_2BeF_4 \cdot CuSO_4$(IVb), $K_2BeF_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot CuSO_4 \cdot 2D_2O$(IV'a), $K_2BeF_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2BeF_4 \cdot ZnSO_4$(V) and $K_2BeF_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2BeF_4 \cdot ZnSO_4$(V').

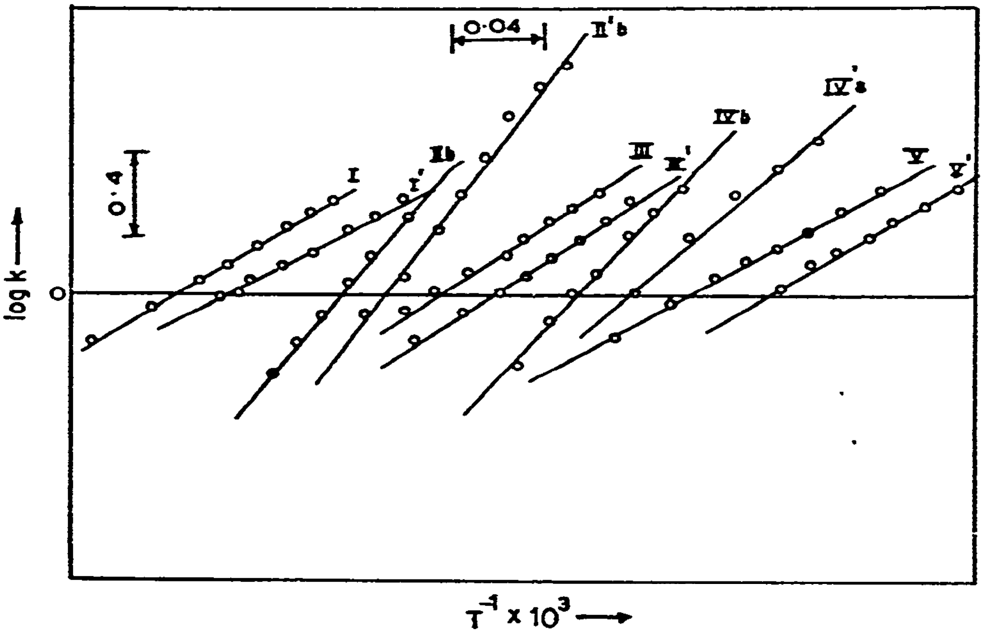

Fig. 8. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from DTA curves for the dehydration of $K_2BeF_4\cdot MgSO_4\cdot 6H_2O \rightarrow K_2BeF_4\cdot MgSO_4$(I), $K_2BeF_4\cdot MgSO_4\cdot 6D_2O \rightarrow K_2BeF_4\cdot MgSO_4$(I'), $K_2BeF_4\cdot CoSO_4\cdot 2H_2O \rightarrow K_2BeF_4\cdot CoSO_4$(IIb), $K_2BeF_4\cdot CoSO_4\cdot 2D_2O \rightarrow K_2BeF_4\cdot CoSO_4$(II'b), $K_2BeF_4\cdot NiSO_4\cdot 6H_2O \rightarrow K_2BeF_4\cdot NiSO_4$(III). $K_2BeF_4\cdot NiSO_4\cdot 6D_2O \rightarrow K_2BeF_4\cdot NiSO_4$(III'), $K_2BeF_4\cdot CuSO_4\cdot 2H_2O \rightarrow K_2BeF_4\cdot CuSO_4$(IVb), $K_2BeF_4\cdot CuSO_4\cdot 6D_2O \rightarrow K_2BeF_4\cdot CuSO_4\cdot 2D_2O$(IV'a), $K_2BeF_4\cdot ZnSO_4\cdot 6H_2O \rightarrow K_2BeF_4\cdot ZnSO_4$(V) and $K_2BeF_4\cdot ZnSO_4\cdot 6D_2O \rightarrow K_2BeF_4\cdot ZnSO_4$(V').

