

# Thermal analysis of some double decavanadates

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*Dedicated to Professor M. Dillinger on his 70th birthday*

The thermal analysis of  $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ ,  $K_2Cd_2V_{10}O_{28} \cdot 14H_2O$ ,  $K_4CdV_{10}O_{28} \cdot 10H_2O$ , and  $Cs_4CdV_{10}O_{28} \cdot 11H_2O$  is described. This analysis is completed with infrared spectra and X-ray diffraction patterns of above compounds and their decomposition products. It was found that the dehydration of these compounds was succeeded by some structural changes within the temperature range between 180 and 290°C. This process also involved a change in  $[V_{10}O_{28}]^{6-}$  ion which was dependent on the presence of different cations.

The double decavanadates hitherto known may be divided approximately into three groups. The first group comprises decavanadates of the type  $M_2^I M_2^I V_{10}O_{28} \cdot nH_2O$  and  $M^I M^I V_{10}O_{28} \cdot nH_2O$  where  $M^I$  is Na, K, Cs,  $NH_4$ , while  $M^{II}$  denotes Mg, Zn, Cd, Mn, or Co. Some of them were described a long time ago [1, 2], the others in recent years [3–5]. The double decavanadates of alkaline and some bivalent metals in which the ratio of cations is varying but cannot be expressed by above-mentioned general formulae belong into the second group [2, 6–8]. The last group includes the double decavanadates of alkaline metals [9]. Since all double decavanadates contain a large number of molecules of crystal water, it is interesting to investigate their dehydration and the eventual changes which take place after the dehydration of these substances. The aim of the thermal analysis of decavanadates described in papers [4, 10] was to complete the characteristics of some compounds prepared. There exist no papers concerned only with the problems of the thermal decomposition of the above group of compounds.

## Experimental

$K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ ,  $K_2Cd_2V_{10}O_{28} \cdot 14H_2O$ ,  $K_4CdV_{10}O_{28} \cdot 10H_2O$ , and  $Cs_4CdV_{10}O_{28} \cdot 11H_2O$  were prepared according to [5].

The thermal analysis was carried out with a derivatograph MOM, Budapest, over the temperature range from 20 to 300°C. The temperature programme was 4°C/min. The weight of sample was 200–530 mg according to the character of species. The products of thermal decomposition destined for further investigation were obtained by the isothermal heating of the sample to constant weight in a vacuum glass apparatus. Salt baths were used for heating to 300°C while above 300°C the samples were heated in a muffle furnace. The temperatures of total dehydration were read off approximately on the DTA thermograms. Anhydrides of decavanadates were obtained at different temperatures but the intervals between these temperatures were 20°C at the very most. To enable the comparison of the results, the maximum heating temperature of 330°C

was used for all compounds. At higher temperatures, the X-ray diffraction patterns and infrared spectra did not change any more with any of the species investigated.

The X-ray powder diffraction patterns of  $\text{K}_4\text{CdV}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$  and  $\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$  as well as of the products of their thermal decomposition were made with a powder goniometer of Czechoslovak production by using a copper anticathode. For  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$  and  $\text{Cs}_4\text{CdV}_{10}\text{O}_{28} \cdot 11\text{H}_2\text{O}$  and the corresponding anhydrides the Debye-Scherer method with silver anticathode was used.

The infrared spectra in the region between  $400-1100\text{ cm}^{-1}$  were made with an instrument UR-20 (Zeiss, Jena) by using the KBr technique. For this purpose 0.75 mg of sample and 500 mg of KBr were weighed.

The melting points of the species were determined in a crucible furnace adapted for this procedure.

For the sake of simplicity, we do not present the plots of all isothermal heatings of substances because many of them are identical.

