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

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ABSTRACT

Dehydration of double salt hydrates of the type $M(I)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ where $M(I) = Rb(I)$ and $M(II) = Mg(II)$, Mn(II), Co(II), Ni(II), Zn(II) and Cu(II) has been studied by derivatograph. Thermal parameters like activation energy, order of reaction, enthalpy change etc. for each step of dehydration have been evaluated from the analyses of TG, DTA and DTG curves and these parameters are compared with the corresponding salt hydrates of the $NH_4(I)$ and K(I) series. These double salt hydrates are deuterated and studied similarly. Activation energies for the first step of dehydration of these salt hydrates increase with the increase of second ionisation potential of the central metal except for Mg. The nature of dehydration changes in the cases of double salt hydrates of Mg(II) and Ni(II) on deuteration. The order of reaction for each case of dehydration has been found to be unity. The enthalpy change per mole of water varies from 11.4 to 17 kcal.

INTRODUCTION

Recently, we reported non-isothermal studies of the 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] or K(I)[2] and M(II) = Mg(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II) and their D_2O analogues. In continuation to these works the present paper deals with the dehydration of similar double salt hydrates of the Rb(I) series and their D_2O analogues. The present paper reports the values of activation energies of all dehydration processes from TG, DTA and DTG curves simultaneously, the order of reaction from TG and the enthalpy changes from DTA peak areas. It also reports the effect of deuteration on the nature of dehydration and a comparison of the effect of deuteration on the thermal properties with the corresponding $NH_4(I)$ and K(I) series.

EXPERIMENTAL

Double salt hydrates were prepared following the standard procedure adopted by earlier workers[3] and their D_2O analogues were prepared by dissolving equimolecular mixtures of anhydrous single salts in D_2O and subsequent crystallisation. A Paulik-Paulik-Erdey type MOM, OD-102 derivatograph has been used for thermal analyses. The particle size of the samples was within 150–200 mesh. The heating rate was about 1.5°C min^{-1}. The volume of the sample in each case was nearly the same.

RESULTS

The double salt hydrate of Mg(II) of the present series loses its water molecules in two distinct steps. In the first step four molecules of water are eliminated and the rest is eliminated in the final step but its D_2O analogue loses its D_2O molecules in a slightly different manner, i.e., $Rb_2Mg(SO_4)_2 \cdot 6D_2O \rightarrow Rb_2Mg(SO_4)_2 \cdot 2D_2O \rightarrow Rb_2Mg(SO_4)_2 \cdot 1.75D_2O \rightarrow Rb_2Mg(SO_4)_2$ which is also shown in Fig. 1. The additional intermediate product, i.e., $Rb_2Mg(SO_4)_2 \cdot 1.75D_2O$, is, however, unstable. Fig. 2 shows that the double salt hydrates of Mn(II), Co(II) and Zn(II) lose their water molecules in a single step and their D_2O analogues also follow the similar fashion of dehydration. The double salt hydrate of Cu(II) loses its water molecules in two steps like the double salt hydrate of Mg(II) of the same series (Fig. 2) and its D_2O analogue behaves similarly. The double salt hydrate of Ni(II) loses all its water molecules in a single step, whereas, its D_2O analogue loses D_2O molecules like the double salt hydrate of Cu(II) of the present series (Fig. 3). All the dehydration processes show the well-resolved DTA and DTG curves except for the double salt hydrate of Mn(II) and its D_2O analogue. DTG peak temperatures and temperature ranges of dehydration of the double salt hydrates and their corresponding D_2O analogues are tabulated in Table 1. Enthalpy changes for each step of dehydration are evaluated by the method of Sano[4] using copper sulphate pentahydrate as the standard (see Table 1). When DTA peaks overlap too much with each other, the ΔH values are evaluated from the overall area of the DTA peaks concerned. Activation energies for each step of dehydration of the salt hydrates and their D_2O analogues are evaluated from the analyses of TG curves using Freeman and Carroll's[5] equation. The results are tabulated in Table 1 and the corresponding curves are shown in Figs. 4 and 5. The activation energies for each step of dehydration are also evaluated from the analyses of DTG curves using the method of Dave and Chopra[6] and the method described in our earlier works[1,2] and also from the analyses of DTA curves using Brochardt's equation[7] for first order reactions. All these values are tabulated in Table 1 and the corresponding Arrhenius plots are shown in Figs. 6 and 7. The order of reaction was found to be unity for each step of dehydration of the double salt hydrates and their D_2O analogues. The IR spectra of the salt hydrates and their D_2O analogues are taken to ensure that deuteration of the hydrates proceeds to the desired extent. X-ray diffraction patterns show that the salt hydrates and their corresponding D_2O analogues are isomorphous to each other.

