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THERMAL DECOMPOSITION OF SOME DIVALENT METAL SELENATES

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ABSTRACT

Thermogravimetry, differential thermal analysis and differential thermogravimetry have been used to study the decomposition of hydrated selenates of manganese(II), cobalt, nickel, copper(II), zinc and cadmium. Based on the results obtained, mechanisms of decomposition have been proposed. The decomposition temperatures of non-hydrates show a gradual increase from manganese(II) selenate to zinc selenate and then a sudden drop for cadmium selenate.

INTRODUCTION

The thermal dehydration decomposition of the divalent metal selenate hydrates has not been so extensively studied as compared to the dehydration of metal sulphates. The available scanty literature has been orientated towards the determination of the lower hydrates and in a few cases the final decomposition products were formed by employing the thermogravimetric techniques. The present paper aims to clarify some of the stages in the thermal decomposition of few less known selenate hydrates of some divalent metals.

EXPERIMENTAL

The divalent metal selenates were prepared by neutralising selenic acid with an excess of the respective metal carbonates, subsequent concentration of filtered solution, followed by crystallisation in vacuum over P_2O_5. All the synthesised selenates were chemically analysed on metal and selenate. The metal contents were determined by direct complexometric titrations. Selenate was estimated after eluting the aqueous salt solution through a cation exchanger Dowex 50X8 followed by simple acid–base titration of the effluent electrolyte.

The intermediate products, particularly the lower hydrates and anhydrides, isolated by static thermal decomposition were determined by chemical analysis. Little dilute hydrochloric acid was used to dissolve the sparingly soluble lower hydrates and anhydrides. These solutions were then analysed on metal components as above. However, the selenate contents were determined gravimetrically by precipitating them as barium selenate from the solutions. Table 1 summarises the results of the chemical analysis of the synthesised selenate hydrates, the isothermally isolated lower hydrates and anhydrous salts. Underlined figures indicate percentage of water obtained during thermal analysis.

TABLE 1

ANALYTICAL AND THERMOANALYTICAL RESULTS

Compound	*Colour*	*Analytical results*					
		Metal (%)		*Selenate* (%)		*Water* (%)[a]	
		Calc.	*Anal.*	*Calc.*	*Anal.*	*Calc.*	*Anal.*
$MnSeO_4 \cdot 2H_2O$	Pale pink	23.49	23.21	61.10	62.48	15.39	$\underline{15.20}$
$MnSeO_4 \cdot H_2O$	Pale pink	25.45	24.61	66.21	68.14	8.34	7.25
$MnSeO_4$·anhyd.	Brown	27.76	27.80	72.24	71.26	—	—
$CoSeO_4 \cdot 4H_2O$	Pink	21.52	21.55	52.18	52.63	26.29	$\underline{26.40}$
$CoSeO_4 \cdot 2H_2O$	Lilac	24.77	24.47	60.09	60.08	15.14	15.43
$CoSeO_4$·anhyd.	Violet	29.17	29.15	70.83	70.34	—	—
$NiSeO_4 \cdot 6H_2O$	Pale green	18.95	18.82	46.13	47.34	34.84	$\underline{33.08}$
$NiSeO_4 \cdot H_2O$	Light brown	26.73	26.49	65.09	65.50	8.18	8.01
$NiSeO_4$·anhyd.	Yellowish green	29.19	29.15	70.89	70.34	—	—
$CuSeO_4 \cdot 5H_2O$	Blue	21.44	21.82	48.20	48.26	30.36	$\underline{30.30}$
$CuSeO_4 \cdot H_2O$	Pale green	28.30	28.48	63.68	63.33	8.02	8.19
$ZnSeO_4 \cdot 3H_2O$	Light cream	24.92	24.86	54.48	55.38	20.58	$\underline{19.04}$
$ZnSeO_4$·anhyd.	Light cream	31.38	30.49	68.62	68.55	—	—
$CdSeO_4 \cdot H_2O$	White	41.12	39.87	52.40	52.29	6.58	$\underline{6.87}$
$CdSeO_4$·anhyd.	White	44.03	42.55	55.97	56.69	—	—

[a] % of water is determined by difference.