### Results and discussion

The thermal analysis of the investigated double decavanadates is presented in Figs. 1-4. The assumption that endothermic processes involving weight losses of compounds are caused by dehydration was confirmed by chemical analysis (Table 1). The dehydration of compounds takes place in several steps. The lower hydrates are characterized by a very low thermal stability so that the corresponding weight losses are sufficiently observable only on DTG curves. The dehydration of compounds finished, various exothermic processes set in. Regarding the weight stability of anhydrous salts and the vanadium content which equals the values given in Table 1, these processes might involve:

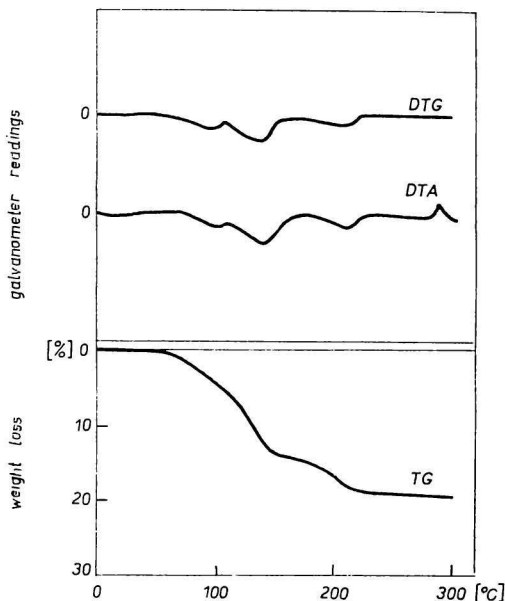


Fig. 1. Thermal analysis of  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$ . Sample weight 200 mg.

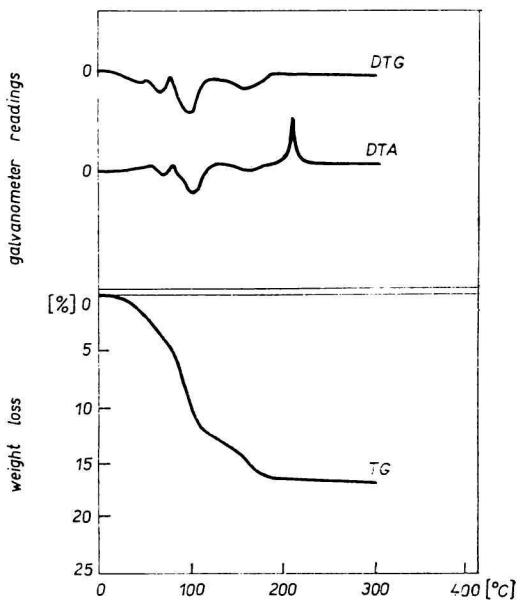


Fig. 2. Thermal analysis of  $\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ . Sample weight 200 mg.

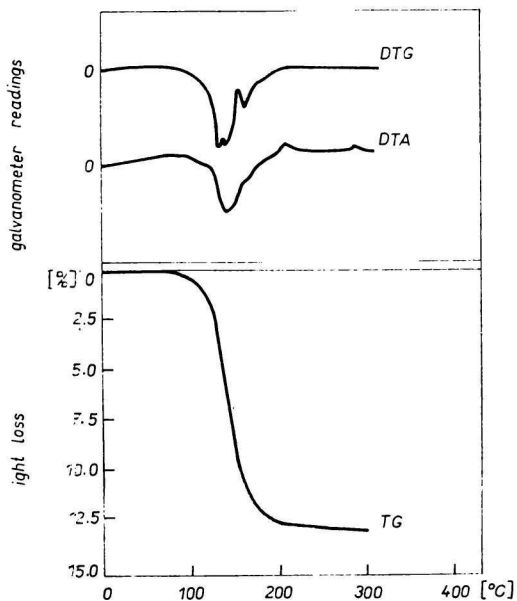


Fig. 3. Thermal analysis of  $\text{K}_4\text{CdV}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$ . Sample weight 400 mg.

