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

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ABSTRACT

Non-isothermal studies of the dehydration of the double salt hydrates of the type $M(I)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues were carried out where $M(I) = Cs(I)$ and $M(II) = Mg(II)$, $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$. The thermal parameters like activation energy, order of reaction, enthalpy change, etc. were evaluated from the analyses of TG, DTA and DTG curves. The activation energies required for dehydration of the salt hydrates and their D_2O analogues did not differ much. The thermal stabilities of the salt hydrates and their D_2O analogues were discussed. The order of reaction was always found unity. The values of ΔH were between ~ 12–~ 16 kcal mol^{-1}.

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], K(I)[2] or Rb(I)[3] 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 Cs 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 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 $NH_4(I)$[1], K(I)[2] and Rb(I)[3] series.

EXPERIMENTAL

The double salt hydrates were prepared according to the procedure adopted by earlier workers[4] and their deuterium oxide analogues were prepared by dissolving equimolecular mixtures of anhydrous single salts in D_2O and subsequent crystallisation. A Paulik–Paulik–Erdey type MOM, Type OD-102, derivatograph has been used for thermal analyses. The particle size of the samples was between 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 dehydration of the double salt hydrates of the present series takes place in two ways. Salt hydrates of Mg(II) and Co(II) lose water molecules in two steps (Fig. 1). The first step corresponds to the elimination of four molecules of water and the second step corresponds to the remaining two molecules of water. The dihydrate of Mg(II) is not thermally stable, whereas, the dihydrate of Co(II) is stable. As a result for Co(II) salt hydrate, well-resolved DTA and DTG curves are observed for both steps and for the Mg(II) salt hydrate the DTA curve of the second step of dehydration is overlapped with that for the first step. The nature of the first step of dehydration of the Mn(II) salt hydrate is like that of the above salt hydrates with respect to the TG curve but its DTA and DTG curves show signs of more intermediate unstable salt hydrates (Fig. 1). Its second step of dehydration is unlike that of the above salt hydrates. The double salt hydrates of Ni(II), Cu(II) and Zn(II) lose water molecules in a single step (Fig. 2). In the case of Ni(II) and Zn(II) both DTA and DTG curves are well resolved. Whereas, this type of resolution is not observed in the case of the Cu(II) salt hydrate. The nature of dehydration of the double salt hydrates of the present series remains unaltered on deuteration. DTG peak temperatures and temperature ranges of dehydration for the double salt hydrates and their D_2O analogues are listed in the second column in Table 1. Enthalpy changes for each step of dehydration of the double salt hydrates and their D_2O analogues are evaluated by the method of Sano[5] using copper sulphate pentahydrate as the standard and the values are tabulated in the last column in Table 1. ΔH values are evaluated from the overall area of the DTA curves of Mg(II), Mn(II) and Cu(II) as these overlap too much. 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 equation[6]. The results are tabulated in Table 1 and the curves are shown in Figs. 3 and 4. The activation energies for each step of dehydration are also evaluated from the analyses of DTG curves using the method of Dave and Chopra[7] and the method described in our earlier work[1] and also from the analyses of DTA curves using Brochardt's equation[8] for first order reactions. All these values are tabulated in Table 1 and the corresponding curves are shown in Figs. 5 and 6. The order of reaction is found unity for dehydration of all the mentioned 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 has taken place to the desired extent. X-ray diffraction patterns show that salt hydrates and their corresponding D_2O analogues are isomorphous to each other.

DISCUSSION

Earlier, the dehydration of $Cs_2Mg(SO_4)_2 \cdot 6H_2O$ was studied by Rassonskaya[9]. He observed a similar nature of dehydration as observed by us but the corresponding DTG curves overlapped and had two peaks. But we observed a prominent break in