TABLE 2

DTA DATA FOR DIVALENT METAL SELENATES

Compound	*No. of bands*	*Temperature* (°C)
$MnSeO_4 \cdot 2H_2O$	6	100, 180, $\underline{270}$, 410, 530, ca. 800
$CoSeO_4 \cdot 4H_2O$	4	130, $\underline{320}$, 545, 605
$NiSeO_4 \cdot 6H_2O$	6	130, 270, $\underline{350}$, 450, 590, 635
$CuSeO_4 \cdot 5H_2O$	8	115, 185, 255, $\underline{480}$, 540, 570, 630, 1050
$ZnSeO_4 \cdot 3H_2O$	7	140, 200, 280, $\underline{535}$, 560, 585, 720
$CdSeO_4 \cdot H_2O$	4	$\underline{165}$, 620, 870, 890

Simultaneous TG, DTA and DTG curves were obtained using the "Mettler Thermoanalyser" which has an accuracy of ±0.05 mg and a temperature range up to 1600°C. Pt/Pt–Rh thermocouples were used as temperature detectors and α-alumina was used as the reference material. Around 100 mg of material are placed in a 0.2-ml platinum crucible and heated at a rate of 10°C min^{-1} under an air flow of 600 ml h^{-1}.

Figures 1–6 represent the thermogravimetric (TG), differential thermal analysis (DTA) and differential thermogravimetric (DTG) curves of $MnSeO_4 \cdot 2H_2O$, $CoSeO_4 \cdot 4H_2O$, $NiSeO_4 \cdot 6H_2O$, $CuSeO_4 \cdot 5H_2O$, $ZnSeO_4 \cdot 3H_2O$ and $CdSeO_4 \cdot H_2O$. Table 2 summarises the DTA data for divalent metal selenates. Peak temperatures associated with complete dehydration are underlined.

RESULTS AND DISCUSSION

Manganese selenate dihydrate, $MnSeO_4 \cdot 2H_2O$

The thermoanalytical curves of manganese selenate dihydrate (Fig. 1) under air, show four major weight loss stages in the range 110–800 °C. At the beginning of the TG curve a gain in weight is observed despite the temperature increase. This phenomenon is due to the reduced buoyancy of air in the furnace. The compound loses weight from 110 till 185 °C whereby manganese selenate monohydrate is produced. In the DTA curve two endothermic peaks are observed in the temperature range 100–180 °C. The peak at 100 °C is assumed to be due to recrystallisation since no accompanying weight loss is found, while the second peak is attributed to the loss of water.

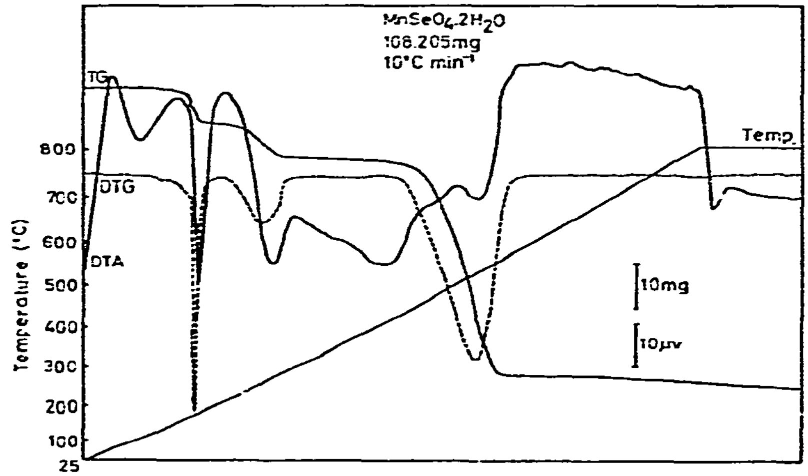

Fig. 1. Simultaneous TG–DTA–DTG of $MnSeO_4 \cdot 2H_2O$.

