

Derivatographic Studies on the Dehydration of Alums^{*1}

Yoshitake YOSHIMURA^{*2} and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University

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Abstract The dehydration was measured by means of derivatography for the following several alums: *i. e.*, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (I), $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (II), $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (III), $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (IV), $\text{RbCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (V), $\text{TiCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (VI), $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (VII) and $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (VIII).

The difference of the dehydration processes depending upon the univalent and trivalent metal ions contained was deduced from the measurements. The enthalpy change and the activation energy for dehydration of these alums were calculated and the order of the magnitude was discussed in relation with the ratio of ionic radius of univalent metal to that of trivalent one.

Introduction

In the crystalline hydrates of the general inorganic salts, a part of water of crystallization coordinates to metal ion and the remainders have a role binding cations and anions by hydrogen bond as lattice water. For example, in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, four water molecules and two sulfate ions coordinate to copper ion, and the fifth water molecule plays a part binding the aquo copper ion and sulfate ion¹⁾, and in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, four water molecules and two chlorine atoms coordinate to cobalt ion and two water molecules bind these coordination units.²⁾

In a series of hydrated compounds which are called alums, on the other hand, the six coordination sites of at least trivalent metal ions are occupied by six water molecules alone in crystalline state. For example, in ammonium iron(III) alum, $(\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O})$, iron(III) ion takes six water molecules in its coordination sphere in a crystal state, showing pale purple, but aquo iron ion undergoes acid dissociation in an aqueous solution, giving light brown; in potassium chromium(III) alum, $(\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O})$, the crystal shows the characteristic purple for hexaaquochromium(III) ion, but the chromium(III) salts and their solutions prepared by the general method give green due to the anion coordination.

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^{*2} Present address: Department of Industrial Chemistry, Fukui Technical College, Sabae, Fukui.

As mentioned above, the alums are unique salts on the point that they have hexaaquo tervalent metal ions in crystalline state. Although the remainder six water molecules are just enough to occupy completely the six coordination sites around univalent metal ions, it is likely to behave only as lattice water.

The structure of alums belongs to the space group of T_h^6 -Pa3 and the chemical unit is four.³⁾ In addition, the alums can be classified to α -,³⁾ β -⁴⁾ and γ -types⁴⁾ from the degree of the ionic radii of univalent metals.

On the dehydration of alums, the thermogravimetry(TG) for $KAl(SO_4)_2 \cdot 12H_2O$ ⁵⁾, $KCr(SO_4)_2 \cdot 12H_2O$ ⁶⁾, $NH_4Al(SO_4)_2 \cdot 12H_2O$,⁷⁾ $NH_4Cr(SO_4)_2 \cdot 12H_2O$ ⁸⁾ and $NH_4Fe(SO_4)_2 \cdot 12H_2O$ ⁹⁾, and the differential thermal analysis (DTA) for $RbGa(SO_4)_2 \cdot 12H_2O$,¹⁰⁾ $CsGa(SO_4)_2 \cdot 12H_2O$,¹⁰⁾ $RbGa(SeO_4)_2 \cdot 12H_2O$,¹¹⁾ $CsGa(SeO_4)_2 \cdot 12H_2O$,¹¹⁾ $KAl(SeO_4)_2 \cdot 12H_2O$,¹²⁾ $RbAl(SeO_4)_2 \cdot 12H_2O$,¹²⁾ $CsAl(SeO_4)_2 \cdot 12H_2O$,¹²⁾ $NH_4Al(SeO_4)_2 \cdot 12H_2O$,¹³⁾ $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ ¹³⁾ and $CH_3NH_3Al(SeO_4)_2 \cdot 12H_2O$ ¹³⁾ had already been measured, but these studies only follow the dehydration process without the further discussion in relation with the structure.

In the present study, the dehydration process of various alums was examined by means of derivatography, and the relationships between the process and the ionic radius of metal ions in the type of α , β or γ of the alums were investigated.