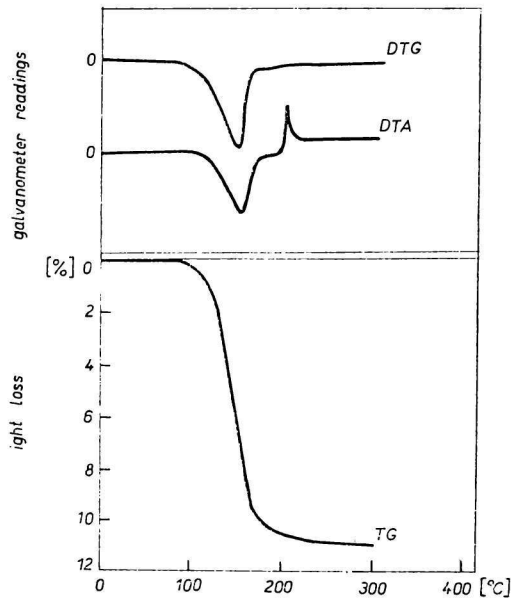


Fig. 4. Thermal analysis of  $\text{Cs}_4\text{CdV}_{10}\text{O}_{28} \cdot 11\text{H}_2\text{O}$ . Sample weight 530 mg.

1. decomposition of anhydrides into corresponding oxides, 2. formation of less condensed polyvanadates, 3. change in the structure of decavanadate ion.

It is obvious from X-ray patterns given in Figs. 5–8 that the dehydration of decavanadates destroys their original structure. In the case of  $\text{Cs}_4\text{CdV}_{10}\text{O}_{28} \cdot 11\text{H}_2\text{O}$  the release of structural water results in such a degree of disorder in the structure that the anhydride gets amorphous according to the analysis with X-rays. This species dried at 170°C gives only one broad line in the X-ray diffraction pattern in the region  $2\theta$  from 8.50 to 10.94°. The heating of anhydride to 180°C produces its recrystallization while the structure formed does not change any more even if the species is heated to higher temperatures (the X-ray patterns of the species heated to 180°C are identical with those

Table 1

Content of vanadium in dehydrated decavanadates

Compound	Weight loss [%]		Vanadium content [%]	
	calculated	found	calculated	found
$\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$	19.80	20.01	43.68	43.52
$\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$	16.66	16.68	40.42	40.31
$\text{K}_4\text{CdV}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$	12.80	12.75	41.55	41.68
$\text{Cs}_4\text{CdV}_{10}\text{O}_{28} \cdot 11\text{H}_2\text{O}$	11.00	11.15	31.81	31.66

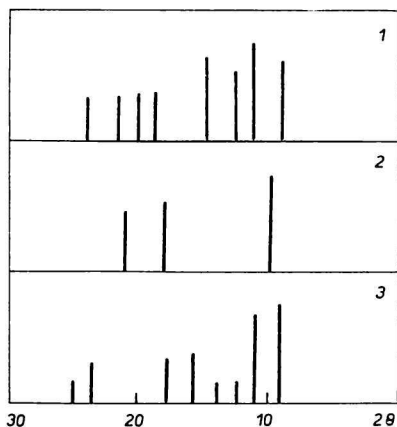


Fig. 5. X-Ray diffraction patterns.  
 1.  $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ ; 2.  $K_2Zn_2V_{10}O_{28}$   
 dehydrated at 250°C; 3.  $K_2Zn_2V_{10}O_{28}$   
 heated to 330°C.

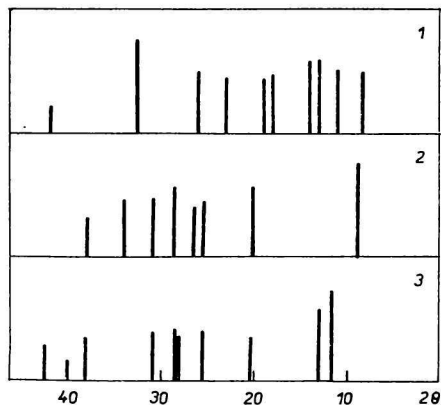


Fig. 6. X-Ray diffraction patterns.  
 1.  $K_2Cd_2V_{10}O_{28} \cdot 14H_2O$ ; 2.  $K_2Cd_2V_{10}O_{28}$   
 dehydrated at 230°C; 3.  $K_2Cd_2V_{10}O_{28}$   
 heated to 330°C.