Manganese selenate monohydrate is quite stable up to 210 °C. Further heating leads to the loss of the remaining water molecule. At 330 °C the compound becomes anhydrous and the endothermic peak at 270 °C in the DTA curve represents this dehydration.

Above 330 °C anhydrous manganese selenate is reduced to selenite and subsequently produces a mixture of dimanganese trioxide, Mn_2O_3, and trimanganese tetraoxide, Mn_3O_4, with the sublimation of selenium dioxide. The endothermal decomposition involves two DTA peaks at 410 and 530 °C. Beyond 800 °C the dimanganese trioxide from the mixture undergoes an endothermal reduction as shown by the peak above ca. 800°C and produces trimanganese tetraoxide which is known to be stable up to 845°C.

Thermal decomposition of manganese selenate pentahydrate has been reported[2] to yield the monohydrate at 126°C. This may suggest lesser stability of the pentahydrate as compared to the present dihydrate. Again, anhydrous manganese selenate is reported to have been formed at a temperature of 280°C, which is lower than the 330°C observed in the present investigation.

The overall decomposition mechanism of manganese selenate dihydrate may be represented as follows:

$$\begin{tikzcd}
MnSeO_4 \cdot 2H_2O \arrow[r, "180\,^{\circ}C"] & MnSeO_4 \cdot H_2O \arrow[r, "330\,^{\circ}C"] & MnSeO_4 \arrow[d, "600\,^{\circ}C"] \\
 & Mn_3O_4 & Mn_3O_4 + Mn_2O_3 \arrow[l, "800\,^{\circ}C"']
\end{tikzcd}$$

Cobalt selenate tetrahydrate, $CoSeO_4 \cdot 4H_2O$

The thermograms of cobalt selenate tetrahydrate are presented in Fig. 2. The TG curve shows a slight weight gain due to reduced buoyancy of air. At 50°C the salt begins to lose water steadily and the process continues up to 170°C. At this temperature a loss corresponding to two molecules of water occurs. This endothermic effect gives a DTA peak at 130°C. The horizontal line of the dihydrate persists from 115 to 255°C, beyond which the remaining water molecules are separated, and anhydrous cobalt selenate is formed. This dehydration is complete at 345°C. The accompanying endothermic reaction is represented by a symmetrical DTA peak with maxima at 320°C.

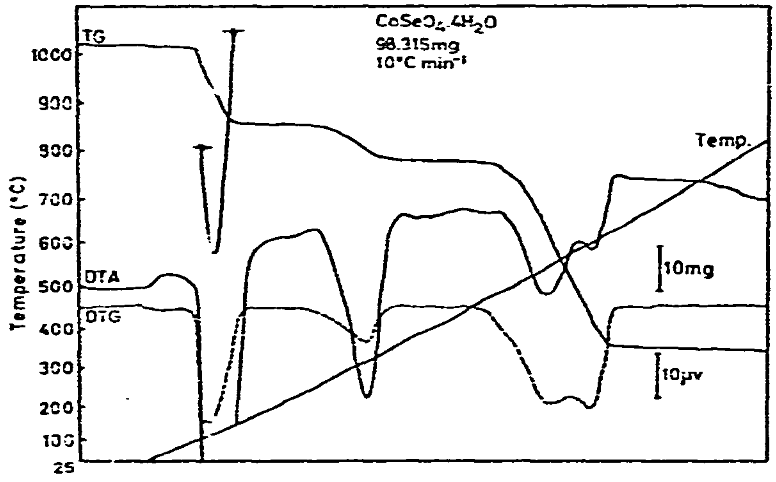

Fig. 2. Simultaneous TG–DTA–DTG of $CoSeO_4 \cdot 4H_2O$.

The plateau of anhydrous cobalt selenate remains perfectly horizontal up to 445 °C, at which temperature the decomposition begins. From the TG curve it appears that the transformation from anhydrous cobalt selenate to oxide is accomplished in only one stage. However, a critical study of DTA and DTG makes it clear that two simultaneous losses occur as seen from the overlapping of two peaks in both cases in the region 545–605 °C. Reduction of selenate to selenite and sublimation of selenium dioxide comprise these two subsequent stages. Conversion to cobalt oxide is complete at 625 °C.