Experimental

Reagents. Alums used in the present work were $KAl(SO_4)_2 \cdot 12H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$ as α -type, $CsAl(SO_4)_2 \cdot 12H_2O$, $CsCr(SO_4)_2 \cdot 12H_2O$, $RbCr(SO_4)_2 \cdot 12H_2O$ and $TlCr(SO_4)_2 \cdot 12H_2O$ as β -type, $NaAl(SO_4)_2 \cdot 12H_2O$ as γ -type and $NH_4Fe(SO_4)_2 \cdot 12H_2O$ for which the type can not be clearly designated. These compounds were obtained by mixing the concentrated solutions containing the equal molar quantities of the desired univalent and tervalent metal sulfates and by recrystallizing them.

Apparatus. The thermochemical reaction process was followed by using a Metrimpex Derivatograph MOM Typ-OD-102 made in Hungary and a Tokyo Koki Pointer SE Type-52 Thermobalance under the heating rate of $1^\circ C \text{ min}^{-1}$. The melting and solidifying points were measured with a melting point apparatus. In order to obtain the informations about the structure, the absorption spectra were measured with a Hitachi Model-124 Double Beam Spectrophotometer, a Hitachi Model-139 UV Spectrophotometer equipped with the attachment for the reflection spectra, and JASCO Type-IR-E Infrared Spectrophotometer. The enthalpy changes, ΔH , and the activation energies, E^\ddagger ,¹⁴⁾ in each step of dehydrations were calculated by analyzing the DTA curves. As a standard for evaluating ΔH , the value for the dehydration of copper(II) sulfate pentahydrate, $\Delta H = 13.6 \text{ kcal/mol}(H_2O)$, was employed.

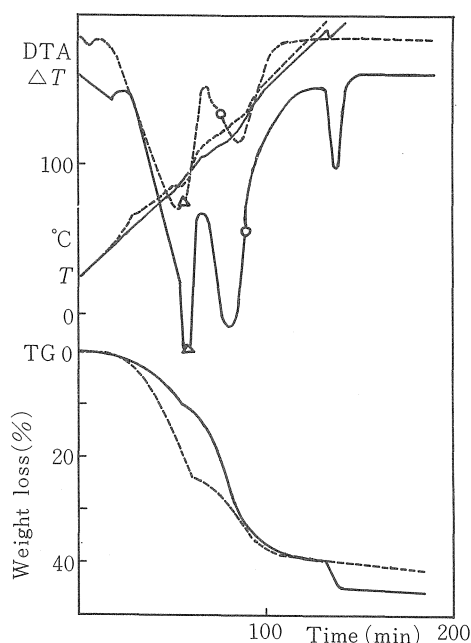


Fig. 1. Derivatograms for $\text{KAl}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (—) and $\text{KCr}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (.....).
 Δ , melting point; o, solidifying point

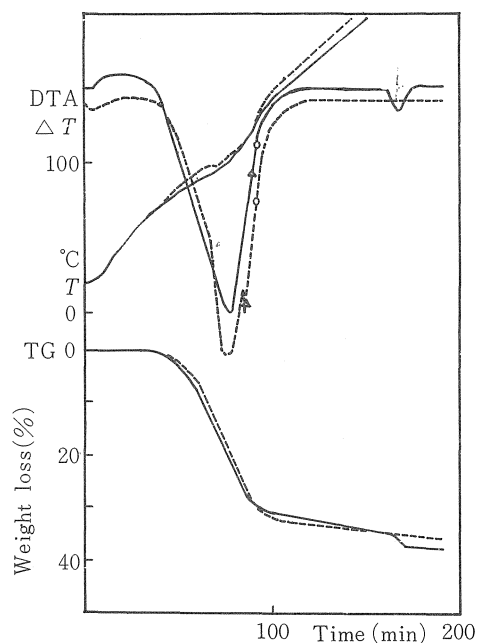


Fig. 2. Derivatograms for $\text{CsAl}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (—) and $\text{CsCr}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (.....).
 Δ , m. p.; o, s. p.