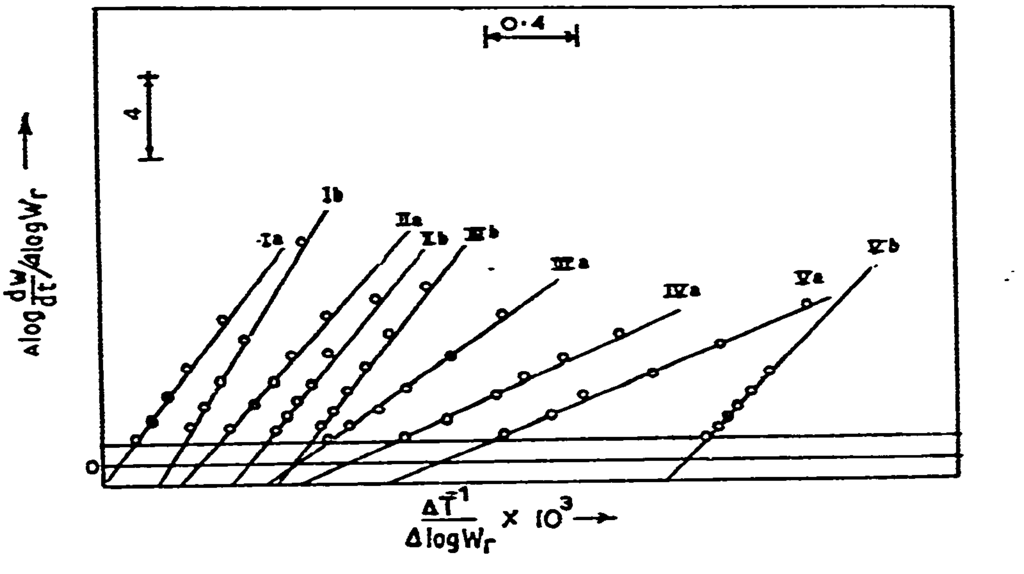

Fig. 9. Plots of $\Delta \log (dw/dt)/\Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from the TG curves for the dehydration of $K_2SeO_4\cdot MgSO_4\cdot 6H_2O \rightarrow K_2SeO_4\cdot MgSO_4\cdot 2H_2O$(Ia), $K_2SeO_4\cdot MgSO_4\cdot 2H_2O \rightarrow K_2SeO_4\cdot MgSO_4$(Ib), $K_2SeO_4\cdot CoSO_4\cdot 6H_2O \rightarrow K_2SeO_4\cdot CoSO_4\cdot 2H_2O$(IIa), $K_2SeO_4\cdot CoSO_4\cdot 2H_2O \rightarrow K_2SeO_4\cdot CoSO_4$(IIb), $K_2SeO_4\cdot NiSO_4\cdot 6H_2O \rightarrow K_2SeO_4\cdot NiSO_4\cdot 2H_2O$(IIIa), $K_2SeO_4\cdot NiSO_4\cdot 2H_2O \rightarrow K_2SeO_4\cdot NiSO_4$(IIIb), K_2SeO_4 $CuSO_4\cdot 6H_2O \rightarrow K_2SeO_4\cdot CuSO_4\cdot 1.5H_2O$(IVa), $K_2SeO_4\cdot ZnSO_4\cdot 6H_2O \rightarrow K_2SeO_4\cdot ZnSO_4\cdot 2H_2O$(Va) and $K_2SeO_4\cdot ZnSO_4\cdot 2H_2O \rightarrow K_2SeO_4\cdot ZnSO_4$(Vb).