In a short note Malard[3] has illustrated the thermal decomposition of cobalt selenate hexahydrate. The range of temperatures for the formation of anhydride and oxide reported by the author is in agreement with the present observation. Since a low-temperature (800 °C) furnace was used, complete conversion of Co_3O_4 to CoO could not be achieved.

The steps occurring during the above thermal decomposition were:

$$\begin{tikzcd} CoSeO_4 \cdot 4H_2O \arrow[r, "170\,^{\circ}C"] & CoSeO_4 \cdot 2H_2O \arrow[r, "345\,^{\circ}C"] & CoSeO_4 \arrow[d, "625\,^{\circ}C"] \\ & & Co_3O_4 + CoO \end{tikzcd}$$

Nickel selenate hexahydrate, $NiSeO_4 \cdot 6H_2O$

The thermal curves (Fig. 3) of nickel selenate hexahydrate show that the salt is stable up to 60 °C and anhydrous nickel selenate is formed in two dehydration stages. The hexahydrate loses part of its water of crystallisation up to 300 °C forming a monohydrate. The endothermic peak maximum which is associated with the loss of five water molecules appears at 130 °C. This is followed by a minor exothermic peak with a maximum at 270 °C. This may probably be due to crystallisation of the monohydrate. A similar observation is reported[4] in the case of nickel sulphate monohydrate.

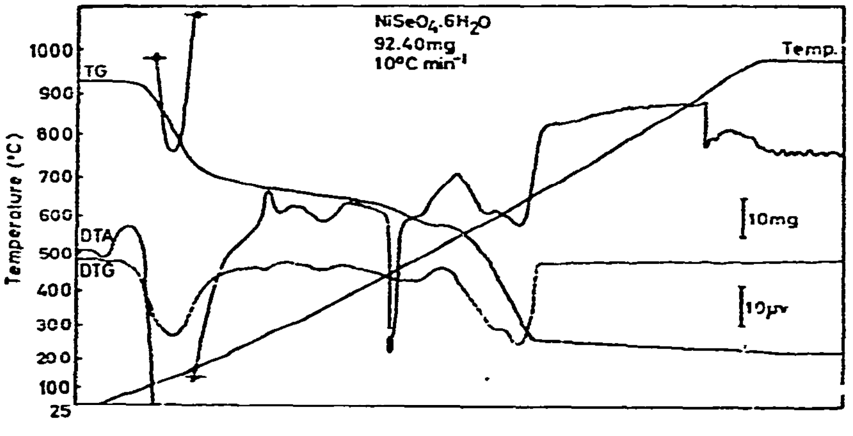

Fig. 3. Simultaneous TG–DTA–DTG of $NiSeO_4 \cdot 6H_2O$.

Directly above 300°C the monohydrate loses its stability and the remaining water molecule begins to separate. At 390°C anhydrous nickel selenate is formed. The weak broad peak existing at 350°C in the DTA curve accounts for this endothermic reaction. A short oblique horizontal of the anhydride persists up to 505°C after which reduction to nickel selenite takes place. The DTA curve shows a very sharp symmetrical endothermic peak at 450°C due to the above change. At 690°C nickel selenite is converted into nickel oxide quantitatively.

The observed mechanism of nickel selenate hexahydrate decomposition can be illustrated as follows:

$$\begin{tikzcd}
NiSeO_4 \cdot 6H_2O \arrow[r, "300\,^{\circ}C"] & NiSeO_4 \cdot H_2O \arrow[r, "390\,^{\circ}C"] & NiSeO_4 \arrow[d, "510\,^{\circ}C"] \\
& NiO & NiSeO_3 \arrow[l, "690\,^{\circ}C"']
\end{tikzcd}$$

Copper selenate pentahydrate, $CuSeO_4 \cdot 5H_2O$

The simultaneous TG–DTA–DTG curves (Fig. 4) of copper selenate pentahydrate show a number of intermediate decomposition stages. The result is stable only up to 40°C, at which the compound starts to lose four molecules of water progressively and the loss is complete at 365°C. At 140°C a loss corresponding to two and half molecules of water occurs and is associated with an endothermic peak at 115°C in the DTA curve. This lower hydrate undergoes a further weight loss of half a water molecule forming copper selenate dihydrate with an endothermic peak at 185°C. Further rise in temperature converts this dihydrate to copper selenate monohydrate at 365°C. This endothermic effect gives a DTA peak at 255°C.

