Table I. Thermogravimetric Analysis of Disodium Hydrogen Phosphate 12-Hydrate

Assumed Product	Composition, Based on $Na_2HPO_4.12H_2O$, % Theoret.	Obsd.	Diff.
Na_2HPO_4	39.64	39.5	−0.1
		39.5	−0.1
$Na_4P_2O_7$	37.13	37.3	+0.2
		37.2	+0.1

circuits. If the sample changes weight, the appropriate photocell will be activated by the beam of light and thus rotate the recording drum back to the null position. With proper adjustment of the photocell sensitivity potentiometers, a smooth curve is recorded.

DISCUSSION

The thermal decomposition curve of disodium hydrogen phosphate 12-hydrate ($Na_2HPO_4.12H_2O$) is given in Figure 4. Water of hydration began to come off at a little above room temperature with a break in the curve corresponding to the 7-hydrate at 105° C. The anhydrous salt, disodium hydrogen phosphate (Na_2HPO_4), was obtained from 185° to 325° C., which then decomposed to give the sodium pyrophosphate ($Na_4P_2O_7$) level, beginning at 375° C. The decomposition temperatures agreed qualitatively with those reported previously (*6*). However, as no weight data have previously been given and no heating rate specified, it is difficult to make a rigorous comparison.

The reproducibility of the thermobalance is given by the data in Table I. The sensitivity (the minimum weight change that can be detected) is about 0.05 mg. with a response time of 2.4 seconds per mg. The maximum weight change that can be recorded is 102 mg.

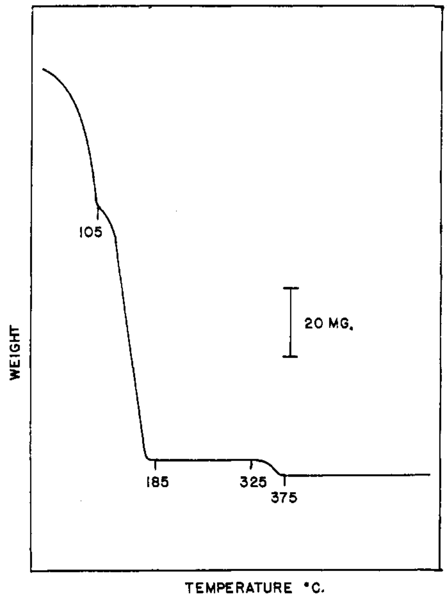

Figure 4. Thermal decomposition curve of sodium dibasic phosphate dodecahydrate

The apparent accuracy for a 100-mg. sample is approximately 0.50%. The reproducibility over the same weight range is approximately 0.2 mg. or 0.20%. The reproducibility of the decomposition temperatures, for duplicate sample weights, is about 1%.

The advantage of this instrument over several of the commercially available models is the low cost of construction. The complete thermobalance, excluding labor, cost about $400. The accuracy and reproducibility of the instrument agreed favorably with the more expensive models.

ACKNOWLEDGMENT

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Thermal Decomposition of Scandium, Yttrium, and Rare Earth Metal Oxalates

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▶ The thermal decomposition of the oxalates of scandium, yttrium, lanthanum, cerium(III), praseodymium, neodymium, samarium, europium, gadolinium, holmium, and erbium was studied on the thermobalance. The hydrate water began to come off in the temperature range of 40° to 60° C. In certain cases, intermediate weight levels were found for the 6- and 2-hydrates. The anhydrous oxalates appear to be very unstable; no weight levels were found with this composition. The oxide levels were obtained in the temperature range of 360° to 800° C.

The rare earth metal ions readily form slightly soluble oxalates in acid solution. Because of the selectivity and insoluble nature of the metal oxalates formed, this procedure has proved useful for separation as well as for gravimetric estimation of these elements. The oxalates, however, cannot be weighed directly as precipitated because of the varying amount of hydrate water present (*6*). This hydrate water was found to be dependent on the temperature of precipitation. For dysprosium, if the precipitation is carried out at 100° C., the 6-hydrate is formed; at 15° C., the 11-hydrate is formed (*4*). Other heavier rare earth metal ions behaved similarly. Consequently, the rare earth metal oxalates must be ignited and weighed as a basic carbonate (*1*) or oxide.

The thermal decomposition of a number of rare earth metal oxalates has been investigated (*3*), but no composition data were given. Hence the hydrated oxalates of scandium, yttrium, lanthanum, cerium(III), praseodymium, neodymium, samarium, europium, gadolinium, holmium, and erbium were prepared and subjected to thermal decomposition on the thermobalance.