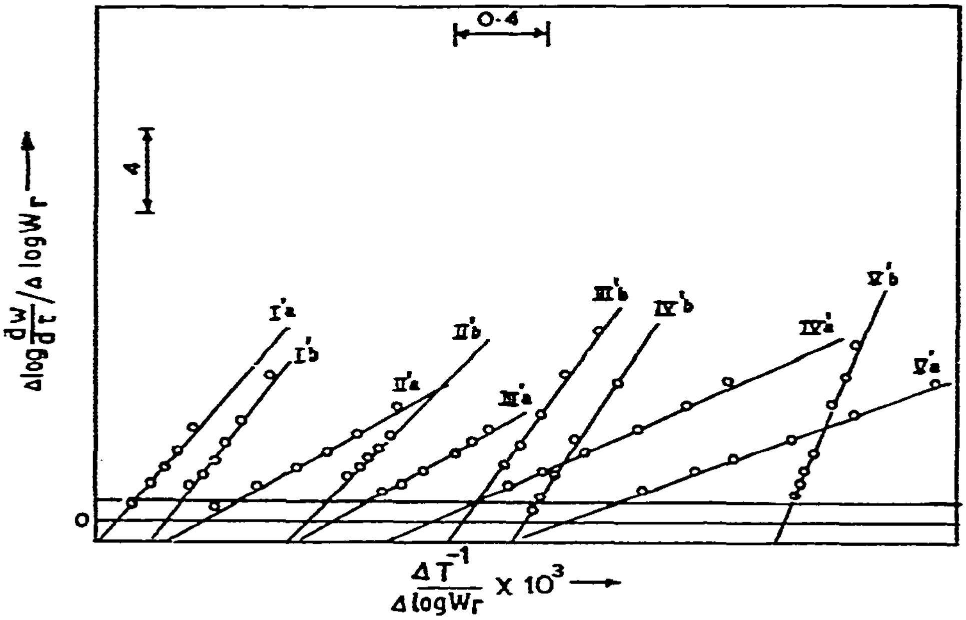

Fig. 10. Plots of Δ log (dx/dt)/Δ log W_r vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from the TG curves for the dehydration of $K_2SeO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O$ (I'a), $K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot MgSO_4$ (I'b), $K_2SeO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O$ (II'a), $K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CoSO_4$ (II'b), $K_2SeO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O$ (III'a), $K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O \rightarrow K_2SeO_4 \cdot NiSO_4$ (III'b), $K_2SeO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O$ (IV'a), $K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CuSO_4$ (IV'b), $K_2SeO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O$ (V'a) and $K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$ (V'b).

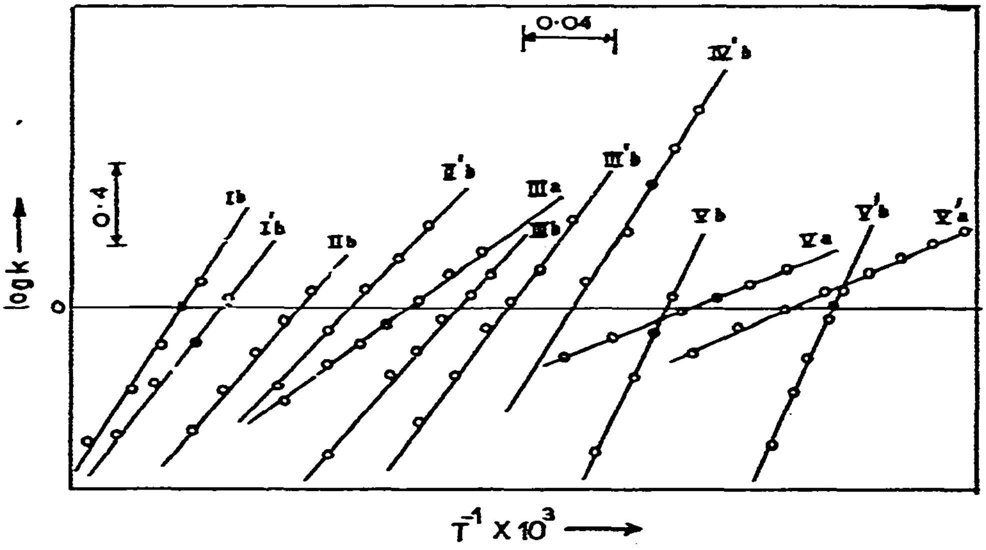

Fig. 11. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTG curves for the dehydration of $K_2SeO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot MgSO_4$ (Ib), $K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot MgSO_4$ (I'b), $K_2SeO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot CoSO_4$ (IIb), $K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CoSO_4$ (II'b), $K_2SeO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot NiSO_4 \cdot 2H_2O$ (IIIa), $K_2SeO_4 \cdot NiSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot NiSO_4$ (IIIb), $K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O \rightarrow K_2SeO_4 \cdot NiSO_4$ (III'b), $K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CuSO_4$ (IV'b), $K_2SeO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2H_2O$ (Va), $K_2SeO_4 \cdot ZnSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$ (Vb), $K_2SeO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O$ (V'a) and $K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$ (V'b).

