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Studies of Rare Earth Acid Oxalates

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Date Author

Studies of Rare Earth Acid Oxalates

(TITLE)

BY

Kenneth Clinton Pyles
B.S. (1969)
Western Illinois University
Macomb, Illinois

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1970
YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

Nov. 11, 1970
DATE

ADVISER

Nov. 11, 1970
DATE

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STUDIES OF RARE EARTH
ACID OXALATES

BY

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June, 1969

Submitted in partial fulfillment
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Charleston, Illinois
November, 1970

STUDIES OF RARE EARTH
ACID OXALATES

Thesis Approved

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Dr. S. R. Steele

DEDICATION

To My Mother and Father

ACKNOWLEDGEMENT

The author expresses his sincere appreciation to Dr. Robert H. Karraker for suggesting this research study and for his guidance and assistance during my graduate program.

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STUDIES OF RARE EARTH
ACID OXALATES

BY

KENNETH CLINTON PYLES

B.S., Western Illinois University, 1969

ABSTRACT OF THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in the
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CHARLESTON, ILLINOIS
1970

The acid oxalate trihydrates of the heavy rare earth elements, $RE(HC_2O_4)(C_2O_4)\cdot 3H_2O$, have been prepared and characterised by X-ray diffraction techniques. These compounds are unique because they contain both the acid radical and the radical of the dibasic acid in the same structure. The acid oxalates of erbium, terbium, dysprosium, holmium, ytterbium, gadolinium, and yttrium are formed when the normal oxalate hydrates, $RE_2(C_2O_4)_3\cdot xH_2O$ (x = 5-10), are dissolved in concentrated hydrochloric acid and the solutions allowed to evaporate slowly in vacuo. Attempts to prepare the acid oxalate trihydrates of the light rare earths, lanthanum through europium, were unsuccessful.

X-ray powder patterns of the prepared acid oxalate trihydrates indicate that they are isomorphous. Confirmation of the lattice parameters ($a_o = 8.6664 \pm 0.0003$ Å, $c_o = 6.4209 \pm 0.0008$ Å) for the erbium compound determined by Steinfink and Brunton has been made. All of the rare earth acid oxalate trihydrates have been indexed and their lattice parameters determined. The indices of refraction of the rare earth acid oxalates have also been measured.

Thermal gravimetric analysis curves of erbium acid oxalate trihydrate indicated that loss of water began at 110° C and continued until a stable monohydrate was reached at 154° C. The monohydrate was stable in the temperature range of 154° C to 192° C, after which the loss of one mole of CO_2 converted the monohydrate to the stable compound $HEr(C_2O_4)\cdot CO_2\cdot H_2O$ at 334° C.

Chapter I.

INTRODUCTION

The rare earth oxalate hydrates, $RE_2(C_2O_4)_3 \cdot xH_2O$ (x = 5-10), have been prepared and characterised optically and by X-ray diffraction powder techniques.$^{(1-3)}$ The oxalate hydrates of some of the light rare earths, lanthanum, neodymium, and gadolinium, have been found to be isomorphous. Detailed X-ray diffraction data on the heavy rare earth oxalate hydrates is practically nonexistent. Karraker found that the X-ray powder patterns of his heavy rare earth oxalate hydrate preparations differed from the reported literature data for lanthanum oxalate decahydrate.$^{(4)}$ A chemical analysis of his compound indicated the formula $Er(HC_2O_4)(C_2O_4) \cdot 3H_2O$.

Möbius and Matthes have also reported the preparation of the acid oxalates of the heavy rare earths.$^{(5,6)}$ They found the erbium analogue to crystallise in the tetragonal system with unit cell parameters of a_o = 12.2 Å and c_o = 6.3 Å.