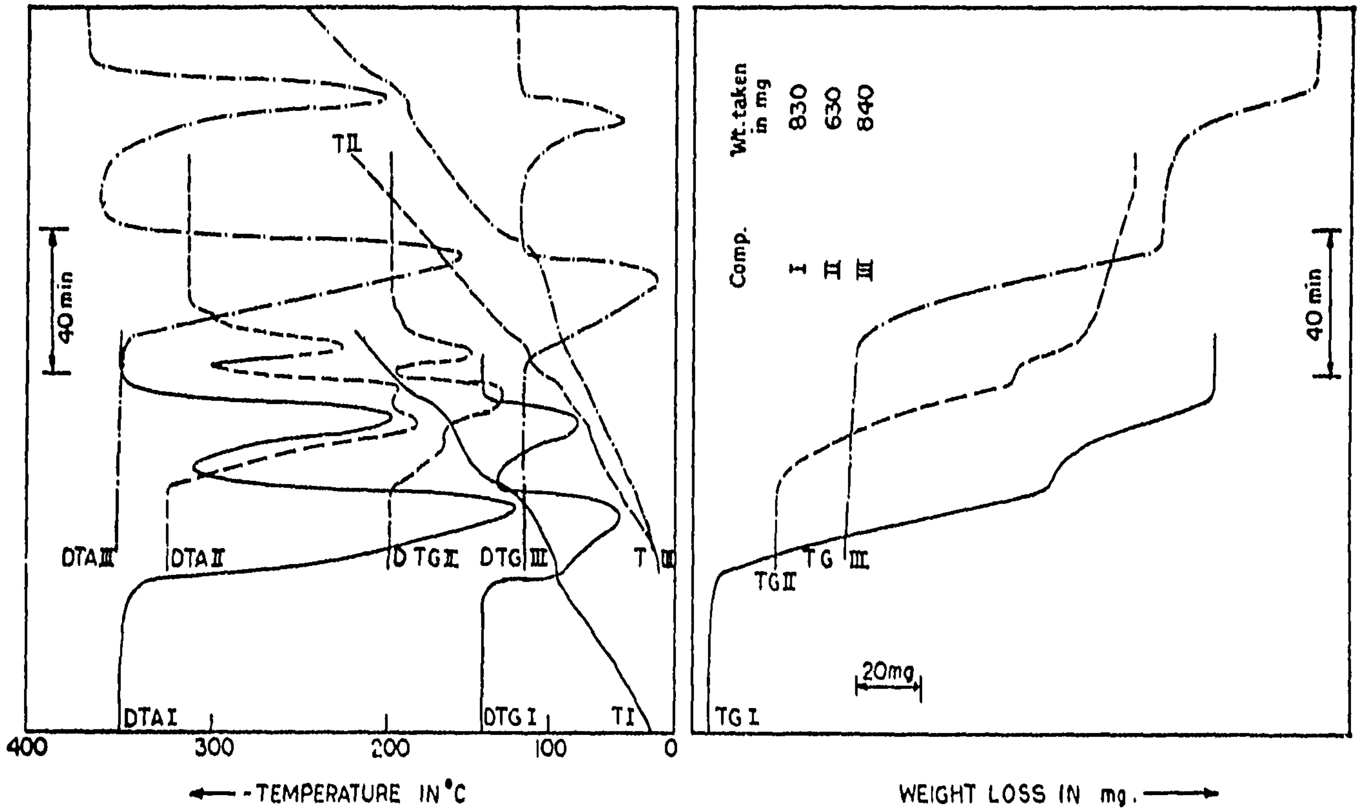

Fig. 1. Derivatograms for the dehydration of $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (I), $Cs_2SO_4 \cdot MnSO_4 \cdot 6H_2O$ (II) and $Cs_2SO_4 \cdot CoSO_4 \cdot 6H_2O$ (III).