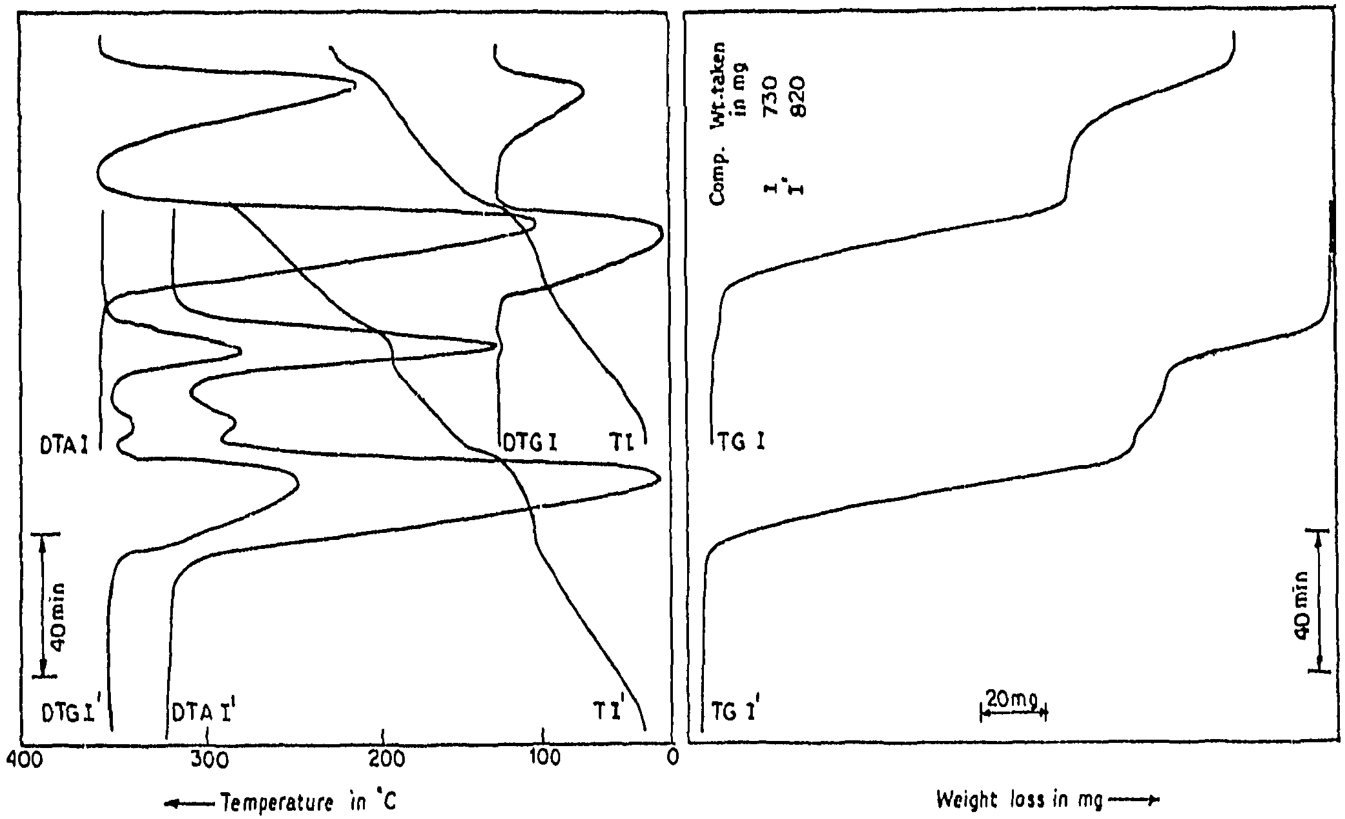

Fig. 1. Derivatograms for $Rb_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (I) and $Rb_2SO_4 \cdot MgSO_4 \cdot 6D_2O$ (I').