Brunton and Steinfink have recently published data on the crystal structure of the same compound, and report the unit cell dimensions to be a_o = 8.6664 Å and c_o = 6.4209 Å.$^{(7)}$

The objective of this research is to 1) prepare and characterise the rare earth acid oxalates by their X-ray diffraction powder patterns and compare these with the powder patterns of the normal rare earth oxalates, 2) determine which of the reported unit cell parameters for the erbium analogue are correct, 3) investigate reasons for the formation of the acid oxalate of terbium, but not of gadolinium, and 4) study the thermal decomposition of the prepared rare earth acid oxalates.

A. Rare Earth Elements

The rare earth elements form the longest continuous series of chemically similar elements in the periodic table. Table 1 lists the atomic number, name, chemical symbol, and abundance in the earth's crust of the rare earth elements.(8)

Scandium, element number 21 and yttrium, element number 39, have electronic configurations very similar to those of the rare earths and are normally studied in conjunction with the rare earths.

The chemistry of the rare earth elements is primarily the chemistry of the 3+ oxidation state. However, europium and ytterbium exist in the 2+ oxidation state in solution, as does tetravalent cerium, while 2+ and 4+ oxidation states are known for some of the light rare earths in the solid state.(9)

The lanthanide ions are very strongly electropositive and have comparatively large ionic radii. Table 2 lists the ionic radii of the trivalent lanthanide ions.(10-12) The shrinkage of the ionic radii of the rare earths as the 4-f sub-shell is progressively filled is known as the "lanthanide contraction." This contraction can be attributed to the imperfect shielding from the nuclear charge of one f electron by another f electron. The high

TABLE 1. NAMES, SYMBOLS, AND ABUNDANCES OF THE RARE EARTH ELEMENTS

Atomic No.	Name	Symbol	Abundance (p.p.m.)
57	Lanthanum	La	30
58	Cerium	Ce	60
59	Praseodymium	Pr	8.2
60	Neodymium	Nd	28
61	Promethium	Pm	Synthetic
62	Samarium	Sm	6
63	Europium	Eu	1.2
64	Gadolinium	Gd	5.4
65	Terbium	Tb	0.9
66	Dysprosium	Dy	3
67	Holmium	Ho	1.2
68	Erbium	Er	2.8
69	Thulium	Tm	0.5
70	Ytterbium	Yb	3.4
71	Lutetium	Lu	0.5
39	Yttrium	Y	33
21	Scandium	Sc	22

TABLE 2. IONIC RADII OF TRIVALENT LANTHANIDE, YTTRIUM, AND SCANDIUM IONS

Ion	Ionic Radii (Å)
Lanthanum	1.061
Cerium	1.034
Praseodymium	1.013
Neodymium	0.995
Promethium	0.979
Samarium	0.964
Europium	0.950
Gadolinium	0.938
Terbium	0.923
Dysprosium	0.908
Holmium	0.894
Erbium	0.881
Yttrium	0.88
Thulium	0.869
Ytterbium	0.858
Lutetium	0.848
Scandium	0.68

polarising power (strong positive fields) of the rare earth ions is also due to this poor screening of the nuclear charge by f electrons.

B. Rare Earth Oxalates

1. Preparation

Historically, the precipitation of the rare earths as oxalates upon the addition of oxalic acid to a solution containing rare earth salts and free mineral acid has made possible the separation of the rare earths from the common metals. Mosander first used oxalic acid to precipitate yttrium from solution in 1843.(13)

In addition to oxalic acid, ammonium oxalate or methyl oxalate, $(CO_2CH_3)_2$, may be used to precipitate the rare earths.

Wendlandt, in preparing the rare earth oxalates, used as the starting material the rare earth nitrate or chloride hydrate.(14) About 0.3 grams of the starting material was dissolved in 200 ml of water, and to this solution was added 2 ml of 6 N nitric acid and a stoichiometric quantity of methyl oxalate solution (3 grams of methyl oxalate in 40 ml of water). After stirring, the solution was placed on a boiling water bath for three hours. After this time, the rare earth oxalate gradually precipitated out of solution. The solution was removed from the water bath and allowed to stand overnight at room temperature. The precipitate was collected on a sintered porcelain crucible, washed four times with 10-ml portions of water, twice with 10-ml portions of 95% ethanol and once with 10 ml of ether. The rare earth oxalate was dried in air for 24 hours at room temperature.