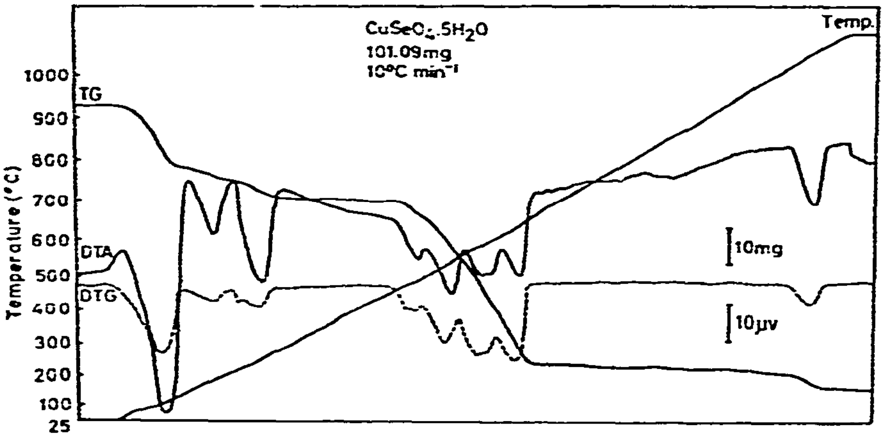

Fig. 4. Simultaneous TG–DTA–DTG of $CuSeO_4 \cdot 5H_2O$.

The moderate horizontal oblique (indicating relatively more stability) of the monohydrate exists up to 465°C. Beyond this temperature the last water molecule from the monohydrate starts to separate. The dehydration of copper selenate is completed at 500°C. The accompanying unsymmetrical peak at 485°C in the DTA curve represents this change.

Further pyrolysis of anhydrous copper selenate shows interesting complex thermal effects. The break on the slope of the TG curve at 580°C indicates the formation of basic copper selenate, $CuO \cdot CuSeO_4$. The DTA peak at 540°C accounts for the endothermic effect during the above reaction. Directly above 580°C the basic copper selenate decomposes into cupric oxide in two very unstable stages. Although these two stages are not distinctly observable on the TG curve, the corresponding DTG curve exhibits the two-stage loss. Besides the DTG peak at 630°C, the peak at 570°C shows overlapping of two peaks clarifying two very unstable intermediate stages in the first of the two stages mentioned above. Thus basic copper selenate yields cupric oxide at 690°C.

Further rise of the temperature up to 1100°C reduces the Cu(II) oxide to Cu(I) oxide. Both DTA and DTG peaks at 1050°C illustrate the endothermic reduction of the oxide.

The TG curves for copper selenate present several short horizontals and sudden breaks. The TG curve shows that there are several unstable intermediates before the formation of copper selenate monohydrate. The difficulty experienced while isolating the intermediates by isothermal dehydration is in agreement with the above observations. Furthermore, copper selenate monohydrate and the anhydride are formed at much lower temperatures during static isothermal heating.