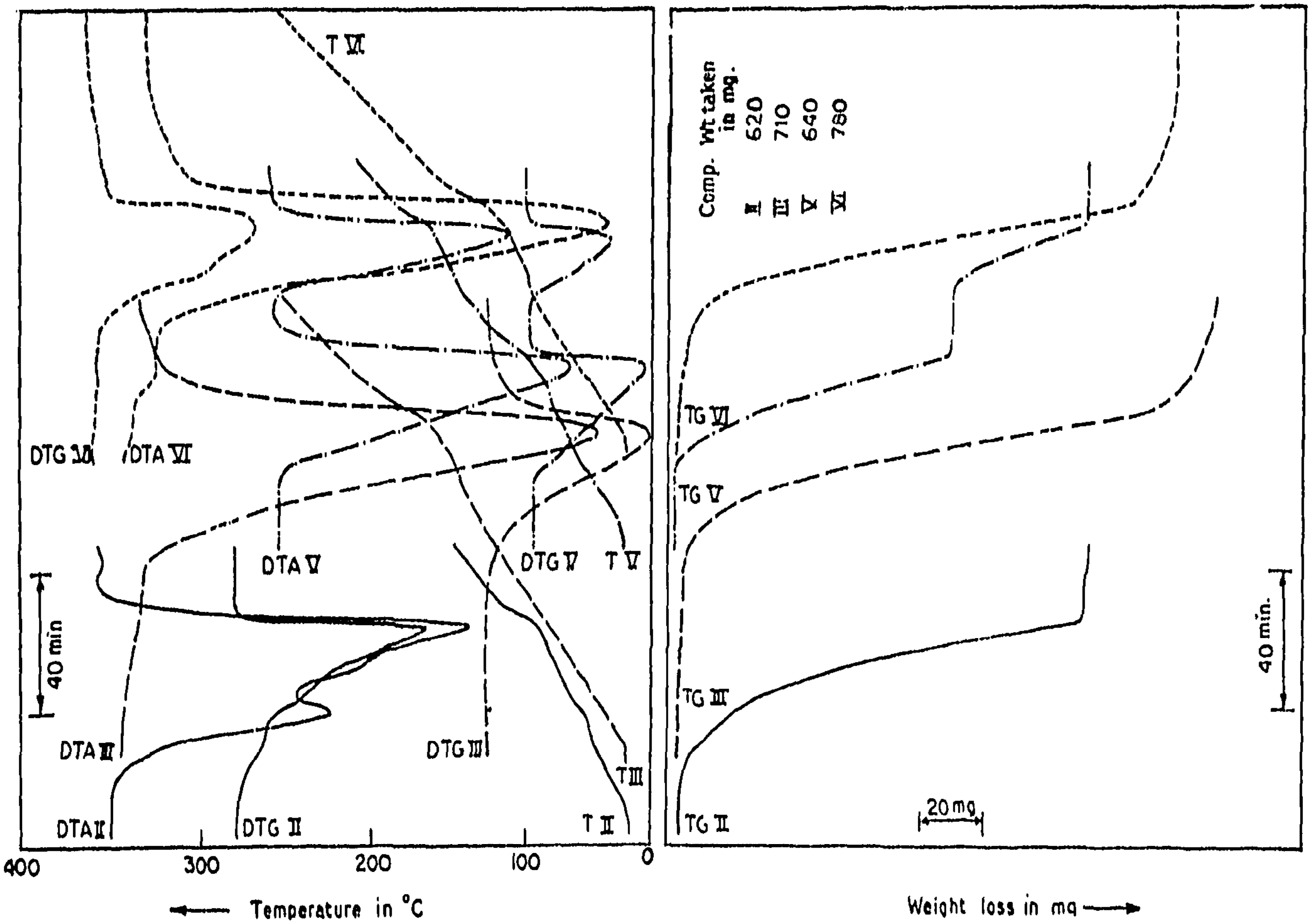

Fig. 2. Derivatograms for $Rb_2SO_4 \cdot MnSO_4 \cdot 6H_2O$(II), $Rb_2SO_4 \cdot CoSO_4 \cdot 6H_2O$(III), $Rb_2SO_4 \cdot CuSO_4 \cdot 6H_2O$(V) and $Rb_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$(VI).