One of the difficulties in preparing pure samples of the rare earth oxalates has been the coprecipitation of soluble oxalates by the rare earths in separation procedures.(15-17) When a rare earth oxalate is precipitated from an acidic solution containing alkali metal ions, the rare earth oxalate is always contaminated with small quantities of alkali oxalates.

Wirth has suggested that the precipitation of the trivalent rare earths with oxalic acid is best carried out in a 5.5 N sulfuric acid solution.(18) If stronger concentrations of acid are used, sulfates may form.

Wenger and Christin prefer precipitating the rare earth oxalates at 55° C in the presence of a small quantity of sulfuric acid and about a 3% excess of oxalic acid.(19)

Brodhead and Heady recommend the following procedures for precipitating the rare earth oxalates: (a) maintain the rare earth metal concentration above 0.01M, (b) stir the mixture for several minutes after precipitation, (c) use an adequate (2-5 fold) excess of oxalic acid, (d) precipitate at room or below room temperatures and digest for at least one hour, (e) avoid an excess of acid, (f) maintain the pH of the solution above 2.0, and (g) avoid an excess of complexing agents such as ethylenediamine tetraacetic acid.(20)

Recently, Ropp and Graff have obtained a patent for increasing the yield of a rare earth oxalate by the addition of ethanol.(21) According to their data, the rare earth oxalate yield is increased by 10% and the amount of oxalic acid required is reduced by 14%.

2. Properties

All of the rare earth oxalates are white powders with the exceptions of cerium (light yellow), praseodymium (light green), neodymium (light blue), holmium (tan), and erbium (pink).

Most of the literature concerning the properties of the rare earth oxalates is restricted to solubility and thermal decomposition studies.(22-26)

Hauser and Wirth have determined the solubility of lanthanum, cerium, and samarium oxalates in sulfuric and oxalic acids, while Korenman has studied the solubility of lanthanum, cerium, and praseodymium oxalates in hydrochloric acid.(27,28)

Korenman noticed that the oxalates of the rare earths were considerably more soluble in sulfuric acid than in hydrochloric acid. This observation can be explained by the fact that in the case of sulfuric acid, the process of solution is accompanied by the formation of complex sulfates. Complex sulfates of the rare earths of composition $Na_3RE(SO_4)_3$ and $NaRE(SO_4)_2$ have been described.(29,30)

3. X-Ray Powder Diffraction Patterns

Jenkins and co-workers have published X-ray powder data and values of the unit cell parameters for the oxalate decahydrates of lanthanum, neodymium, and gadolinium.(2,31) The crystal system of these compounds was found to be monoclinic and all of the compounds examined were isomorphous. Table 3 lists the crystal system and unit cell parameters for these compounds.(2)

Gilpin and McCrone have also determined from a single crystal study the unit cell parameters for lanthanum oxalate decahydrate. Their values are in close agreement with those of Jenkins. Table 4 gives the observed d values of lanthanum oxalate decahydrate as observed by Gilpin and McCrone.

Weigel and associates have indexed and shown the isomorphism of the oxalate hydrates of neodymium, promethium, and samarium.(32) Table 5 lists the X-ray powder data for these compounds.

Barrett and co-workers studied the X-ray diffraction patterns of all the rare earth oxalates and observed four different powder patterns.(3) The lanthanum oxalate decahydrate type of structure was found for the oxalates of yttrium and of the elements lanthanum through terbium. X-ray powder data for cerium oxalate decahydrate, a member of this group, is given in Table 6. Dysprosium oxalate decahydrate gave a powder pattern which appeared to be unique, in that it did not resemble the patterns of any of the other rare earth oxalate hydrates. The X-ray powder data for dysprosium oxalate decahydrate is given in Table 7. The oxalate