The overall decomposition mechanism of copper selenate pentahydrate may be presented as follows:

$$\begin{tikzcd}
CuSeO_4 \cdot 5H_2O \arrow[r, "140\,^{\circ}C"] & CuSeO_4 \cdot 2.5H_2O \arrow[r, "210\,^{\circ}C"] & CuSeO_4 \cdot 2H_2O \arrow[d, "365\,^{\circ}C"] \\
CuO \cdot CuSeO_4 \arrow[d, "690\,^{\circ}C"'] & CuSeO_4 \arrow[l, "580\,^{\circ}C"'] & CuSeO_4 \cdot H_2O \arrow[l, "500\,^{\circ}C"'] \\
CuO \arrow[r, "1100\,^{\circ}C"] & Cu_2O &
\end{tikzcd}$$

Zinc selenate trihydrate, $ZnSeO_4 \cdot 3H_2O$

The thermoanalytical curves (Fig. 5) of zinc selenate trihydrate show progressive loss in weight immediately as soon as the temperature is above room temperature. The salt reaches a quite stable stage at 305°C after two subsequent unstable intermediate hydrates. The weight loss up to 305°C agrees well with that required for the removal of half the number of water molecules from the trihydrate. Three endothermic peaks in the DTA curve with maxima at 140, 200 and 280°C indicate the respective endothermal effects which occur during the dehydration.

Zinc selenate sesquihydrate which is stable over a long range of temperatures (as indicated by the horizontal in the TG curve running from 305 to 525°C), starts losing weight gradually beyond 525°C and becomes anhydrous at 615°C. The dehydration is associated with three distinct endothermic peaks at 535, 580 and 585°C in

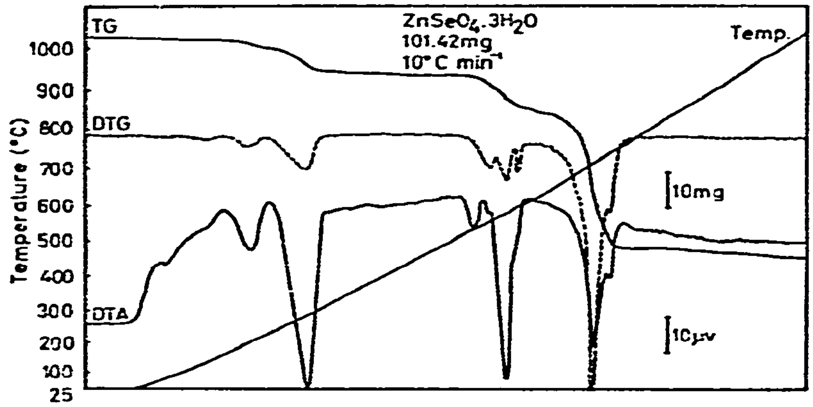

Fig. 5. Simultaneous TG–DTA–DTG of $ZnSeO_4 \cdot 3H_2O$.

a triplet form, which could be due to two subsequent unstable intermediates formed during the dehydration. The existence of a triplet in DTG curve also confirms this.

Anhydrous zinc selenate shows immediate weight loss, just above 615°C, and it gradually begins to decompose. The anhydride undergoes a reduction and finally decomposes to zinc oxide at 760°C. A very sharp endothermic peak with a maximum at 720°C is attributable to the above dissociation reaction.

The following mechanism can thus be proposed for the decomposition of zinc selenate trihydrate:

$$\begin{tikzcd} ZnSeO_4 \cdot 3H_2O \arrow[r, "305^\circ C"] & ZnSeO_4 \cdot 2.5H_2O \arrow[d, "615^\circ C"] \\ ZnO & ZnSeO_4 \arrow[l, "760^\circ C"'] \end{tikzcd}$$

Cadmium selenate monohydrate, $CdSeO_4 \cdot H_2O$

The simplest thermal curves (Fig. 6) are found for cadmium selenate monohydrate with loss of water of crystallisation in one step. The compound loses its stability just above 70°C and is dehydrated completely at 195°C. The simultaneously obtained DTA curve accounts for the endothermic activity at 165°C during this dehydration.

The horizontal of cadmium selenate persists up to 550°C and exhibits thermal stability of the anhydrous salt over a long range of temperatures. Above 550°C the anhydride starts decomposing and is reduced to cadmium selenite at 675°C. The peak in the DTA curve associated with this reduction gives a maximum at 620°C. The selenite appears to be very susceptible to temperature as it starts decomposing little above 675°C. Further heating brings about the sublimation of selenium dioxide and leads to the formation of cadmium oxide. This decomposition involves an endothermic effect marked by peaks with maxima at 870 and 890°C in the DTA curve. The part of the TG curve at higher temperatures exhibits a gradual weight loss indicating the sublimation of cadmium oxide without decomposition.