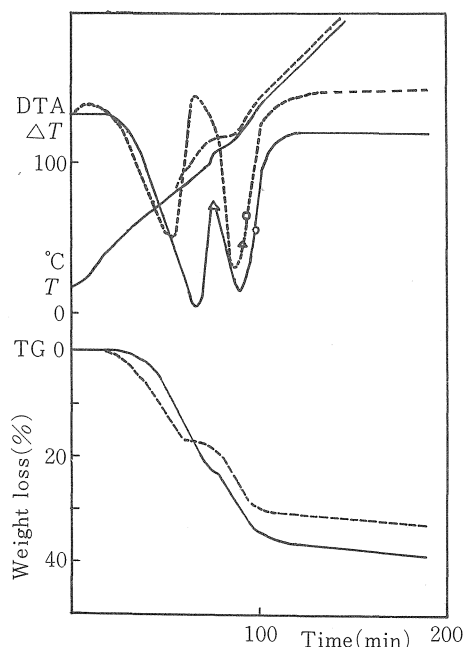


Fig. 3. Derivatograms for $\text{RbCr}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (—) and $\text{TiCr}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (.....).
 Δ , m. p.; o, s. p.

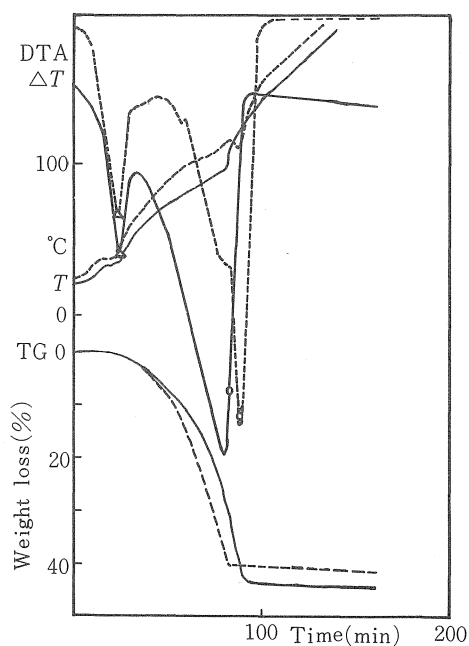


Fig. 4. Derivatograms for $\text{NaAl}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (—) and $(\text{NH}_4)\text{Fe}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (.....).
 Δ , m. p.; o, s. p.

Results

Derivatograms for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (I) and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (II) as α -type alums are shown in Fig. 1. Derivatograms for $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (III) and $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (IV) and those for $\text{RbCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (V) and $\text{TlCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (VI) as β -type alums are shown in Figs. 2 and 3, respectively. The derivatograms for $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (VII) of γ -type alum and $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (VIII) the type of which is ambiguous are shown in Fig. 4. The thermochemical functions for each step of dehydration evaluated by the analysis of the above diagrams are summarized in Table 1, together with the radius ratios of univalent to tervalent ion and the color changes of samples upon heating.

TABLE 1. THERMOCHEMICAL FUNCTIONS FOR THE DEHYDRATION OF ALUMS.

Chemical formula	Type	Dehydration temperature (°C)	Number of water molecules dehydrated	ΔH (kcal mol ⁻¹)	E^\neq (kcal mol ⁻¹)	Ionic radius ratio univalent/tervalent
(I) $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	α	60~85	3	14.2	36.9	2.61
		85~150	6	7.3	38.3	
		150~190	2	7.3	—	
		190~210	1	7.9	73.2	
(II) $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	α	45~110	6	11.8	21.8	1.93
		110~140	4	10.2	26.8	
		140~	2	—	—	
(III) $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	β	65~120	9	13.9	35.6	3.57
		120~200	2	—	—	
		210~240	1	—	—	
(IV) $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	β	70~140	10	12.2	26.9	2.64
		140~	2	—	—	
(V) $\text{RbCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	β	45~ 95	6	12.4	22.5	2.32
		95~120	4	11.9	60.7	
		120~	2	—	—	
(VI) $\text{TlCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	β	25~ 80	6	9.7	19.6	2.32
		80~140	4	12.7	—	
		140~	2	—	—	
(VII) $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	γ	45~ 95	12	11.1	26.5	1.90
(VIII) $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	—	45~115	11.5	8.9	—	2.26
		115~200	0.5	—	—	

Discussion

α -Type Alums. It is found from Fig. 1 and Table 1 that the alum I shows four steps of dehydration, stepwise liberating 3, 6, 2 and 1 mol of water and that the alum II gives three steps of dehydration, successively evolving 6, 4 and 2 moles of water, where, in I, the steps for the liberation of 6 and 2 moles of water overlap with each other in DTA, and, in II, the last step is only shown by the gradual descent of TG curve due to the gentle loss of water over 140°C without the distinct peak in DTA.