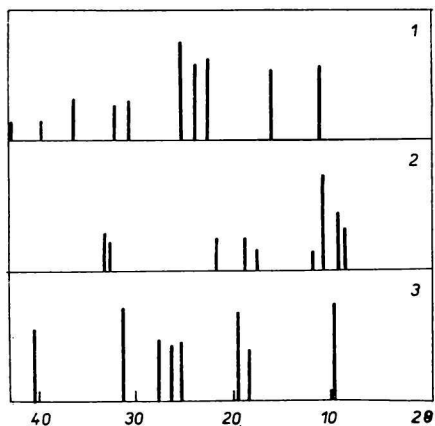


Fig. 7. X-Ray diffraction patterns.  
 1.  $K_4CdV_{10}O_{28} \cdot 10H_2O$ ; 2.  $K_4CdV_{10}O_{28}$   
 dehydrated at 250°C; 3.  $K_4CdV_{10}O_{28}$   
 heated to 330°C.

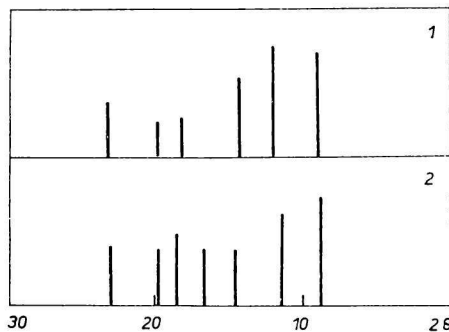


Fig. 8. X-Ray diffraction patterns.  
 1.  $Cs_4CdV_{10}O_{28} \cdot 11H_2O$ ; 2.  $Cs_4CdV_{10}O_{28}$   
 heated to 330°C.

obtained at 330°C). Similarly in the case of dehydrated potassium zinc decavanadate the most intense diffraction is also relatively diffuse what indicates a certain degree of amorphousness of this anhydride, too. On account of dehydration, a change in the structure of substances appears also with both potassium cadmium salts. By heating all anhydrides of double decavanadates to temperature higher than that necessary to release structural water, other changes manifested by a change in diffraction patterns appear in these substances.

*Table*  
Frequencies of polyvanadates in  $\text{cm}^{-1}$

Compound	$\gamma_1$		$\gamma_3$	$\gamma_4$	$\gamma_5$	$\gamma_6$	$\gamma_7$
$\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$	417 w 465 w	550 w	600 m	760 m	850 s	962 vs	
$\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28}$ (255°C)	410 w	560 vs		770 m	880 m	970 m	
$\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28}$ (330°C)	410 w 470 m	505 m 545 s	610 m	745 vs	850 w 880 w	940 s 985 s 990 s	1010 s
$\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$	415 m 465 w	535 m 560 m	600 m	760 m	825 s 840 s	955 s	
$\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28}$ (230°C)	405 w	555 vs 590 vs		745 m	830 m	950 m	
$\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28}$ (330°C)	425 m 470 m	585 vs		742 s	862 m	948 w 973 s	1010 m
$\text{K}_4\text{CdV}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$	417 m 465 w	535 m 595 m		760 m	835 s 855 m	955 vs	
$\text{K}_4\text{CdV}_{10}\text{O}_{28}$ (250°C)	405 w	550 vs		735 m	898 w	948 m 970 m 995 w	
$\text{K}_4\text{CdV}_{10}\text{O}_{28}$ (330°C)	425 m 467 m	535 m	600 vs 675 m	750 vs	845 m	900 w 948 m 975 vs	1000 m 1010 m
$\text{Cs}_4\text{CdV}_{10}\text{O}_{28} \cdot 11\text{H}_2\text{O}$	415 m 465 w	530 m	600 m	755 m 790 w	820 m 840 m	960 vs	
$\text{Cs}_4\text{CdV}_{10}\text{O}_{28}$ (170°C)	435 w		655 s	770 s	830 s	968 vs	
$\text{Cs}_4\text{CdV}_{10}\text{O}_{28}$ (330°C)	410 m 430 m		600 vs	715 vs	855 m	968 m 993 s	
$\text{V}_2\text{O}_5$	480 s	590 m			820 vs		1020 m
$\text{Ti}_3\text{V}_5\text{O}_{14}$	405 m 435 m 468 m		667 m	722 s 782 vs		928 m 973 s	

w — weak, m — medium, s — strong, vs — very strong.