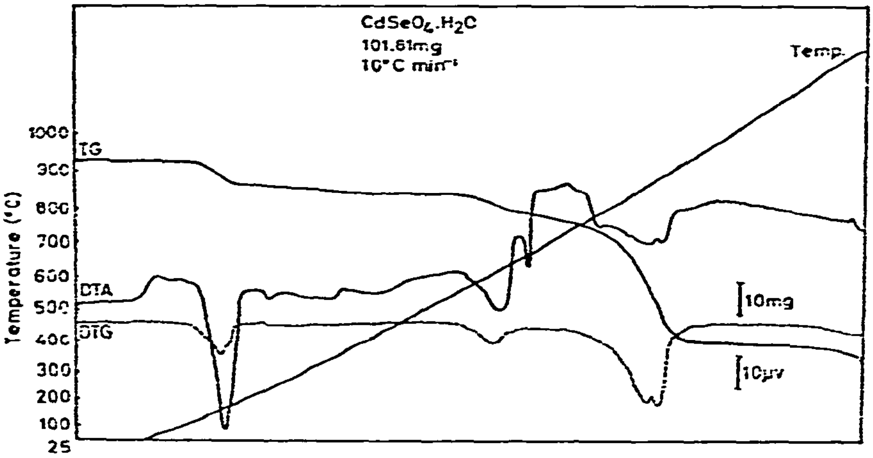

Fig. 6. Simultaneous TG–DTA–DTG of $CdSeO_4 \cdot H_2O$.

The decomposition of cadmium selenate monohydrate may be illustrated according to:

$$CdSeO_4 \cdot H_2O \xrightarrow{195\,^{\circ}C} CdSeO_4 \xrightarrow{675\,^{\circ}C} CdSeO_3 \xrightarrow{945\,^{\circ}C} CdO$$

CONCLUDING REMARKS

Decomposition of the divalent metal selenates confirmed that oxides are produced in all the cases described. When comparing the TG curves no definite trend of dehydration is observed. However, although the decomposition of the anhydride to metal oxides appears to be a one-stage process, the DTG curves indicate that it certainly involves two subsequent stages, namely reduction to selenite followed by immediate conversion to metal oxide. The inflection points at these stages could have

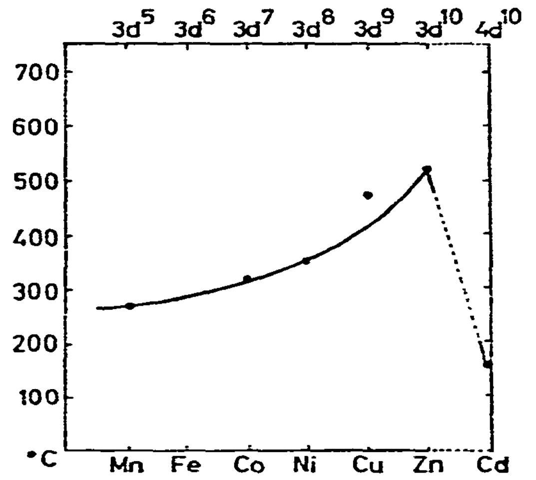

Fig. 7. The dehydration temperatures of the divalent metal selenates.

possibly been resolved into plateaus on the TG curves with a heating rate slower than that employed in the present case.

The DTA data also prove the exceptional thermal stability of the polyhydrates accompanied by a comparatively high dehydration energy. It is well known that the hydration energies of transitional elements increase with the number of 3d electrons. The temperature of the final dehydration to non-hydrates follows the same trend (Fig. 7). Starting from Mn^{2+} there is a continual rise in the dehydration temperature until Zn^{2+}. Furthermore, there is a sudden drop in this temperature on going from Zn^{2+} to Cd^{2+}. Similar results were obtained by Ben-Dor and Margalith[4] for the dehydration of the transitional metal sulphates monohydrates.

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