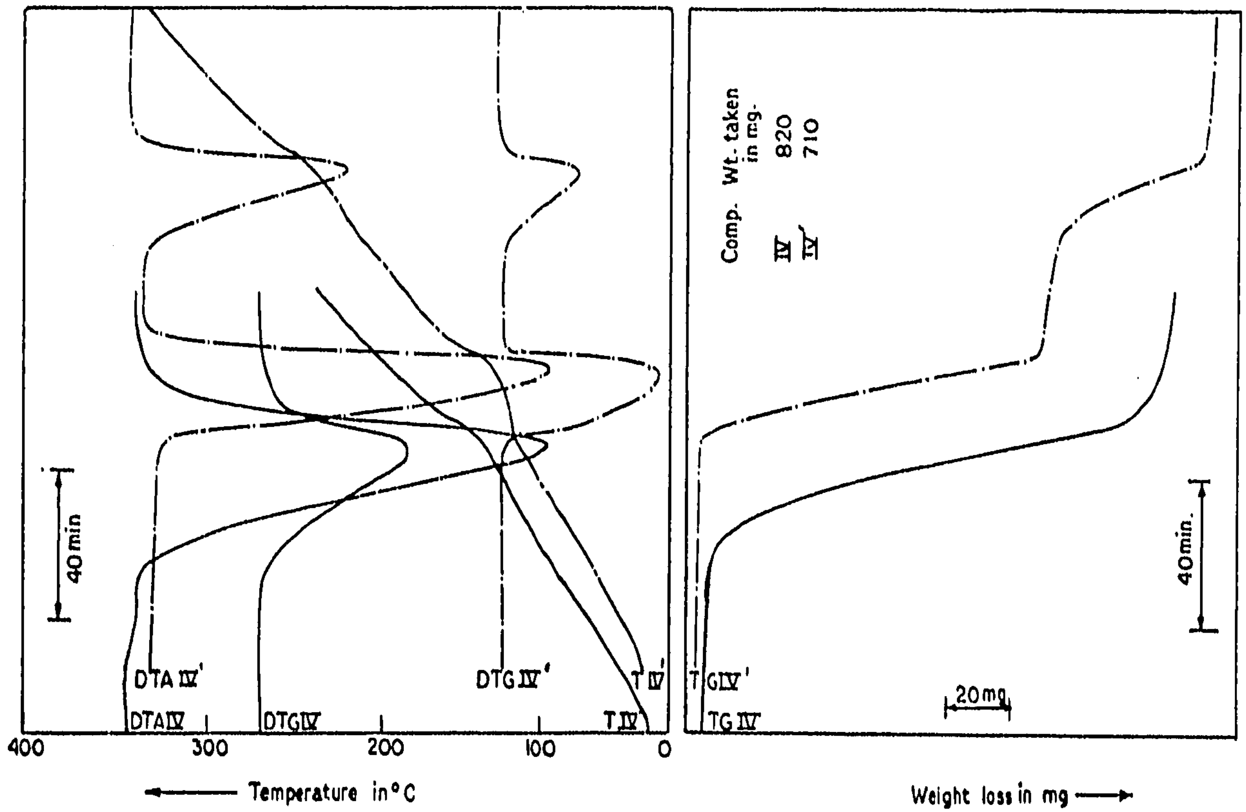

Fig. 3. Derivatograms for $Rb_2SO_4 \cdot NiSO_4 \cdot 6H_2O$(IV) and $Rb_2SO_4 \cdot NiSO_4 \cdot 6D_2O$(IV').

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)	$Rb_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O$	90–125	110	33.0	38.3	38.3	13.7
(Ib)	$Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$	160–225	196	55.0	57.6	57.6	13.5
(I'a)	$Rb_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2D_2O$	80–140	115	34.5	42.0	42.0	16.3
(I'a')	$Rb_2SO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 1.75D_2O$	140–170	162	—	—	—	—[a]
(Ib)	$Rb_2SO_4 \cdot MgSO_4 \cdot 1.75D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$	190–210	195	84.3	84.3	84.3	15.4
(II)	$Rb_2SO_4 \cdot MnSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot MnSO_4$	32–100	88	19.7	—	—	11.4[b]
(II')	$Rb_2SO_4 \cdot MnSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot MnSO_4$	33–100	89	19.7	—	—	13.4[b]
(III)	$Rb_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$	85–220	132	23.0	27.6	29.9	13.0
(III')	$Rb_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$	85–225	132	27.6	27.6	30.6	14.5
(IV)	$Rb_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$	105–270	165	26.3	30.6	30.6	14.8
(IV'a)	$Rb_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O$	115–155	130	56.2	56.2	57.5	14.8
(IV'b)	$Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$	205–265	240	69.0	69.0	69.0	14.4
(Va)	$Rb_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O$	55–105	95	32.8	32.8	32.8	15.6
(Vb)	$Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$	140–170	160	92.0	92.0	92.0	14.9
(V'a)	$Rb_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O$	55–105	95	29.3	29.3	29.3	17.0
(V'b)	$Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$	145–170	162	107.0	107.0	107.0	16.4
(VI)	$Rb_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$	70–165	115	27.6	27.6	30.6	13.6
(VI')	$Rb_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$	70–165	115	26.3	30.6	30.6	13.8

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

DISCUSSION

Earlier, the dehydration of $Rb_2Mg(SO_4)_2 \cdot 6H_2O$ was studied by Rassonskaya[8]. He observed the similar nature of dehydration as observed by us but the corresponding DTA and DTG curves overlapped, having both two peaks. But we found a prominent break in the TG curve and two well-resolved DTA and DTG curves. He evaluated the activation energy for the first step of dehydration from DTA curve by Piloyan's method and found a value of 26.0 kcal mol^{-1} and a value of 27.5 from the analysis of the TG curve. In our case, the value for the activation energy for the first step of dehydration is high in comparison to Rassonskaya's value. This difference is probably due to the difference in heating rate, the nature of the crucible etc. Moreover, he did not determine the activation energy from the DTG curve. The nature of dehydration of this salt hydrate is quite different from the corresponding $NH_4(I)^1$ and $K(I)^2$