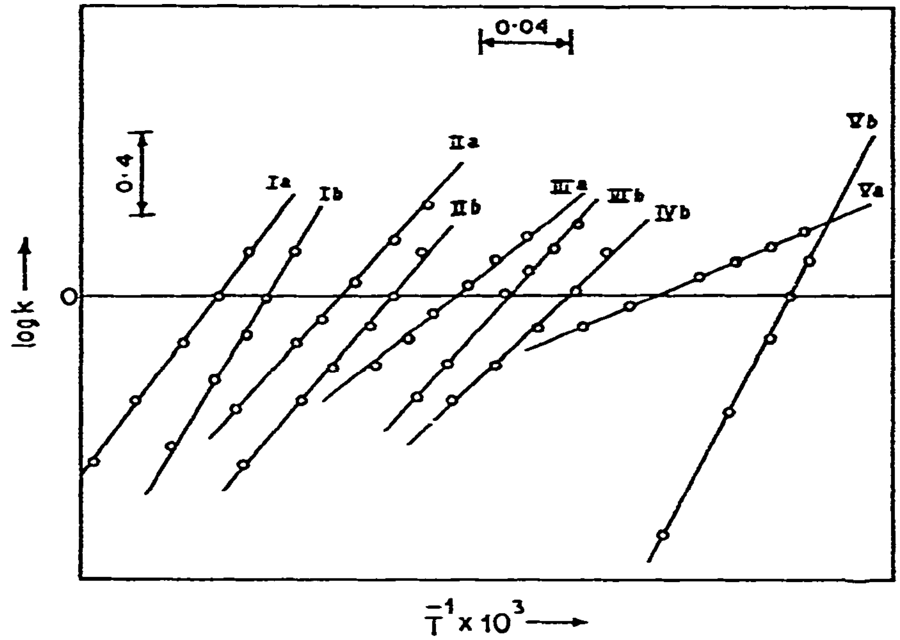

Fig. 12. Arrhenius plots of log *k* vs. T^{-1} from the DTA curves for the dehydration of $K_2SeO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot MgSO_4 \cdot 2H_2O$(Ia), $K_2SeO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot MgSO_4$(Ib), $K_2SeO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot CoSO_4 \cdot 2H_2O$(IIa), $K_2SeO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot CoSO_4$(IIb), $K_2SeO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot NiSO_4 \cdot 2H_2O$(IIIa), $K_2SeO_4 \cdot NiSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot NiSO_4$(IIIb), $K_2SeO_4 \cdot CuSO_4 \cdot 1.5H_2O \rightarrow K_2SeO_4 \cdot CuSO_4 \cdot 0.5H_2O$(IVb), $K_2SeO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2H_2O$(Va) and $K_2SeO_4 \cdot ZnSO_4 \cdot 2H_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$(Vb).

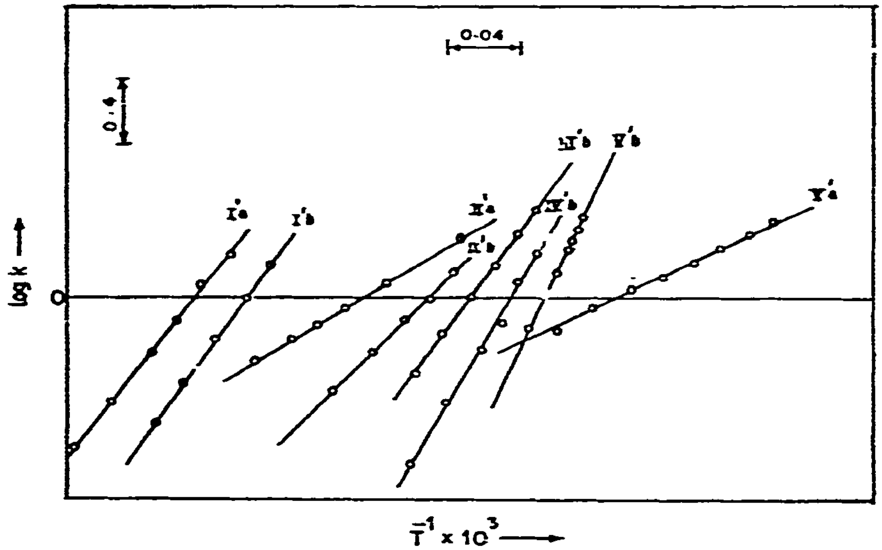

Fig. 13. Arrhenius plots of log *k* vs. T^{-1} from the DTA curves for the dehydration of $K_2SeO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O$(I'a), $K_2SeO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot MgSO_4$(I'b), $K_2SeO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O$(II'a), $K_2SeO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CoSO_4$(II'b), $K_2SeO_4 \cdot NiSO_4 \cdot 1.5D_2O \rightarrow K_2SeO_4 \cdot NiSO_4$(III'b), $K_2SeO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot CuSO_4$(IV'b), $K_2SeO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O$(V'a) and $K_2SeO_4 \cdot ZnSO_4 \cdot 2D_2O \rightarrow K_2SeO_4 \cdot ZnSO_4$(V'b).