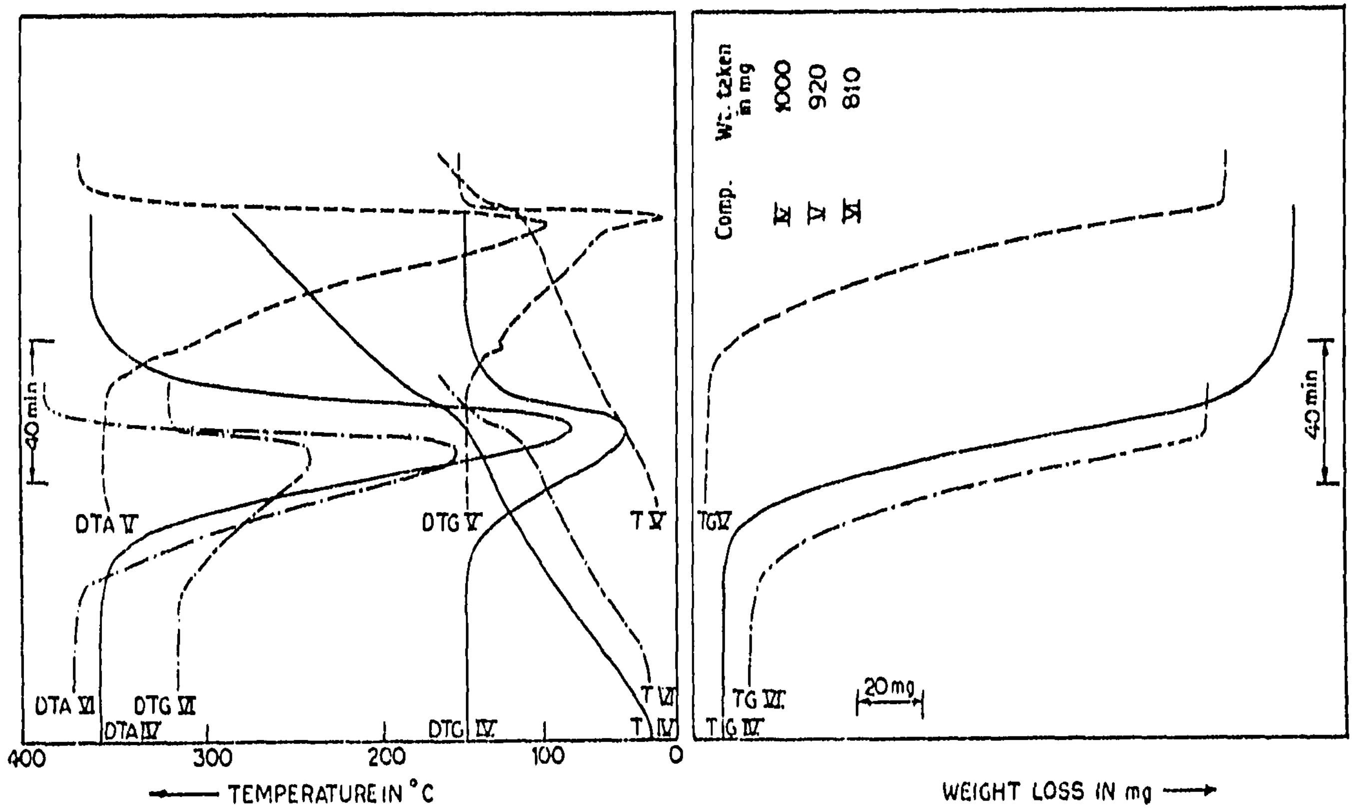

Fig. 2. Derivatograms for the dehydration of $Cs_2SO_4 \cdot NiSO_4 \cdot 6H_2O$(IV), $Cs_2SO_4 \cdot CuSO_4 \cdot 6H_2O$(V) and $Cs_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$(VI).

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*	
(Ia) $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot MgSO_4 \cdot 2H_2O$	90–117	110	32.2	32.2	—	14.3[a]
(Ib) $Cs_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot MgSO_4$	118–195	161	41.0	41.0	—	—
(I'a) $Cs_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot MgSO_4 \cdot 2D_2O$	95–128	117	30.6	34.5	—	14.3[a]
(I'b) $Cs_2SO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot MgSO_4$	129–207	167	40.3	40.3	—	—
(IIa) $Cs_2SO_4 \cdot MnSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot MnSO_4 \cdot 2H_2O$	43– 95	89	26.3	—	—	13.9[a]
(IIb) $Cs_2SO_4 \cdot MnSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot MnSO_4$	97–224	115	—	—	—	—[b]
(II'a) $Cs_2SO_4 \cdot MnSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot MnSO_4 \cdot 2D_2O$	49– 98	90	23.0	—	—	13.9[a]
(II'b) $Cs_2SO_4 \cdot MnSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot MnSO_4$	100–226	116	—	—	—	—[b]
(IIIa) $Cs_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O$	80–117	107	46.0	46.0	46.0	15.5
(IIIb) $Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$	165–215	190	69.0	69.0	69.0	14.9
(III'a) $Cs_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O$	75–120	107	36.8	36.8	36.8	12.8
(III'b) $Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$	157–225	192	70.0	69.0	69.0	13.7
(IV) $Cs_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$	100–230	147	26.0	26.0	26.0	14.4
(IV') $Cs_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$	100–225	143	27.6	30.6	30.6	13.4
(V) $Cs_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot CuSO_4$	57–149	115	23.0	—	—	12.3[a]
(V') $Cs_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot CuSO_4$	55–145	110	25.5	—	—	14.8[a]
(VI) $Cs_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$	60–151	110	23.0	23.0	23.0	14.6
(VI') $Cs_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$	62–153	113	26.3	23.0	27.6	16.3