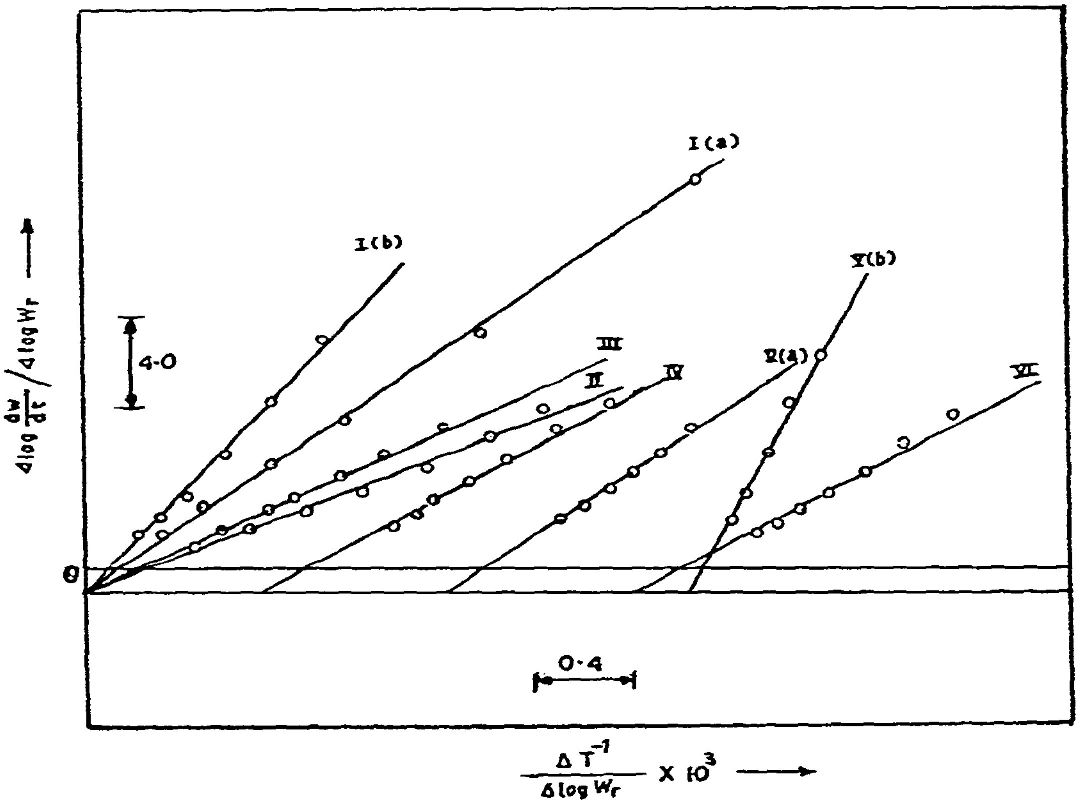

Fig. 4. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ vs. $\frac{\Delta T^{-1}}{\Delta \log W_r} \times 10^3$ from TG for the dehydration of $Rb_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O$(Ia), $Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$(Ib), $Rb_2SO_4 \cdot MnSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot MnSO_4$(II), $Rb_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$(III), $Rb_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$(IV), $Rb_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O$(Va), $Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$(Vb) and $Rb_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$(VI).

series. In the case of the corresponding NH_4(I) series, the first step of dehydration took place with five molecules of water and the rest was eliminated in the final step, the monohydrate, however, was unstable. A similar way of dehydration was also observed on deuteration. In the case of the corresponding K(I) series dehydration took place in three equal steps, whereas, on dueteration, dehydration took place in a single step. With respect to the first DTG peak temperature, the thermal stability of Mg(II) double salt hydrates of the NH_4(I), K(I) and Rb(I) series follows the order: $NH_4(I) > Rb(I) > K(I)$ but the thermal stability of the corresponding D_2O analogues follows a different order: $NH_4(I) > Rb(I) = K(I)$. The activation energy* of dehydration is less than that of K(I) and higher than that of NH_4(I). On deuteration this value of activation energy remains the same, but the D_2O analogue follows the order: $Rb(I) > K(I) > NH_4(I)$. This change is due to a fall in the value of activation energy of