in Tables 1 and 2 and the corresponding Arrhenius plots are shown in Figs. 7, 8 and 11–13. The order of reaction for each step of dehydration was found to be unity. The IR spectra of the salt hydrates and their D_2O analogues are taken to ensure the deuteration of the hydrates to the desired extent. X-ray diffraction patterns show that the salt hydrates and their corresponding D_2O analogues are isomorphous to each other.

DISCUSSION

The nature of dehydration of the salt hydrate of Mg(II) of 'A' differs from the corresponding salt hydrate of 'B' and also from that of 'C' studied earlier[2], where 'C' denotes $K_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$. Our earlier work showed that the salt hydrate of Mg(II) of 'C' lost D_2O molecules in single step on deuteration like the corresponding salt of 'A', instead of in three equal steps. But the salt hydrates of 'A' and 'B' of Mg(II) do not show any change in the nature of dehydration on deuteration. The thermal stability with respect to the first DTG peak temperature of this salt hydrate of 'A' is high in comparison to that of 'B'. It is observed that the thermal stability of the corresponding salt hydrate of 'C' is lowest with respect to that of 'A' and 'B'. On deuteration thermal stabilities of the salt hydrates of 'A' and 'B' remain unaltered, whereas, the thermal stability of the corresponding deuterated salt hydrate of 'C' increases and becomes equal to that of 'A'. The activation energy* of dehydration of the salt hydrate of 'B' is high in comparison to that of 'A' and is equal to that of 'C' studied already by us. On deuteration the value of the activation energy decreases slightly in both the salt hydrates of Mg(II) of 'A' and 'B' but decreases noticeably in the case of the corresponding salt hydrate of 'C'. Thereby, the value of activation energy of dehydration of Mg(II) salt hydrate of 'A' becomes equal to that of C. The enthalpy change of dehydration of this salt hydrate of 'B' is greater than that of 'A'. It is noticed in our earlier work that this value of the corresponding salt hydrate of 'C' is lowest with respect to the other two types. On deuteration these values increase.

The nature of dehydration of the double salt hydrate of Co(II) of 'A' is similar to that of 'B' and also to that of 'C' as observed from TG. But the DTA and DTG curves for the first step of dehydration of this salt hydrate of 'A' show two peaks indicating the existence of an unstable intermediate. Whereas, for the corresponding salt hydrate of 'B', DTG curves for the first step of dehydration show a shoulder accompanied by a peak indicating here also the existence of an intermediate, although the corresponding DTA curve does not respond well to the inference drawn from the DTG curve. On deuteration, a similar phenomenon is observed in the corresponding salt hydrate of 'A', whereas, in the case of the corresponding salt hydrate of 'B' another shoulder which is not prominent in the DTA curve is observed in the DTG curve during the first step of dehydration in addition to that of its H_2O analogue.

---

*Average of the values obtained from TG, DTA and DTG curves.

The thermal stability with respect to the first DTG peak temperature of this salt hydrate of 'A' is slightly high in comparison to that of 'B' and is close to that of 'C'. The corresponding D_2O analogues do not show any variation in thermal stability. The value of activation energy of dehydration of this salt hydrate of 'B' is high in comparison to that of 'A'. It is observed that both values are high in comparison to the value evaluated from that of 'C'. The value decreases in the corresponding salt hydrate of 'B' and remains the same in 'A' on deuteration and order with respect to the present deuterated salt hydrates and that of 'C' follows as: 'A'>'C'>'B'. Activation energies for the second step of dehydration of salt hydrate of 'A' and 'B' are close and the similar value is also obtained in the corresponding step of dehydration of 'C'. It is observed that the value of activation energy for the second step of dehydration of the deuterated salt hydrate of 'C' decreases. This decrease in the value of activation energy due to deuteration observed in the case of the salt hydrate of 'A' shows no change in the activation energy value on deuteration. The enthalpy changes of dehydration of these salt hydrates and their D_2O analogues do not differ much and the values are close to that of 'C'. It is observed in our earlier work that $K_2Co(SO_4)_2 \cdot 2H_2O$ is thermally stable. This type of thermal stability is observed in the case of the corresponding dihydrates of 'A' and 'B'.