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

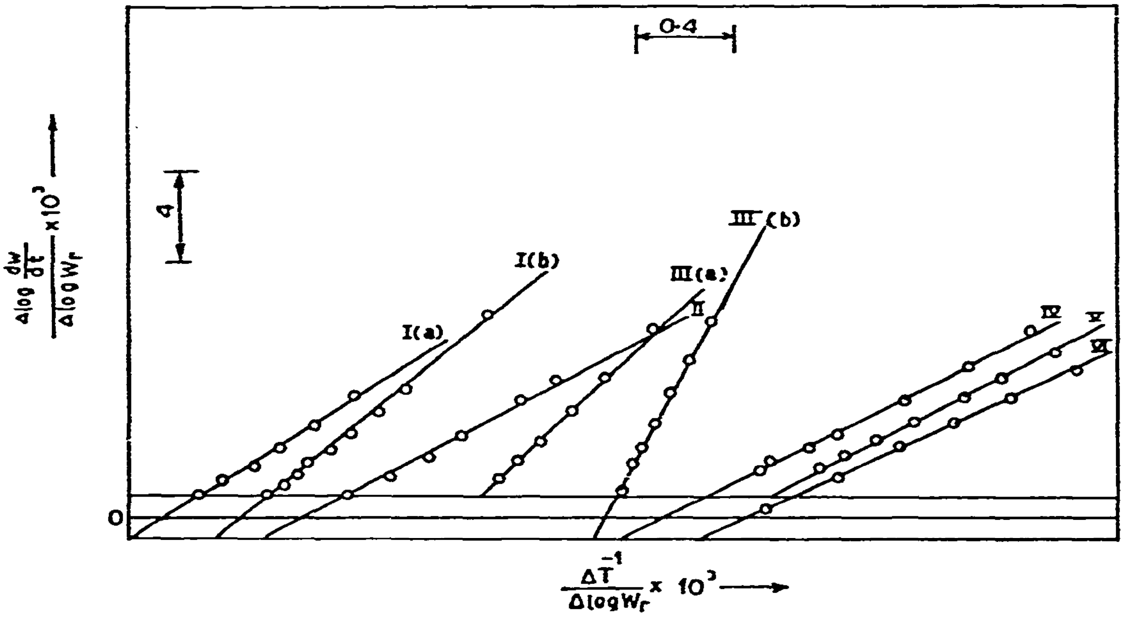

Fig. 3. Plots of $\Delta \log \frac{dw}{dT} \Big/ \Delta \log w_r$ vs. $\frac{\Delta T^{-1}}{\Delta \log w_r} \times 10^3$, from the TG curves for dehydration of $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot MgSO_4 \cdot 2H_2O$(Ia), $Cs_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot MgSO_4$(Ib), $Cs_2SO_4 \cdot MnSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot MnSO_4 \cdot 2H_2O$(II), $Cs_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O$(IIIa), $Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$(IIIb), $Cs_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$(IV), $Cs_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot CuSO_4$(V) and $Cs_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$(VI).

TG and two well-resolved DTG curves. He evaluated the activation energy for the first step of dehydration from the DTA curve by Piloyan's method and his value was 36 kcal mol^{-1} and 38 kcal mol^{-1} from the analysis of the TG curve. He did not determine the value of activation energy from the second step of dehydration from the TG curve. In our case the value of the activation energy for the first step of dehydration is slightly low in comparison to Rassonskaya's value. But in the case of the corresponding Rb(I) series, Rassonskaya's[9] value is high in comparison to the value evaluated in our earlier work[3]. This difference is probably due to the heating rate, the nature of the crucible, etc. Moreover, he did not determine the activation energy of dehydration from DTG curves. The nature of dehydration of this salt hydrate differs from the corresponding NH_4(I)[1], K(I)[2] and Rb(I)[3] series. In the case of the NH_4(I) series, the first step of dehydration took place with five molecules of water and the remaining water molecule was eliminated in the second step, the monohydrate was, however, unstable. The nature of dehydration did not change on deuteration. In the case of the corresponding K(I) series, dehydration took place in three equal steps, whereas, its D_2O analogue dehydrates in a single step. The dihydrate of caesium magnesium double sulphate is less stable than the corresponding dihydrate of Rb(I). As a result during dehydration of the corresponding Rb(I) series, both DTA curves