The character of the changes which occur as a result of the dehydration of decavanadates and further heating of anhydrides is obvious from the infrared spectra of these substances presented in Table 2. With all crystalline hydrates an intense absorption band appears in the region between 950 and 960  $\text{cm}^{-1}$ . It remains unchanged if the dehydrated compounds have been heated only to the temperature necessary to release the structural water. This absorption band is considered [11] to correspond to the V—O stretching vibrations characteristic of the decavanadate ion which consists of ten  $\text{VO}_6$  octahedra bound together by edges. The shift or disappearance of some bands in the spectrum of dehydrated compounds is evidently due to the release of water molecules among which some may be linked with the cation as well as through hydrogen bonds with the terminal oxygen atoms of  $\text{VO}_6$  octahedra. Thus it may be concluded that the dehydration of crystalline hydrates of decavanadates cannot be responsible for the change in the structure of anion. The decavanadate ion changes only after heating the anhydrides to higher temperatures what is accompanied by a qualitative change in the infrared spectra of these species. The alternatives of a possible transformation of the investigated decavanadates have already been stated in this discussion. A comparison of the infrared spectrum of vanadium pentoxide (Table 2) with the spectra of anhydrides excludes the decomposition into vanadium pentoxide and other corresponding oxides. Provided some other less polymerized vanadates were formed, only the conversion into pentavanadates would be possible because of the weight stability of heated substances. For comparison, the spectrum of thallium(I) pentavanadate [12] is presented in Table 2. It follows from this spectrum that such a transformation does not occur either. This conclusion conforms with the fact that only the pentavanadates of some univalent metals with relatively large ionic radius are known for the time being. With respect to the structure of anion [13], it is therefore probable that the size of cation should have a decisive influence on the existence of a certain pentavanadate. A formation of pentavanadates of bivalent elements with relatively small ionic radii is therefore very little likely. Hence, a change in the character of infrared spectrum is caused by a change in the structure of  $[\text{V}_{10}\text{O}_{28}]^{3-}$  ion. The relatively high stability of original configuration of this ion is in a certain inconsistency with the fact that the  $\text{VO}_6$  octahedra possess several common edges what ought to produce an opposite phenomenon. The stability of this ion must be enhanced by a considerable polarization of V—O bonds. It can be seen on the DTA records (Figs. 1—4) that the structural changes follow almost immediately after dehydration what means that a labile crystal structure formed by a voluminous anion and relatively very small cations has arisen after releasing the structural water which extended the space effect of cation. Therefore, the stability of the structure as a whole and not only that of the anion itself must be taken into consideration. Thus it may be assumed that a further heating of anhydrous decavanadates produces a less compact configuration of anion which is responsible for the greater stability of lattice.

Another piece of knowledge is based on the comparison of absorption bands at higher values of wavenumbers. In the case of  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28}$ ,  $\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28}$ , and  $\text{K}_4\text{CdV}_{10}\text{O}_{28}$  an absorption band appears at 1010  $\text{cm}^{-1}$  while it is absent in the case of  $\text{Cs}_4\text{CdV}_{10}\text{O}_{28}$ . For this reason this species was gradually heated to temperatures exceeding 330°C until it melted. The infrared spectra as well as X-ray powder diffraction patterns were equal and identical with the results obtained at 330°C. Thus it may be concluded that the newly produced constitution of decavanadate ion may be strongly affected by cations — their size and polarization properties. The simultaneous effect of these factors on the stability of the structures formed manifests itself in the melting points of  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28}$  (446°C) and  $\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28}$  (434°C) as well as  $\text{K}_4\text{CdV}_{10}\text{O}_{28}$  (387°C) and  $\text{Cs}_4\text{CdV}_{10}\text{O}_{28}$  (374°C).

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