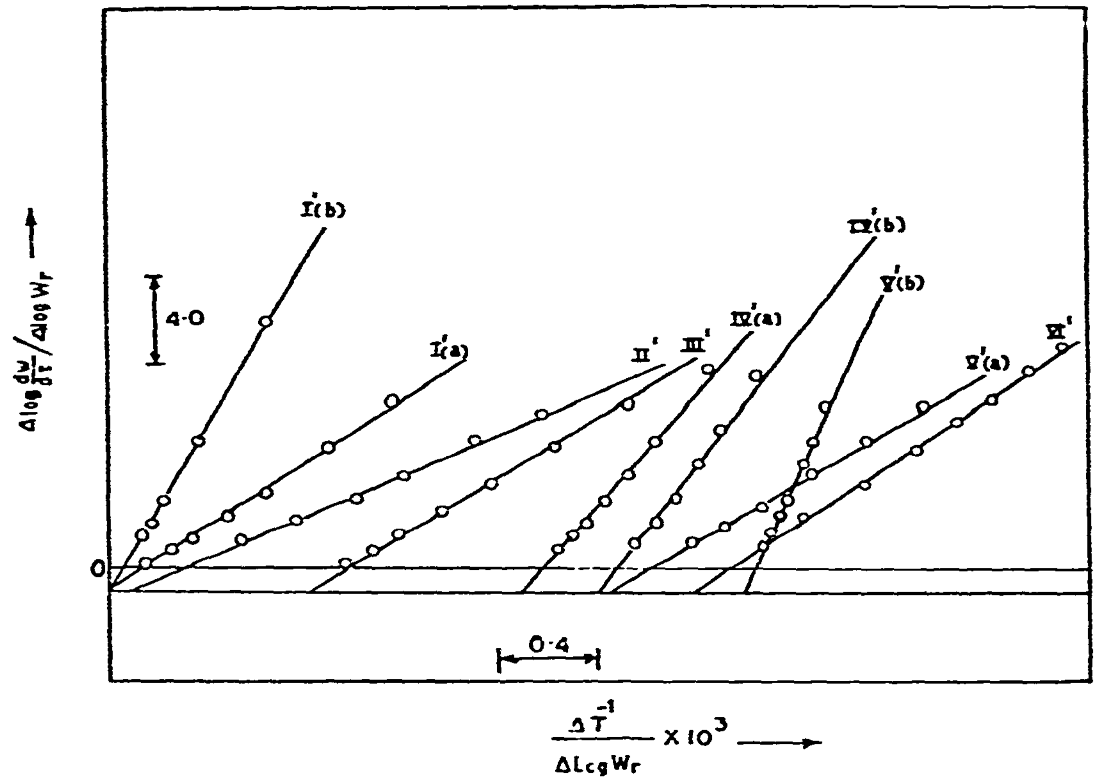

Fig. 5. Plots of $\Delta \log \frac{dw}{dt} \Big/ \Delta \log W_r$ vs. $\frac{\Delta T^{-1}}{\Delta \log W_r}$ from TG for the dehydration of $Rb_2SO_4 \cdot MgSO_4$ $6D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2D_2O$(I'a), $Rb_2SO_4 \cdot MgSO_4 \cdot 1.75D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$(I'b), $Rb_2SO_4 \cdot MnSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot MnSO_4$(II'), $Rb_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$(III'), $Rb_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O$(IV'a), $Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$(IV'b), $Rb_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O$(V'a), $Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$(V'b) and $Rb_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$(VI').

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

the corresponding K(I) series due to deuteration. The enthalpy changes for the first step of dehydration of the double salt hydrates of Mg(II) of the present series, NH_4(I) and K(I) series do not differ much, but the enthalpy change of the deuterated salt hydrate differs from the aquated one.

The nature of dehydration of the double salt hydrate of Mn(II) of this series is similar to the corresponding NH_4(I) series. Comparison with that of the K(I) series is not possible, as this compound undergoes dehydration as soon as the crystals are removed from its mother liquor. The first DTG peak temperature and enthalpy change of of the present salt hydrate are less than the corresponding NH_4(I) series but its activation energy is higher than that of NH_4(I). There is no significant change in the thermal properties on deuteration.

The process of dehydration of the double salt hydrate of Co(II) of the present series is similar to the dehydration of that of the NH_4(I) series and is different from that

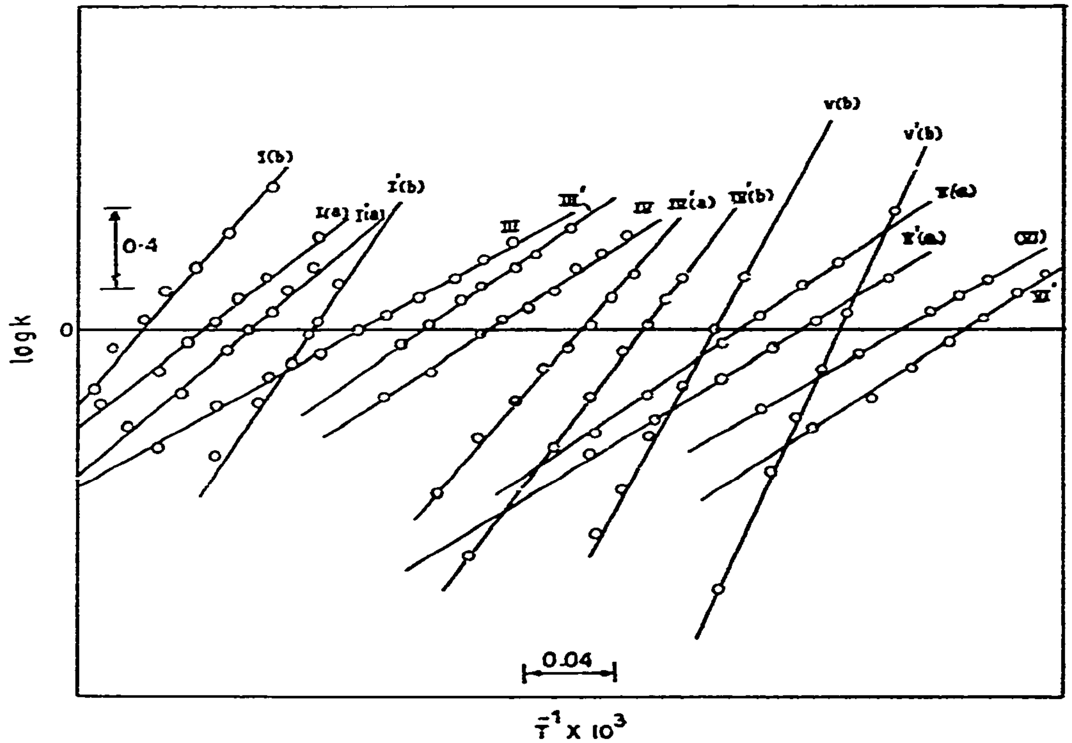

Fig. 6. Arrhenius plots, log k vs. $T^{-1} \times 10^3$, from DTG curves for dehydration of $Rb_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O$(Ia), $Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$(Ib), $Rb_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2D_2O$(I'a), $Rb_2SO_4 \cdot MgSO_4 \cdot 1.75D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$(I'b), $Rb_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$(III), $Rb_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$(III'), $Rb_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$(IV), $Rb_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O$(IV'a), $Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$(IV'b), $Rb_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O$(IVa), $Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$(Vb), $Rb_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O$(V'a), $Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$(V'b), $Rb_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$(VI) and $Rb_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$(VI').

of the K(I) series whose nature of dehydration is similar to $Rb_2Mg(SO_4)_2 \cdot 6H_2O$. The first DTG peak temperature of the present salt hydrate does not differ much from the corresponding NH_4(I) but is higher than the corresponding K(I). The activation energy of dehydration of the same salt hydrate is less than the corresponding K(I) series and higher than that of the NH_4(I) series. The enthalpy change of dehydration is minimal with respect to the corresponding NH_4(I) and K(I) series. On deuteration the enthalpy change increases slightly (13 to 14.5) and thereby the enthalpy changes of dehydration of the Rb(I) and the corresponding NH_4(I) and K(I) follow the order NH_4(I) > Rb(I) > K(I).