EXPERIMENTAL

Reagents. The yttrium and rare earth metal compounds of 99.9% purity were obtained as the chlorides or oxides from Research Chemicals, Inc., Burbank, Calif., Lindsay Chemical Co., West Chicago, Ill., and Research Laboratories, Inc., Division of St. Eloi Corp., Newtown, Ohio. Scandium oxide of 99.8% purity was obtained from A. D. Mackay, Inc., New York, N. Y. The listed purities are those given by the supplier.

Methyl oxalate (melting point 53° C.) was prepared as described (*2*).

All other chemicals used were of C.P. quality.

Thermobalance. The thermobalance has been described (*7*). A heating rate of 5.4° C. per minute was employed.

Preparation of Oxalates. About 0.3 grams of the metal nitrate or chloride hydrate was dissolved in 200 ml. of water. To this solution were added 2 ml. of 6*N* nitric acid and the methyl oxalate solution (3 grams of methyl oxalate in 40 ml. of water). Although methyl oxalate was used as a source of oxalate ion, there is no reason why a solution of oxalic acid could not be used as well. After stirring, the solution was placed on a boiling water bath for 3 hours. During this time, the metal oxalate gradually precipitated out of solution. The solution was then removed from the water bath and allowed to stand overnight at room temperature. The resulting precipitate was collected on a sintered porcelain crucible, washed four times with 10-ml. portions of water, twice with 10-ml. portions of 95% ethyl alcohol, and then once with 10 ml. of ether. After drying in air for 24 hours at room temperature, the metal oxalate was pyrolyzed on the thermobalance.

DISCUSSION

The thermal decomposition curves of the metal oxalates are given in Figures 1 to 3. The composition data are given in Table I.

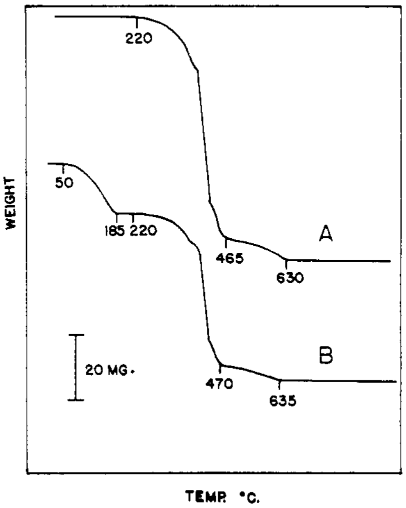

Figure 1. Thermal decomposition curves of scandium oxalate

A. Scandium oxalate 2-hydrate
B. Scandium oxalate 6-hydrate

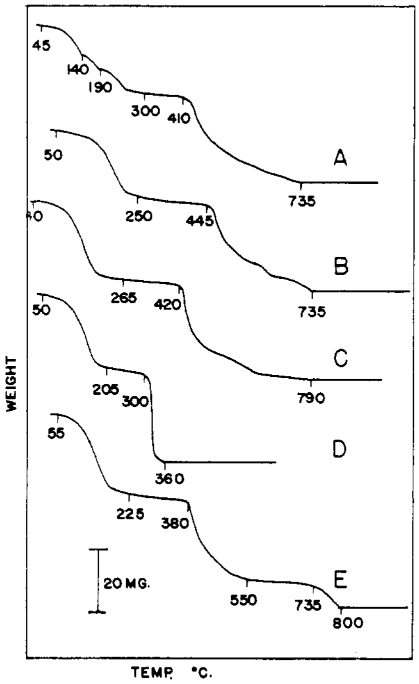

Figure 2. Thermal decomposition curves of rare earth metal oxalates

A. Samarium oxalate 10-hydrate
B. Neodymium oxalate 10-hydrate
C. Praseodymium oxalate 10-hydrate
D. Cerium oxalate 10-hydrate
E. Lanthanum oxalate 10-hydrate

Thermal Decomposition Curves. **SCANDIUM OXALATE.** The thermal decomposition curves of scandium oxalate are given in Figure 1: one for the 6-hydrate and the other for the 2-hydrate.

The composition of the oxalate as precipitated from solution, in agreement with Riley (*5*), corresponded to the formula $Sc_2(C_2O_4)_3 \cdot 6H_2O$. This compound began to lose water of hydration at 50° C. From 185° to 220° C. a horizontal weight level was found which corresponded to the 2-hydrate, $Sc_2(C_2O_4)_3 \cdot 2H_2O$. Beyond 220° C. additional water of hydration was evolved as well as carbon monoxide and carbon dioxide, to give the Sc_2O_3 level at 635° C. A level corresponding to anhydrous scandium oxalate was not found. The thermal decomposition curve of the 2-hydrate revealed that decomposition began above 220° C. The Sc_2O_3 level began at 630° C.