The latter result that the last two molecules of water are particularly difficult to be liberated from metal in II is likely to be due to the strong polarizing power of trivalent chromium. The another marked characteristic for II is that the first six molecules of water are more easily expelled than the other six. It exhibits that there is a remarkable difference in the binding force against metal ions between the six water molecules coordinated to trivalent metal and six lattice water molecules.¹⁵⁾ Such phenomena were also observed in the alums V and VI as shown in Table 1.

The alum II gave the distinct color change from purple to green at 78°C. The absorption spectra in the aqueous solution for the alum II and for the compound obtained by heating II over 80°C are shown in Fig. 5, and the corresponding spectra in solid state are in Fig. 6. It is found from these figures that the first and the second

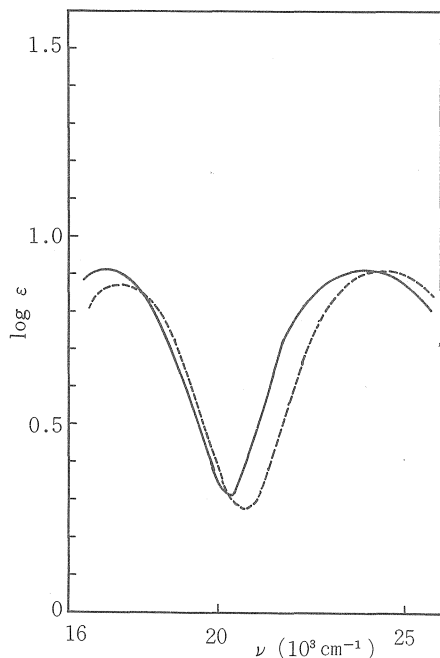


Fig. 5. Absorption spectra in the aqueous solution for $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (II) (.....) and for the compound obtained by heating II over 80°C (—).

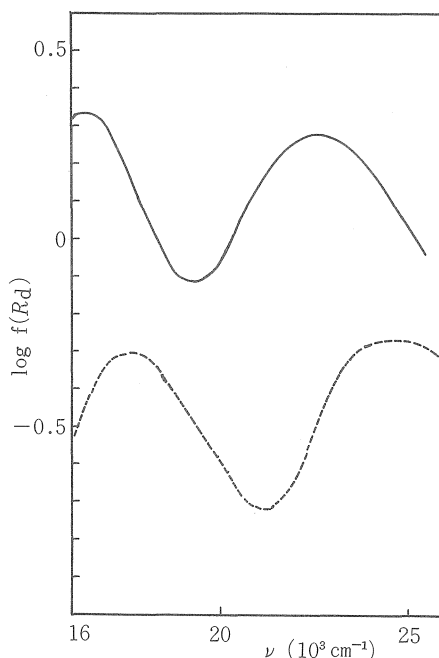


Fig. 6. Absorption spectra in the solid state for II (.....) and for the compound obtained by heating II over 80°C (—).

absorption bands for d-d transition in chromium(III) ion are shifted by about 10nm toward longer wavelength region upon heating II at 80°C. This will suggest the formation of sulfato complex species such as $[\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4]^+$ by replacing a part of water molecules coordinated to chromium(III) by SO_4^{2-} as counter-anion. Such phenomena were also observed for the other chromium(III) alums, III, V and VI.

It should be noted that in the dehydration of I and II, the values of the enthalpy change in the second step are smaller than those of the corresponding first step, as seen in Table 1. This fact can be explained by the following consideration: as shown in Fig. 1, the enthalpy change obtained by the analysis of the first DTA peak contains the heat of fusion of the salt ($\Delta H > 0$) besides the essential endothermicity in dehydration, and the enthalpy change for the second DTA peak includes the heat of solidification ($\Delta H < 0$), because the melting points of these alums (90°C for both I and II) lie within the temperature range where DTA peak of the first step of dehydration appears and the solidifying points (130°C for I, 120°C for II) fall within the temperature range where DTA peak of the second step appears.