The nature of dehydration of the salt hydrate of Ni(II) of 'A' differs from that of 'B' and also from that of 'C' studied earlier. The corresponding salt hydrate of 'C' lost five and half molecules of water in the first step and the remaining half molecule in the second step. Similar nature of dehydration is observed also on deuteration. Like the salt hydrate of 'C' the present deuterated salt hydrate of 'A' loses D_2O molecules similar to its H_2O analogue, whereas, this similarity in the nature of dehydration is not observed in the corresponding salt hydrate of 'B'. The thermal stability with respect to first DTG peak temperature of the salt hydrate of 'A' is high in comparison to that of the salt hydrate of 'B' and is close to that of 'C'. It is noticed that the thermal stability of the salt hydrate of 'C' remains unaltered on deuteration. Here a similar phenomenon is observed, though the deuterated salt hydrate of 'B' eliminates D_2O molecules in a different fashion in comparison to its H_2O analogue. The activation energy of dehydration of this salt hydrate of 'B' is close to that of 'A' and is high with respect to that of 'C' studied earlier. On deuteration of the salt hydrate of 'B' the value of activation energy decreases (37.1 → 30.6). Whereas, the value of that of 'A' remains unaltered like the corresponding deuterated salt hydrate of 'C'. The values of enthalpy changes of dehydration of the salt hydrates of 'A' and 'B' are close and these are also close to that of 'C'.

The nature of dehydration of the Cu(II) salt hydrate of 'A' is apparently similar to that of 'C' and unlike that of 'B'. The salt hydrate of 'C' showed a shoulder accompanied by a prominent DTA peak during the dehydration of the first four molecules of water and two overlapped DTA peaks for the elimination of the last two molecules of water indicating the existence of a more thermally unstable intermediate. Its DTG curve also supported the above fact. Whereas, the salt hydrate of 'A' shows two peaks overlapped to each other, for the elimination of the first four molecules of water and shows a single peak in DTA curve for the elimination of the last two molecules of water. It was noticed that none of the intermediate salt hydrates of Cu(II) of 'C' was thermally stable. It was also noticed that the D_2O analogue of the salt hydrate of 'C' showed two peaks overlapped by each other for the elimination of the first four molecules of D_2O and showed DTA peaks for the elimination of the last two molecules of D_2O like its H_2O analogue, but the peaks were weak in resolution. Here also this type of change on deuteration occurs in the case of the salt hydrate 'A', whereas, a prominent change appears in the case of the deuterated salt hydrate of 'B'. The thermal stability of the Cu(II) salt hydrate of 'B' with respect to the first DTG peak temperature is slightly high in comparison to that of 'A' and is close to that of 'C'. On deuteration the thermal stability of the salt hydrate of 'B' remains almost the same like that of 'C', whereas, the thermal stability of that of 'A' decreases slightly. The activation energy for the first step of dehydration of the Cu(II) salt hydrate of 'B' is close to that of 'C' and is appreciably low in comparison to that of 'A'. It is noticed that the Cu(II) salt hydrates of 'A', 'B' and 'C' do not show any change in the value of activation energy due to deuteration, though D_2O effects the nature of dehydration. The enthalpy change for the first step of dehydration of the salt hydrate of 'B' is close to that of 'C' and is high in comparison to that of 'A'. The enthalpy changes of dehydration of the salt hydrates of 'A' and 'B' increase on deuteration, whereas, a slight decrease in the value of enthalpy change was observed in the corresponding salt hydrate of 'C'.

The nature of dehydration of the salt hydrate of Zn(II) of 'B' is similar to that of the corresponding salt hydrate of 'C' but unlike to that of 'A'. Neither of the salt hydrates of Zn(II) shows any change in the nature of dehydration due to deuteration like that of 'C'. The thermal stability with respect to first DTG peak temperature of this salt hydrate of 'A' is close to that of 'C' studied earlier and is high in comparison to that of 'B'. The thermal stability of the D_2O analogues also remains practically same. The dihydrate of the salt hydrate of 'B' is more thermally stable than that of 'C'. The values of activation energies of dehydration of the present salt hydrate of Zn(II) are close to each other but the values are low in comparison to that of 'C'. On deuteration the values remain unaltered like the salt hydrate of 'C'. The value of enthalpy change of dehydration of the salt hydrate of Zn(II) of 'B' differs from that of 'A' and also from that of 'C' and the order is as follows: 'B'>'A'>'C'. On deuteration the value for 'A' is close to that of 'C' and the value of 'B' increases to a certain extent, i.e., 14.1 to 18.4 kcal mol^{-1}.