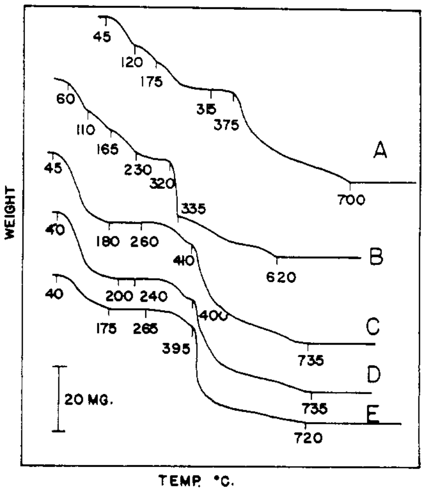

Figure 3. Thermal decomposition curves of yttrium and rare earth metal oxalates

A. Gadolinium oxalate 10-hydrate
B. Europium oxalate 10-hydrate
C. Yttrium oxalate 9-hydrate
D. Holmium oxalate 10-hydrate
E. Erbium oxalate 6-hydrate

These results are in disagreement with those of Duval (*3*), who stated that the initial oxalate corresponded to the 10-hydrate. At 227° C. he noted a 5-hydrate, which subsequently decomposed to give the Sc_2O_3 level at 608° C. However, it appears doubtful that the 5-hydrate would be so thermally stable. Furthermore, a level corresponding to the anhydrous metal oxalate was not found in his investigation.

YTTRIUM OXALATE (Figure 3). The compound as precipitated corresponded to the formula, $Y_2(C_2O_4)_3 \cdot 9H_2O$. Hydrate water began to come off at 45° C., resulting in a horizontal weight level from 180° to 260° C., which corresponded to the 2-hydrate, $Y_2(C_2O_4)_3 \cdot 2H_2O$. The 2-hydrate began to decompose at 260° C., giving a break in the curve at 410° C. The composition of the compound at 410° C. corresponded closely to the anhydrous oxalate, $Y_2(C_2O_4)_3$. Beyond this temperature the compound decomposed rapidly to give the Y_2O_3 level at 735° C.

LANTHANUM OXALATE (Figure 2). The compound as precipitated corresponded to the formula, $La_2(C_2O_4)_3 \cdot 10H_2O$. Water of hydration began to come off at 55° C. No intermediate hydrates were detected in the curve; instead, the composition approached the anhydrous oxalate, $La_2(C_2O_4)_3$, at 380° C. Decomposition was rapid beyond 380° C., giving a nearly horizontal weight level from 550° to 735° C. The composition of this weight level corresponded approximately to the

$La_2O_3 \cdot CO_2$ found by Backer and Klaassens (*1*). Beyond 735° C. further decomposition occurred to give the La_2O_3 level at 800° C.

Cerium Oxalate (Figure 2). The compound as precipitated corresponded to the formula, $Ce_2(C_2O_4)_3 \cdot 10H_2O$. Water of hydration began to come off at 50° C., a break in the curve appearing at 205° C. The decomposition became rapid above 300° C., to give the CeO_2 level at 360° C. As expected, the oxide level temperature found was the lowest for any of the rare earth metal oxalates.

Praseodymium Oxalate (Figure 2). The compound as precipitated corresponded to the formula, $Pr_2(C_2O_4)_3 \cdot 10H_2O$. Water of hydration began to come off at 40° C., with the composition of the resulting mixture gradually approaching the anhydrous oxalate, $Pr_2(C_2O_4)_3$, at 420° C. Beyond 420° C. the decomposition was rapid, resulting in the Pr_6O_{11} level at 790° C.

Neodymium Oxalate (Figure 2). The precipitated compound corresponded to the formula, $Nd_2(C_2O_4)_3 \cdot 10H_2O$. The decomposition curve was similar to that of praseodymium. Water of hydration began to come off at 50° C., resulting in a break in the curve at 250° C. The weight loss was slower beyond 250° C., the composition approaching that of the anhydrous oxalate, $Nd_2(C_2O_4)_3$, at 445° C. Beyond this temperature the weight loss was rapid, giving the Nd_2O_3 level at 735° C.

Samarium Oxalate (Figure 2). The composition of the precipitated compound corresponded to the formula, $Sm_2(C_2O_4)_3 \cdot 10H_2O$. The water of hydration began to come off at 45° C. Several breaks in the curve, which were not present in the decomposition curves of the metal oxalates of lower atomic number, indicated that lower hydrates of varying stability were present during the decomposition. After the two breaks at 140° and 190° C., a nearly horizontal weight level was found from 300° to 410° C., which corresponded to the anhydrous oxalate, $Sm_2(C_2O_4)_3$. Beyond 410° C. the decomposition was more rapid, resulting in the Sm_2O_3 level at 735° C.