β -Type Alums. In α -type alums, six water molecules coordinate to the tervalent metal ion such as aluminum or chromium ion, forming the regular octahedron and the other six molecules are lattice waters which cooperate rather to potassium ion. On the other hand, in β -type alums, although the tervalent metal ion is coordinated by six water molecules in the same manner to that in α -type alum, the univalent ion which is larger in size than potassium ion is surrounded by six oxygen molecules of sulfate ion as well as by six oxygen of water molecule.⁶⁾

Although β -alums, V and VI, show the same dehydration process with that for α -type chromium(III) alums as seen in Fig. 3, the alums, III and IV, have the tendency liberating 9~10 moles of water in single step as shown in Fig. 2, differing from V and VI. Moreover, the dehydration temperatures of two steps in both V and VI are remarkably lower than those of the corresponding steps of the α -alums, whereas the dehydration endothermic peaks of one step in both alums III and IV lie in the intermediate range between the dehydration peaks of the first and the second steps of the α -alums, I and II. As seen from the derivatograms, the alums, V and VI, may behave as α -alums rather than β -alums. It is probably attributed mainly to the results that the radius ratios of the univalent to tervalent ion in V and VI are situated in the intermediate between those of I and IV as shown in Table I, and is due to the facts that the dimension of the unit cubic lattice of V, $a = 12.227 \text{ \AA}$, is fairly close to that of II, $a = 12.175 \text{ \AA}$, whereas that of IV, $a = 12.405 \text{ \AA}$, is considerably larger than that of II.⁵⁾

The dehydration temperatures in the first step for V and VI are lower than the corresponding ones of II. It may suggest that the rubidium and thallium ions form the relatively unstable crystal structure because their ionic radii are not so sufficiently large to form β -type structure.

On the other hand, III and IV underwent dehydration in a single step. It seems to

be explained by the consideration that the cesium ion has the large size enough to form the stable β -type structure, and as soon as some molecules of water surrounding cesium are liberated, the resulting product becomes unstable, the remaining water molecules coordinated to tervalent metal ion being evolved at once.

The enthalpy changes for the first and second step of dehydrations are almost equal in V and VI, differing from the general case that the enthalpy change for the second step is larger than that for the first one. It will be explained by the results that, in these alums, differing from α -type alums, both melting and solidifying points lie within the range of the DTA peak for the second step (for V, m.p., 120°C, s.p., 127°C; for VI, m.p., 99°C, s.p., 120°C), the heat of fusion and heat of solidification being canceled by each other.

Since the melting point and the solidifying point of III are very close to each other, and those of IV are also the same (for III, m.p., 124°C, s.p., 130°C; for IV, m.p., 122°C, s.p., 127°C), and they lie all within the DTA peak of the single step of dehydration, the enthalpy changes show normal values.

So far as the chromium(III) alums are concerned, the activation energies are increasing in the order, VI < II < V < IV. This order is in agreement with that of the dehydration temperature in the first step, as VI < V < II < IV, except that the order of II and V is exchanged. Consequently, the order of the activation energies is considered to be approximately parallel to the stability for the dehydration.

The enthalpy changes for the aluminum alums I and III are not so different from each other, and the activation energies are also the same. And they show the considerably higher values than those of the corresponding chromium alums; *i. e.*, the values for I are higher than those for II and the values for III are higher than those for IV. In addition, the temperature initiating dehydration for I is a little higher than that for II and that for III is a little higher than that for IV. It may be explained by the reason that the force constant of Cr-O(H₂O) is larger than that of Al-O(H₂O),¹⁶⁾ and the binding force of water molecules against chromium is stronger than that against aluminum, and as a result, the degree of contribution of chromium on the binding force of water molecules against potassium or cesium is smaller than that of aluminum.

The chromium(III) alums, II, IV, V and VI, because of the higher temperature of the last dehydration step for two molecules of water and the smallness of the dehydration rate, do not show an endothermic DTA peak based on the dehydration, and consequently the enthalpy change can not be obtained. As stated above, six moles of water surrounding univalent metal ion and four moles of water coordinated to chromium(III) ion were relatively easily liberated as the first and the second steps of dehydration, respectively, and the last two moles of water were difficult to be dehydrated.