TABLE 3. CRYSTAL SYSTEM AND UNIT CELL PARAMETERS FOR LIGHT RARE EARTH OXALATE DECAHYDRATES

Compound	Crystal System	Unit Cell Parameters			
		a(Å)	b(Å)	c(Å)	β (degrees)
$La_2(C_2O_4)_3 \cdot 10H_2O$	Monoclinic	11.830 ± 0.004	9.658 ± 0.006	10.492 ± 0.003	119.14 ± 0.01
$Nd_2(C_2O_4)_3 \cdot 10H_2O$	Monoclinic	11.662 ± 0.003	9.669 ± 0.002	10.227 ± 0.003	118.62 ± 0.01
$Gd_2(C_2O_4)_3 \cdot 10H_2O$	Monoclinic	11.516 ± 0.003	9.640 ± 0.001	10.097 ± 0.003	118.81 ± 0.01

TABLE 4. X-RAY POWDER DATA FOR LANTHANUM OXALATE DECAHYDRATE

d	Intensity
10.55	0.5
6.76	1.0
5.28	0.5
5.07	0.5
4.86	0.7
4.57	0.1
4.32	0.1
3.79	0.2
3.58	0.3
3.05	0.5
2.96	Very weak
2.91	Very weak
2.83	0.2
2.78	0.1
2.70	Very weak
2.63	0.1
2.39	Very weak
2.33	Very weak
2.29	Very weak
2.26	Very weak
2.21	Very weak

TABLE 4. (CONTINUED)

d	Intensity
2.11	Very weak
2.08	Very weak
2.03	Very weak
1.99	Very weak
1.58	Very weak
1.54	0.1

TABLE 5. X-RAY POWDER DATA FOR NEODYMIUM, PROMETHIUM, AND SAMARIUM OXALATE DECAHYDRATES

	$Nd_2(C_2O_4)_3\cdot 10H_2O$		$Pm_2(C_2O_4)_3\cdot 10H_2O$		$Sm_2(C_2O_4)_3\cdot 10H_2O$	
hkl	d	I	d	I	d	I
$\bar{1}11$ 011	6.52	10	6.70	9	6.76	10
$\bar{1}02$ 200	5.17	6	5.05	6	5.08	8
$\bar{2}11$	4.96	8	4.87	7	4.96	9
020 111	4.77	9	4.84	10	4.82	10
120 $\bar{1}21$	4.30	5	——	—	4.29	8
021	4.20	5	——	—	——	—
012	——	—	——	—	4.04	7
$\bar{3}02$	3.65	2	3.73	5	3.72	5
102 $\bar{1}22$ 220	3.48	7	3.53	6	3.54	9
300 $\bar{2}22$ 112	3.35	2	3.37	4	3.39	5

TABLE 5. (CONTINUED)

	$Nd_2(C_2O_4)_3 \cdot 10H_2O$		$Pm_2(C_2O_4)_3 \cdot 10H_2O$		$Sm_2(C_2O_4)_3 \cdot 10H_2O$	
hkl	d	I	d	I	d	I
022 $\bar{2}13$ 030	3.27	2	3.21	2	3.19	1
130	3.06	6	3.09	2	3.09	3
$\bar{3}13$	2.98	3	2.97	3	2.96	3
$\bar{4}02$	2.91	3	2.88	2	2.87	6
013	2.87	3	—	—	—	—
$\bar{4}01$	2.84	3	—	—	—	—
$\bar{2}31$	—	—	2.79	2	—	—
$\bar{2}23$ 202	2.78	3	—	—	—	—
$\bar{1}23$	2.74	3	—	—	—	—
230 $\bar{4}11$	—	—	—	—	2.71	5
$\bar{4}03$	2.69	2	2.68	2	—	—
$\bar{2}32$	—	—	—	—	2.64	8

TABLE 5. (CONTINUED)