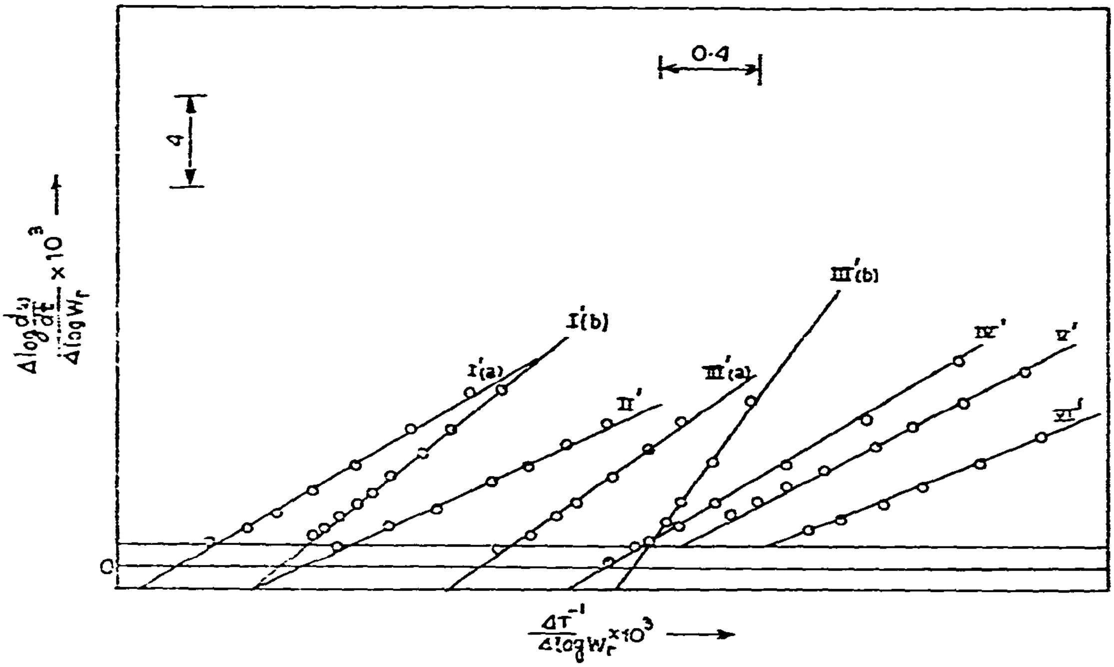

Fig. 4. Plots of $\Delta \log \frac{dw}{dt} \Big/ \Delta \log w_r$ vs. $\frac{\Delta T^{-1}}{\Delta \log w_r} \times 10^3$, from the TG curves for dehydration of $Cs_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot MgSO_4 \cdot 2D_2O$(I'a), $Cs_2SO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot MgSO_4$(I'b)' $Cs_2SO_4 \cdot MnSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot MnSO_4$(II'), $Cs_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O$(III'a), $Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$(III'b), $Cs_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$(IV'), $Cs_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot CuSO_4$(V'), $Cs_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$(VI').

are well resolved which is not so for the dihydrate of caesium magnesium double sulphate. But unlike the dehydration of the latter, the nature of dehydration of the dihydrate of Rb(I) changes on deuteration as stated earlier[3], i.e., $Rb_2Mg(SO_4)_2 \cdot 6D_2O \rightarrow Rb_2Mg(SO_4)_2 \cdot 2D_2O \rightarrow Rb_2Mg(SO_4)_2 \cdot 1.75D_2O \rightarrow Rb_2Mg(SO_4)_2$. With respect to the first DTG peak temperature the thermal stability of the $Cs_2Mg(SO_4)_2 \cdot 6D_2O$ shows the following order with respect to the corresponding NH_4(I), K(I) and Rb(I) series: NH_4(I) > Rb(I) = Cs(I) > K(I). But the thermal stability of the corresponding D_2O analogues follows a different order, i.e., NH_4(I) > K(I) = Cs(I) > Rb(I). This change in order is probably due to a change in the nature of dehydration of that of K(I) due to deuteration. The activation energy* of dehydration of the Cs(I) salt shows the following order: K(I) > Rb(I) > Cs(I) > NH_4(I), but on deuteration this order changes as follows: Rb(I) > Cs(I) > K(I) > NH_4(I). This change in the order is also due to a change in the nature of dehydration due to deuteration. The enthalpy change for the first step of dehydration of the Cs(I) salt does not differ much from that of the other corresponding salt hydrates and remains practically the same on deuteration.