Europium Oxalate (Figure 3). The precipitated compound corresponded to the formula, $Eu_2(C_2O_4)_3 \cdot 10H_2O$. Hydrate water began to come off at 60° C., giving two breaks in the curve: one at 110° C. and the other at 165° C. Beyond 230° C. the rate of decomposition became slower, approaching the anhydrous oxalate, $Eu_2(C_2O_4)_3$, at 320 °C. The decomposition became very rapid beyond 320° C., resulting in the Eu_2O_3 level at 620° C.

Gadolinium Oxalate (Figure 3). The precipitated compound corresponded to the formula, $Gd_2(C_2O_4)_3 \cdot 10H_2O$. The decomposition curve was very similar to that of europium. The first weight loss occurred at 45° C., giving two intermediate breaks, one at 120° C. and the other at 175° C. The composition of the compound at 120° C. corresponded approximately to the 6-hydrate, $Gd_2(C_2O_4)_3 \cdot 6H_2O$. The anhydrous oxalate, $Gd_2(C_2O_4)_3$, was found at 315° C. but began to decompose rapidly beyond 375° C. The Gd_2O_3 level began at 700° C.

Holmium Oxalate (Figure 3). The precipitated compound corresponded to the formula, $Ho_2(C_2O_4)_3 \cdot 10H_2O$. Water of hydration began to come off at 40° C., resulting in a horizontal weight level from 200° to 240° C. This level corresponded to the 2-hydrate, $Ho_2(C_2O_4)_3 \cdot 2H_2O$. Beyond 240° C. the 2-hydrate began to lose water, approaching the composition of the anhydrous oxalate, $Ho_2(C_2O_4)_3$, at 400° C. The anhydrous oxalate decomposed rapidly above this temperature to give the Ho_2O_3 level at 735° C.

Erbium Oxalate (Figure 3). The precipitated compound, in contrast with the other rare earth oxalates, corresponded to the formula, $Er_2(C_2O_4)_3 \cdot 6H_2O$. Water of hydration began to come off at 40° C. to give a horizontal weight level from 175° to 265° C., which corresponded to the 2-hydrate, $Er_2(C_2O_4)_3 \cdot 2H_2O$. Above 265° C. additional water of hydration began to come off, approaching the anhydrous oxalate, $Er_2(C_2O_4)_3$, at 395° C. The anhydrous oxalate began to decompose rapidly above this temperature to give the Er_2O_3 level at 720° C.

GENERAL OBSERVATIONS

The thermal decomposition curves of the rare earth metal oxalates studied in this investigation can be roughly classified in three groups. The first includes

Table I. Composition Data for Metal Oxalates

(% metal oxide)

Rare Earth Metal	$M_2(C_2O_4)_3.10H_2O$		$M_2(C_2O_4)_3.xH_2O$			$M_2(C_2O_4)_3$			$La_2O_3.CO_2$	
	Found	Theor.	Found	Theor.	Temp., ° C.	Found	Theor.	Temp., ° C.	Found	Theor.
Lanthanum	45.4 45.6	45.13	...	...	...	59.9 60.5	60.13	380	86.4 86.4	88.18
Cerium	47.8 47.6	47.52	...	...	...	...	...	...		
Praseodymium	46.9 46.3	46.99	...	...	...	61.1 61.5	62.38	420		
Neodymium	46.7 46.7	45.93	...	...	...	61.3 61.4	60.91	445		
Samarium	47.5 47.4	46.83	...	...	...	62.6 62.4	61.76	410		
Europium	47.7 47.5	47.04	...	...	...	62.7 62.4	61.95	320		
Gadolinium	48.4 48.4	47.73	53.6 53.5	52.75 ($6H_2O$)	120	62.3 62.9	62.61	315		
Holmium	49.4 49.7	48.81	60.9 61.3	60.00 ($2H_2O$)	200	65.7 65.6	63.62	400		
Erbium	...	...	54.1 54.5	54.12 ($6H_2O$)		63.7 63.7	63.90	395		
			60.7 61.6	60.27 ($2H_2O$)	175					
Yttrium	...	...	37.2 37.2	37.39 ($9H_2O$)		52.8 52.4	51.10	410		
			48.2 47.9	47.25 ($2H_2O$)	180					
Scandium	...	...	30.5 30.6	29.89 ($6H_2O$)						
			36.3 36.3	35.41 ($2H_2O$)						

the oxalates of lanthanum, praseodymium, and neodymium; the second consists of samarium, europium, and gadolinium; the third contains yttrium, holmium, and erbium.