The nature of dehydration of the double salt hydrate of Ni(II) of the present series is similar to that of corresponding NH_4(I)[1] and unlike that of K(I)[2], but this picture changes completely on deuteration of this salt hydrate as stated earlier. The first DTG peak temperature is higher than that of the corresponding K(I) and NH_4(I)

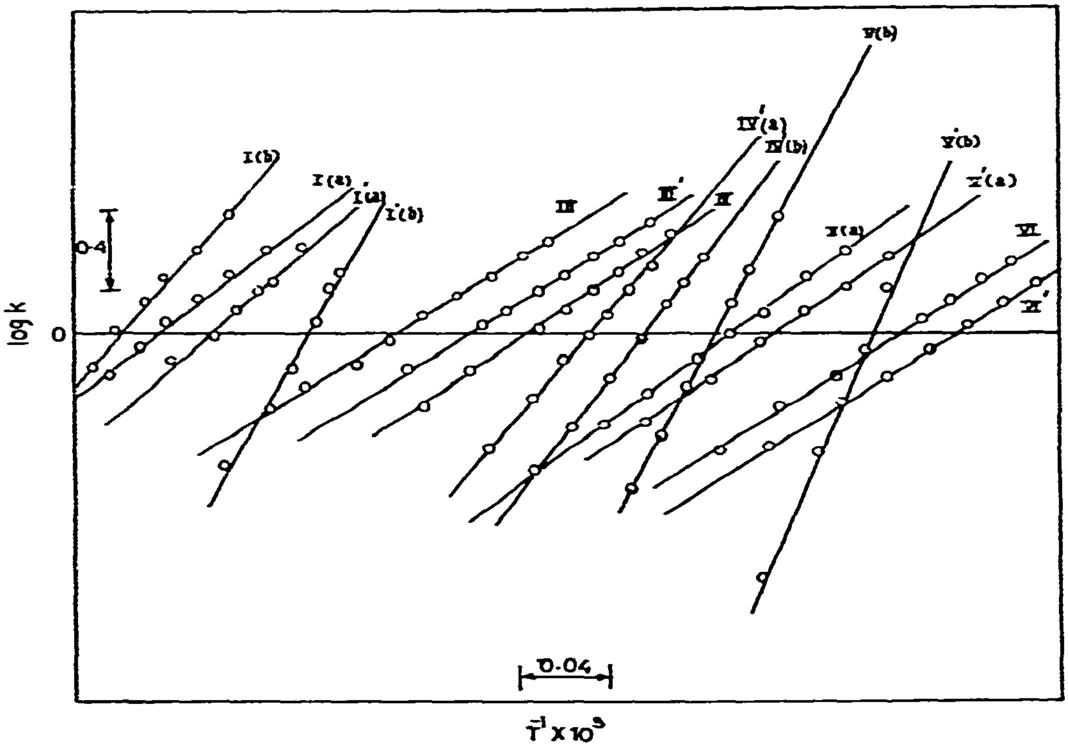

Fig. 7. Arrhenius plots, log *k* vs. $T^{-1} \times 10^3$, from DTA curves for dehydration of $Rb_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O$(Ia), $Rb_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$(Ib), $Rb_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4 \cdot 2D_2O$(I'a), $Rb_2SO_4 \cdot MgSO_4 \cdot 1.75D_2O \rightarrow Rb_2SO_4 \cdot MgSO_4$(I'b), $Rb_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$(III), $Rb_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CoSO_4$(III'), $Rb_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$(IV), $Rb_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O$(IV'a), $Rb_2SO_4 \cdot NiSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot NiSO_4$(IV'b), $Rb_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O$(Va), $Rb_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$(Vb), $Rb_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O$(V'a), $Rb_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Rb_2SO_4 \cdot CuSO_4$(V'b), $Rb_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$(VI) and $Rb_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Rb_2SO_4 \cdot ZnSO_4$(VI').

series [Rb(I) > K(I) > NH_4(I)] but on deuteration the order changes as follows: K(I) ⩾ NH_4(I) > Rb(I). The value of enthalpy change of dehydration is higher than that of the corresponding K(I) series and lower than that of the NH_4(I) series. On deuteration the value of enthalpy change remains practically unaltered. The activation energy for the first step of dehydration of the Rb(I) series is maximal with respect to the corresponding NH_4(I) and K(I) series. On deuteration the activation energy for the first step of dehydration becomes high, whereas, the values for the corresponding NH_4(I) and K(I) series do not show any significant change.