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

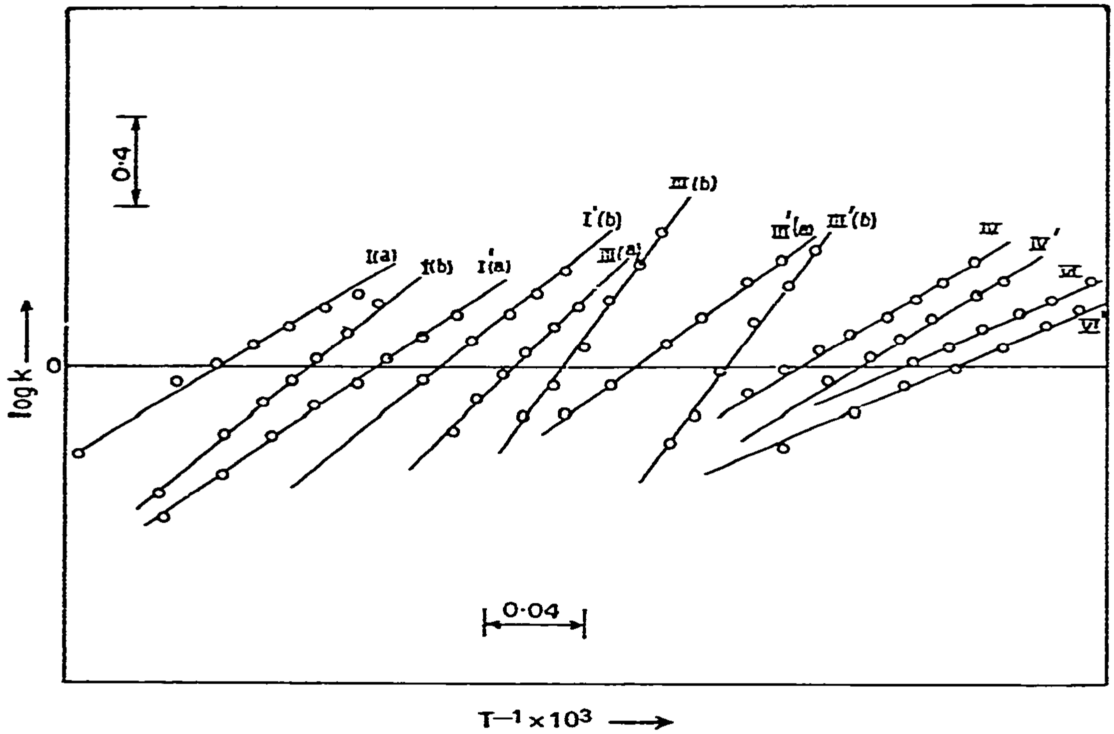

Fig. 5. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTG curves for the dehydration of $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ (Ia), $Cs_2SO_4 \cdot MgSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot MgSO_4$ (Ib), $Cs_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot MgSO_4 \cdot 2D_2O$ (I'a), $Cs_2SO_4 \cdot MgSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot MgSO_4$ (I'b), $Cs_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O$ (IIIa), $Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$ (IIIb), $Cs_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O$ (III'a), $Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$ (III'b), $Cs_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$ (IV), $Cs_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$ (IV'), $Cs_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$ (VI), $Cs_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$ (VI').

The nature of dehydration of the double salt hydrate of Mn(II) of the present series is different from the corresponding NH_4(I) and Rb(I) series. Comparison with that of the K(I) series is not possible as it loses its crystal hydrates at room temperature. It is observed that although the corresponding salt hydrates of NH_4(I) and Rb(I) lose water molecules in a single step as indicated from their respective thermograms, their DTA and DTG curves clearly indicate the presence of thermally unstable intermediate products. The first DTG peak temperature of dehydration of the present salt hydrate is equal to that of the corresponding Rb(I) series and less than that of the NH_4(I) series. The thermal stability remains unaltered on deuteration. Whereas, the activation energy of dehydration of the Cs(I) salt is maximal in comparison to the other corresponding hydrates of NH_4(I) and Rb(I), their order is as follows: Cs(I) > Rb(I) > NH_4(I) and this order remains the same on deuteration. The value of the enthalpy change of dehydration of the Cs(I) salt lies in between the value derived from the corresponding salt hydrates of NH_4(I) and Rb(I) where the former occupies the top position.