In the first group, there was no evidence for the formation of intermediate hydrates. The 10-hydrates decomposed directly to the anhydrous oxalates. However, the anhydrous oxalates were very unstable and immediately decomposed to give the oxides. In only one case, lanthanum, was a basic carbonate observed. The minimum oxide level temperatures in this group were higher than in the other two groups.

In the second group, the formation of intermediate hydrates was first observed. No levels were obtained, perhaps because of the heating rate employed, but breaks in the curve were found for the 6- and the 2-hydrates. Again, the composition for the anhydrous oxalates was approached, but no horizontal weight levels were obtained. The oxide levels were obtained at slightly lower temperatures than in the first group. The oxide level temperature for europium was anomalously lower than for the other two elements in this group.

In the third group, the first stable intermediate hydrate levels were observed. The 2-hydrates appeared to be stable, giving stable levels over a temperature interval of 40° to 90°. Breaks in the curve were noted for the anhydrous oxalates, which immediately decomposed to give the oxides.

ACKNOWLEDGMENT

The author would like to thank James R. Slagle for preparing the methyl oxalate used in this investigation.

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Thermolysis of Oxine Molybdophosphate

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▶The thermal decomposition of precipitated oxine molybdophosphate was reinvestigated on the thermobalance. The air-dried precipitate was converted to the anhydrous compound in the range 60° to 85° C. The anhydrous compound was found over the range 85° to 285° C. The results confirm a previous conclusion that 140° C. is a good drying temperature.

THE detailed investigation of the precipitation of phosphorus as the oxine salt of molybdophosphoric acid has presented new information as to the composition of the precipitated compound. Brabson and Edwards (*2*) found that if the precipitate was carefully prepared, properly washed, and dried at 140° C., the composition corresponded to the formula $3C_9H_7ON \cdot H_3(PMo_{12}O_{40})$. On the basis of phosphorus content, the precipitate gave accurate and reproducible results.

Their results were in disagreement with previous work. Berg (*1*) concluded that the dried precipitate corresponded to the 2-hydrate, $3C_9H_7ON \cdot H_7[P(Mo_2O_7)_6] \cdot 2H_2O$. Duval (*3*), from his study of the thermolysis of this compound, reported that the 2-hydrate was stable from 176° to 225° C. The organic part of the molecule was eliminated starting at 300°, without evidence for the formation of the anhydrous compound.

Duval prepared the precipitate according to the instructions of Hecht and Donau (*4*), taken from the original work of Scharrer (*5*), which specify that the precipitate be washed with an ammonium nitrate solution prior to drying. Ignition of the organic compound with ammonium nitrate might be expected to cause accelerated decomposition.

As it appeared that the compound prepared by Brabson and Edwards (*2*) would exhibit different properties upon ignition, it was of interest to investigate the thermolysis of the ammonium nitrate–free compound on the thermobalance.

EXPERIMENTAL

Thermobalance. An automatic recording thermobalance was used (*6*). The sample sizes weighed between 80 and 100 mg. The heating rate was 5.4° C. per minute.

Preparation of Precipitate. The oxine molybdophosphate was prepared as previously described (*2*). Samples of the air-dried and oven-dried (140° C. for 2 hours) compounds were studied on the thermobalance.

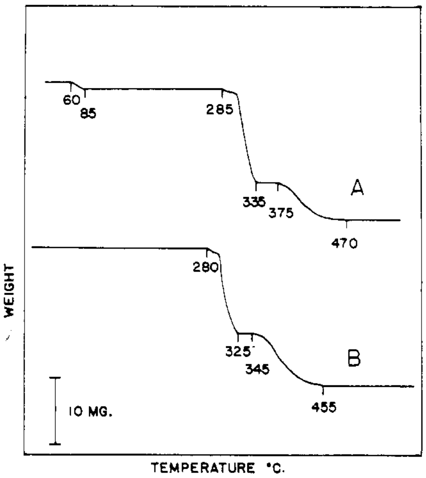

Figure 1. Thermal decomposition curves of oxine molybdophosphate

A. Air-dried
B. Oven-dried at 140° C.

DISCUSSION

The thermal decomposition curves are given in Figure 1 with the composition data in Table I.

The air-dried precipitate began to lose weight at 60° C. At 85° C., a horizontal weight level appeared which extended to 285° C. Calculations from the resulting weight data indicated that air-dried compound corresponded to the