The fashion of dehydration of double salt hydrate of Cu(II) of the present series is unlike the corresponding NH_4(I) and K(I). It is observed that the nature of the TG curve of the corresponding K(I) series is similar to that of the present salt hydrate, but both steps showed overlapping DTA and DTG curves indicating the existence of more unstable intermediate salt hydrates, which is not found in the present salt hydrate. In the corresponding NH_4(I)[1] series dehydration took place in three steps which was stated earlier. On deuteration of the Cu(II) compound, the nature of dehydration is not altered, whereas, for the corresponding K(I) series, the nature of dehydration differed slightly[2]. The first DTG peak temperature of the present salt hydrate is lower than that of the corresponding NH_4(I) series and equal to that of the K(I) series. The enthalpy change for the first step of dehydration is lower than for the corresponding NH_4(I) series and higher than that of the K(I) series. On deuteration the values increase slightly. The activation energy for the first step of dehydration is equal to that of the corresponding NH_4(I) series and higher than that of the K(I) series. On deuteration the value becomes slightly lower.

The nature of dehydration of the double salt hydrate of Zn(II) of the present series is like that of the corresponding NH_4(I)[1] series but is different from the corresponding K(I)[2] series whose nature of dehydration is similar to that of the double salt hydrate of Cu(II) of the present series. The D_2O analogue dehydrates similarly. DTG peak temperature and enthalpy change for the first step of dehydration are higher than those of the corresponding NH_4(I) series and less than those of K(I). The value of activation energy for the first step of dehydration of the present salt hydrate is higher than that of the corresponding K(I) series and less than that of NH_4(I). On deuteration, the above order also remains unaltered.

It is noticed that the thermal stability of the double salt hydrates of Rb(I) is greater than that of the corresponding K(I) series and less than that of the NH_4(I) series, whereas, the activation energy for the first step of dehydration of the present series is greater than that of NH_4(I) and less than for the corresponding K(I) series.

The first DTG peak temperatures of the double salt hydrates of the present series show that the salt hydrates are thermally stable in the following order: Ni(II) > Co(II) > Zn(II) > Mg(II) > Cu(II) > Mn(II). This order is almost maintained in the NH_4(I) series except for the double salt hydrates of Zn(II) and Co(II) whose order is reversed. But the above order is not maintained in the K(I) series. D_2O analogues of the present series show a similar order of thermal stability except for Ni(II). In the case of $Rb_2Ni(SO_4)_2 \cdot 6H_2O$, on deuteration the thermal stability decreases to a great extent. This change is probably due to the change in the nature of dehydration.

The variation of the values of activation energies for the dehydration process evaluated from TG, DTA and DTG curves is not too much. This shows that all the methods used for the evaluation of activation energies are standard. It is observed that on deuteration of the single salt hydrates[9] activation energies of dehydration of the corresponding D_2O analogues increase. But in the case of double salt hydrates there is no significant change in the value of activation energy on deuteration where the nature of dehydration remains unaltered. In general, salt hydrates[1,2,9] which lose water molecules in more than one step, the activation energy for the latter step of dehydration gives a larger value than the previous step. In the present series a similar phenomenon is observed. It is observed in our earlier work[2] that where the deuteration effect completely changes the nature of dehydration, the value of the activation energy of dehydration changes markedly, i.e., in the case of $K_2Mg(SO_4)_2 \cdot 6H_2O$, on deuteration dehydration took place in a single step instead of dehydrating in three equal steps. As a result the value of activation energy of dehydration fell markedly on deuteration. Whereas, $Rb_2Ni(SO_4)_2 \cdot 6H_2O$ dehydrates in two steps on deuteration instead of in a single step. Due to this change in the nature of dehydration the activation energy for the dehydration of $Rb_2Ni(SO_4)_2 \cdot 6D_2O$ is markedly high in comparison to that of its H_2O analogue. The above observations show that the value of the activation energy of dehydration increases with increase in the number of steps during dehydration due to deuteration and vice versa. The activation energies for the first step of dehydration of the double salt hydrates of the present series do not show any systematic variation with increase in atomic number of the cation, whereas, a systematic order was maintained in the NH_4(I) series. It is noticed, however, that the activation energies of the double salt hydrates of the present series increase with rise of the 2nd ionisation potential of the central metal except for Mg. But this trend is not observed between the corresponding D_2O analogues due to abrupt rise in the value of activation energy for dehydration of $Rb_2Ni(SO_4)_2 \cdot 6D_2O$.

It is also observed that the value of enthalpy change of dehydration of the double salt hydrates of this series ranges from 11.4–17 kcal mol^{-1}. There is little effect on the value of ΔH on deuteration.

The differences in thermal properties of dehydration between the NH_4(I), K(I) and Rb(I) series is due to a natural cause, i.e., slight difference in ionic size of NH_4(I) (1.43), K(I) (1.33) and Rb(I) (1.48). We attempted to isolate $Rb_2Cd(SO_4)_2 \cdot 6H_2O$ but could not succeed as the compound loses water as soon as the crystals are removed from its mother liquor.

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