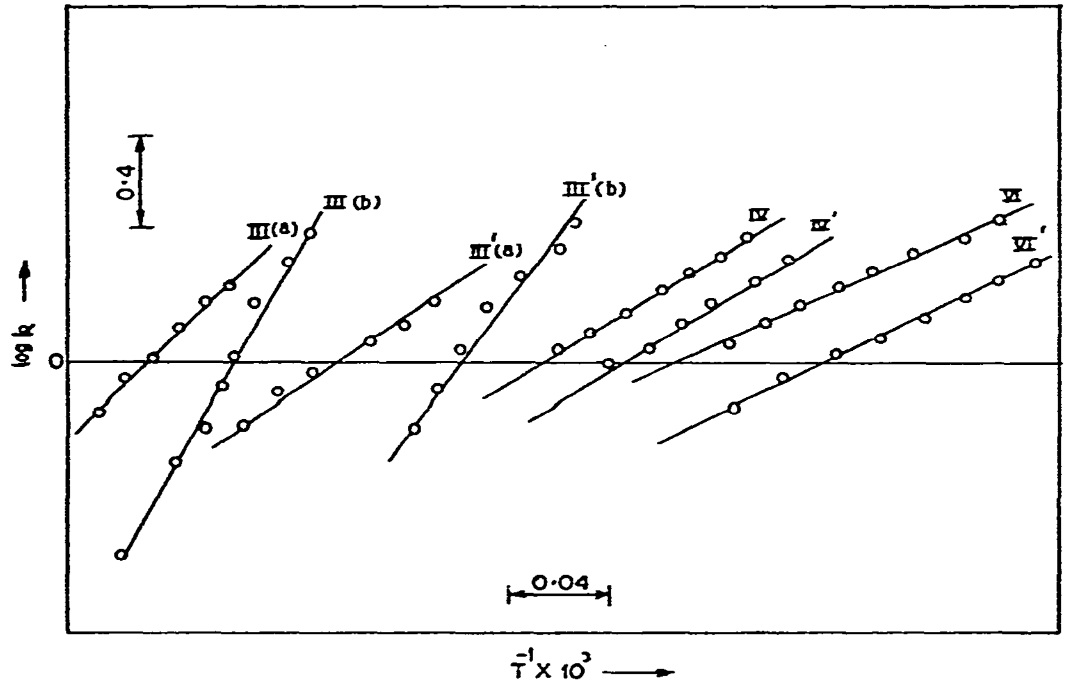

Fig. 6. Arrhenius plots of log *k* vs. $T^{-1} \times 10^3$ from DTA curves for the dehydration of $Cs_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O$(IIIa), $Cs_2SO_4 \cdot CoSO_4 \cdot 2H_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$(IIIb), $Cs_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O$(III'a), $Cs_2SO_4 \cdot CoSO_4 \cdot 2D_2O \rightarrow Cs_2SO_4 \cdot CoSO_4$(III'b), $Cs_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$(IV), $Cs_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot NiSO_4$(IV'), $Cs_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$(VI), $Cs_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Cs_2SO_4 \cdot ZnSO_4$(VI').

The nature of dehydration of the double salt hydrate of Co(II) of the present series is similar to that of the corresponding K(I) series. But the corresponding NH_4(I) and Rb(I) series, unlike the Cs(I) and K(I), lose all their water molecules in a single step. It is observed that these salt hydrates also follow the similar manner of dehydration on deuteration. With respect to the first DTG peak temperature the thermal stability of the Cs(I) salt is low in comparison to the corresponding NH_4(I) and Rb(I) series and slightly higher than that of K(I). The order is as follows: Rb(I) > NH_4(I) > Cs(I) > K(I) and this order is maintained on deuteration. The activation energy for dehydration of the Cs(I) compound is high in comparison to the other salt hydrates of Co(II) of the NH_4(I), K(I) and Rb(I) series and the order is as follows: Cs(I) > K(I) > Rb(I) > NH_4(I) and this order is maintained on deuteration. The enthalpy change for the first step of dehydration of the Cs(I) is equal to that of NH_4(I) but is slightly higher than that of the corresponding K(I) and Rb(I) series. On deuteration the value of enthalpy change decreases and thereby the order changes as follows: NH_4(I) > Rb(I) > K(I) > Cs(I).

The nature of dehydration of the double salt hydrate of Ni(II) of the present series is similar to the corresponding NH_4(I) and Rb(I) series but unlike to that of

K(I)[2]. But it is also observed that the nature of dehydration of the deuterated salt hydrate of Cs(I) is not similar to that of Rb(I), the latter on deuteration eliminates heavy water molecules in two steps in the ratio of 4:2. The DTG peak temperature of Cs(I) is equal to the corresponding NH_4(I) and K(I) series and is low with respect to the Rb(I) series. But on deuteration the first DTG peak temperature of Cs(I) is low with respect to the corresponding NH_4(I) and K(I) and is higher than that of Rb(I). The DTG peak temperature of Cs(I) decreases slightly on deuteration. The change in the order of thermal stability on deuteration is probably due to a change in the nature of dehydration of the Rb(I) series as stated earlier[3]. The activation energy of dehydration of Cs(I) is slightly high with respect to the corresponding NH_4(I) and K(I) series and is lower than that of Rb(I), whereas the values of activation energies for the K(I) and NH_4(I) series are the same. On deuteration of the Cs(I) salt the value of the activation energy increases slightly and this trend is also observed in the NH_4(I), K(I) and specially in the Rb(I) series. The value of activation energy for the Rb(I) series is abruptly high which may be accounted for by the same reason, i.e., due to the change in the nature of dehydration. The value of enthalpy change of the Cs(I) salt with respect to the corresponding NH_4(I), K(I) and Rb(I) series follows the order: NH_4(I) > Rb(I) > Cs(I) > K(I) and this order remains the same on deuteration.