These results were also ascertained stepwise by the isothermal experiments at the several fixed temperatures, which are shown in Fig. 7 for III and V as representative examples. As seen in Fig. 7, the alum V loses six moles of water upon heating at 50°C

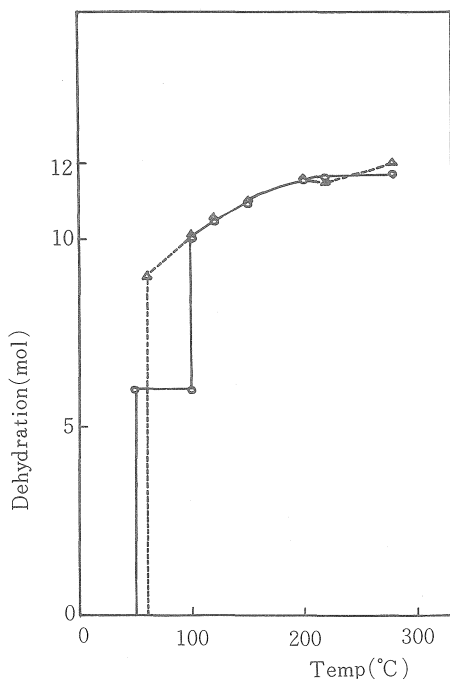


Fig. 7. TG curves obtained by the isothermal heating at the stepwise several fixed temperatures for $\text{RbCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (—○—) and $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (···△···).

isothermally, loses four moles of water upon the successive heating at 100°C and loses two moles of remaining water gently as the fixed heating temperatures are raised.

Fig. 7 also contains the isothermal heating diagram for III, where III loses nine moles of water at a time upon heating at 60°C and afterwards loses three moles of remaining water slowly as the temperature rising.

γ -Type Alum and Ammonium Iron Alum. The dehydration processes of the alum VII as γ -type and VIII the type for which is not ascertained show the strikingly characteristic features quite different from those of α -type and β -type alums, as shown in Fig. 4. The first of them is that the fusion of the salts appears prior to dehydration. The second is that the dehydration of twelve moles of water occurs in a single step, and hence, in this case, the endothermic peak of DTA only based on the fusion appears clearly at considerably lower temperature (for VII, 37°C ; for VIII, 39°C). Solidification points (for VII, 110°C ; for VIII, 115°C) lie within the range of the dehydration peak for the first step.

In the alum VII, which is one of the γ -type alums investigated in detail in the present work, since the radius of sodium ion is small, the sulfate ion takes somewhat different orientation along the three-folded axis to perform the closepacking as completely as possible. It will make the melting point lower, but the reason is not clear.

Although the alums, I through VII, are melt to form the homogeneous liquid phase,

VIII is clearly separated to two layers of the homogeneous liquid and solid phases and their colors both change from pale purple to light brown. The liquid phase component gives the absorption maximum of the spectrum at 290nm in 1×10^{-4} M solution. This maximum is shifted toward longer wavelength side with the concentration until it gets to 320nm in the solution beyond 1×10^{-3} M.

The latter wavelength is coincident with that appearing in the absorption spectra of $[\text{Fe}(\text{SO}_4)_2(\text{H}_2\text{O})_2]^-$ in sulfuric acid solution.¹⁷⁾

When the materials of the solid phase separated out are heated with the thermobalance, they lose three moles of water of crystallization at $50^\circ\text{C} \sim 210^\circ\text{C}$ which amount to 18% of the gross weight. It is consequently considered that a very small DTA peak appearing at near 190°C in Fig. 4 is due to the liberation of the water of crystallization contained in the materials of the solid phase.

It is obvious that an endothermic peak appearing at near 40°C in VII and VIII depends on thier heat of fusion, but an endothermic peak appearing at near 110°C is owing to the enthalpy change based on the dehydration partially cancelled by the heat of solidification. Thus, the enthalpy changes of VII and VIII may show a little smaller values than those in the general dehydration as shown in Table 1.

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