It is observed that the nature of dehydration and also the thermal parameters of the salt hydrates $K_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues change with the replacement of one sulphate anion which is linked to the monovalent cation, i.e., K(I), by SeO_4^{2-} or BeF_4^{2-}. It is also observed that the thermal stabilities of the salt hydrates of 'A' are higher than those of the other salt hydrates of 'B' and 'C' in most of the cases. It is noticed, that where the salt hydrates of the same metal(II) lose H_2O or D_2O molecules in a similar fashion, thermal parameters become close to each other. Although, this is not observed in the case of Zn(II). The nature of dehydration of the

Cu(II) salt hydrate of 'B' is not similar to that of 'C', but their thermal parameters are very close to each other. On deuteration the thermal properties of the salt hydrates of 'A' and 'B' are effected except the salt hydrate of Zn(II), whereas, this effect was less in the corresponding salt hydrate of 'C'.

The first DTG peak temperatures of the salt hydrates of 'A' show the following order in thermal stability: Ni(II) > Mg(II) > Zn(II) > Co(II) > Cu(II). The same order is almost maintained in their D_2O analogues. Similarly the first DTG peak temperatures of the salt hydrates of 'B' show the following order of thermal stability: Ni(II) > Mg(II) > Co(II) = Cu(II) ≥ Zn(II). Here also their D_2O analogues show no change in the order of thermal stability. The order of thermal stability of the salt hydrate of 'A' is maintained in the corresponding deuterated salt hydrates of 'C' where this is not maintained properly in 'B'.

The activation energy for the latter step of dehydration gives a larger value than the earlier. This phenomenon is observed in our earlier works[1-5] and also in Tsuchiya's[14] work. The order of the value of activation energies of the salt hydrates of 'C' is not maintained in both 'A' and 'B'.

It is observed that the values of enthalpy change of dehydration of salt hydrates of 'A' and 'B' ranges from $\sim 11 - \sim 19$ kcal mol^{-1}. There is little effect on the value of ΔH on deuteration.

The differences in the value of the thermal parameters are due to different states of bonding between the two elements of the anions of SO_4^{2-}, SeO_4^{2-} and BeF_4^{2-}, although these anions have the same size and symmetry.

ACKNOWLEDGEMENT

The authors are grateful to Prof. N. K. Dutt, Head of this laboratory, for various help and stimulating interest in this work.

REFERENCES

1 N. Ray Chaudhuri, G. K. Pathak and S. Mitra, *Proc. 4th Int. Conf. Therm. Anal.*, 1974.
2 N. Ray Chaudhuri and G. K. Pathak, *Thermochim. Acta*, 12 (1975) 71.
3 N. Ray Chaudhuri and G. K. Pathak, *Thermochim. Acta*, 12 (1975) 287.
4 N. Ray Chaudhuri and G. K. Pathak, *Thermochim. Acta*, 12 (1975) 397.
5 N. Ray Chaudhuri and G. K. Pathak, *Thermochim. Acta*, 13 (1975) 71.
6 P. C. Ray and P. B. Sarkar, *J. Ind. Chem. Soc.*, 6 (1929) 987.
7 P. C. Ray and P. B. Sarkar, *Nature*, 124 (1929) 481.
8 T. K. Ghose, T. N. Chakrabarty and N. N. Ray, *J. Ind. Chem. Soc.*, 42 (1965) 847.
9 E. Von Gerichten, *Liebig's Ann.*, 168 (1873) 225.
10 K. Sano, *Sci. Rep. Tohoku. Imp. Univ., Ist Ser.*, 24 (1936) 719.
11 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
12 N. G. Dave and S. K. Chopra, *Z. Phys. Chem.*, 48 (1966) 257.
13 H. J. Brochardt and F. Daniels, *J. Amer. Chem. Soc.*, 79 (1957) 41.
14 H. Oki, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Jap.*, 43 (1970) 3263.