The nature of dehydration of the double salt hydrate of Cu(II) of the present series differs from the corresponding NH_4(I), K(I) and Rb(I) series. Besides the corresponding Cs(I) salt, other salt hydrates lose water molecules in more than one step, though these steps are not thermally stable except for the dihydrate of that of Rb(I). Similar to the corresponding NH_4(I) and Rb(I) series, here also the effect on deuteration is not observed. But the corresponding K(I) shows a slight effect on deuteration stated earlier[2]. The thermal stability with respect to the first DTG peak temperature of the Cs(I) salt is maximal in comparison to the corresponding NH_4(I), K(I) and Rb(I) series. On deuteration the thermal stability of the Cs(I) salt slightly decreases and occupies a similar position as the salt hydrate. The activation energy for the first step of dehydration of the Cs(I) salt is equal to that of the K(I) series and is low with respect to the NH_4(I) and Rb(I) series. It is also observed that the activation energy of dehydration of the NH_4(I) and Rb(I) series are practically the same. On deuteration the value of activation energy of dehydration of the Cs(I) salt slightly increases and this trend was observed in the corresponding NH_4(I) and K(I) series. In the case of the Rb(I) series the value decreased and the order of activation energy is as follows: NH_4(I) > Rb(I) > Cs(I) > K(I). It is observed that other salt hydrates of Cu(II) except the corresponding Rb(I) series show overlapped DTA curves, thereby, we evaluated the value of enthalpy change from the overall area of the DTA curve. Enthalpy change of the Cs(I) salt is minimal in comparison to other Cu(II) salt hydrates studied earlier[1–3] and occupies the minimum position as follows: NH_4(I) > Rb(I) > K(I) > Cs(I). On deuteration of the Cs(I) salt the value increases and thereby this order changes as follows: NH_4(I) > Rb(I) > Cs(I) > K(I).

The nature of dehydration of the double salt hydrate of Zn(II) of the present series is similar to its corresponding NH_4(I) and Rb(I) series and unlike that of

K(I). On deuteration the nature of dehydration does not change. It is observed that the thermal stability of the Cs(I) salt with respect to the first DTG peak temperature is close to that of the corresponding K(I) and Rb(I) series and is low with respect to that of NH_4(I). On deuteration this stability order remains practically constant. The activation energy of dehydration of the Cs(I) salt is close to NH_4(I) and lower than that of K(I) and Rb(I) and the order is as follows: K(I) > Rb(I) > Cs(I) > NH_4(I). On deuteration this order remains unchanged, but the value of the Cs(I) salt and that of NH_4(I) becomes less close due to slight increase in the value of the former. The value of enthalpy change of dehydration of the Cs(I) salt is low in comparison to that of the corresponding NH_4(I) and higher than that of K(I) and Rb(I). On deuteration of the Cs(I) salt this value increases and thereby it occupies the top position exceeding the value of NH_4(I).

The first DTG peak temperatures of the double salt hydrates of the present series show that the double salt hydrate of Ni(II) is thermally most stable and that of Mn(II) is least stable. The thermal stability of the other salt hydrates are close to each other. In other series like NH_4(I)[1], K(I)[2] and Rb(I)[3], the salt hydrates of Mn(II) are also the least stable and those of Ni(II) are thermally most stable. It is observed from our earlier observations that the thermal stability of the salt hydrates changes markedly where the nature of dehydration changes on deuteration. In the present series, the nature of dehydration of the salt hydrates remains the same. As a result, a significant change in the thermal stability is not observed in the present series due to deuteration. Like the NH_4(I) series, the thermal stability of the present series is not effected on deuteration, whereas, the deuteration effect is observed in some of the hydrates of K(I) and Rb(I) series.

The values of activation energies for dehydration processes, evaluated from TG, DTA and DTG curves are close to each other like other series carried out earlier[1-3], thereby justifying the methods used. In the present series, the values of activation energies of the salt hydrates and their corresponding D_2O analogues are very close to each other which is not observed in some of the salt hydrates of K(I) and Rb(I) series. The activation energy for the later step of dehydration gives a larger value than the earlier step. This phenomenon is observed in our earlier works[1-3] and also Tsuchiya's[10] work. The value of activation energy for the first step of dehydration of the double salt hydrate of Co(II) of the present series is maximal, whereas, it is minimal for Zn(II) and Cu(II). The values of the activation energies of the present series do not show any systematic variation with increase in atomic number, whereas, a systematic order is maintained in the NH_4(I) series[1]. It is also noticed that the activation energies do not follow the order maintained in the case of Rb(I) series[3] where they increased with the rise of 2nd ionisation potential of the central metal except Mg.

It is also observed that the values of enthalpy change of dehydration of double salt hydrates of this series range from $\sim 12 \sim -16$ 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), Rb(I) and Cs(I) series are due to a natural cause, i.e., slight difference in ionic size of NH_4(I) (1.43), K(I) (1.33), Rb(I) (1.48) and Cs(I) (1.67). Repeated attempts of isolation of $Cs_2Cd(SO_4)_2 \cdot 6H_2O$ were made, but these failed as the salt hydrate loses water molecules at room temperature as soon as the crystals are removed from its mother liquor.

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