	$Nd_2(C_2O_4)_3 \cdot 10H_2O$		$Pm_2(C_2O_4)_3 \cdot 10H_2O$		$Sm_2(C_2O_4)_3 \cdot 10H_2O$	
hkl	d	I	d	I	d	I
$\bar{3}23$ 032	2.61	6	2.61	5	—	—
023	2.54	1	—	—	2.55	2
$\bar{3}04$	—	—	2.50	1	—	—
$\bar{4}22$ $\bar{1}04$	2.47	1	—	—	—	—
040	—	—	2.41	4	—	—
140 $\bar{4}23$ 233 $\bar{4}04$ $\bar{1}41$	—	—	2.33	5	2.33	7
$\bar{4}14$	2.27	10	2.27	3	2.24	9
$\bar{5}01$	2.23	8	2.23	3	—	—
$\bar{1}42$ 240	2.16	8	—	—	2.17	3

TABLE 6. X-RAY POWDER DATA FOR CERIUM OXALATE DECAHYDRATE

d	Intensity
10.27	m
7.01	w
6.66	s
5.19	mw
4.99	m
4.82	ms
4.35	w
4.24	w
3.73	w
3.53	mw
3.42	w
3.05	mw
2.99	mw
2.80	mw
2.74	w
2.67	w
2.62	mw
2.33	mw

TABLE 6. (CONTINUED)

d	Intensity
2.28	mw
2.25	mw

s = high intensity

ms = moderate to high intensity

m = moderate intensity

mw = moderate to low intensity

w = low intensity

TABLE 7. X-RAY POWDER DATA FOR DYSPROSIUM OXALATE DECAHYDRATE

d	Intensity
5.84	mw
5.23	ms
4.86	m
4.67	mw
4.15	w
3.49	w
3.37	w
3.11	mw
2.87	mw
2.80	mw
2.61	mw
2.56	mw
2.17	mw
2.10	mw
2.05	w
1.91	w
1.88	w

m = moderate intensity
ms = moderate to high intensity
mw = moderate to low intensity
w = low intensity

hydrates of ytterbium and thulium gave very similar powder patterns. Table 8 gives the X-ray powder data for ytterbium oxalate pentahydrate. Erbium and lutetium oxalate hydrates yielded almost identical patterns. X-ray powder data for lutetium oxalate hexahydrate is given in Table 9.

4. Thermal Decomposition Data

Thermal decomposition studies on the rare earth oxalate hydrates by the techniques of thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) are abundant, but inconsistent.(33-36)

Wendlandt has studied by TGA methods the thermal decomposition of all the rare earth oxalate hydrates, and found that loss of water began to occur in the range of 40° to 60° C.(14,37) After various stages of intermediate hydrate formation and decomposition, the metal oxide levels were obtained in the 620° to 800° C range.

Analysis of the TGA curves indicate that the rare earth oxalate hydrates can be divided into three distinct groups.

The oxalate hydrates of lanthanum, praseodymium, and neodymium constitute group I. The TGA curves for this group are given in Figure 1. The significant feature of this group is the absence of evidence for the formation of any intermediate hydrates. The oxalate decahydrates decompose directly to the anhydrous oxalates. The anhydrous oxalates, being very unstable, then decompose

TABLE 8. X-RAY POWDER DATA FOR YTTERBIUM OXALATE PENTAHYDRATE

d	Intensity
9.25	mw
8.68	w
6.00	s
5.73	w
5.43	m
5.01	mw
4.77	ms
4.56	w(d)
4.17	mw(d)
3.87	mw(d)
3.48	vw
3.08	m
2.98	w
2.89	ms

s = high intensity
ms = moderate to high intensity
m = moderate intensity
mw = moderate to low intensity
w = low intensity
vw = very low intensity
(d) = diffuse

TABLE 9. X-RAY POWDER DATA FOR LUTETIUM OXALATE HEXAHYDRATE

d	Intensity
9.13	w
7.19	m
5.89	ms
5.72	vs
4.77	s
4.61	m
4.38	mw
4.11	w
3.59	m
3.53	m
3.46	m
3.18	w
3.08	m
2.97	mw
2.86	ms
2.81	w
2.77	mw
2.60	w

TABLE 9. (CONTINUED)

d	Intensity
2.37	w
2.30	w

vs = very high intensity

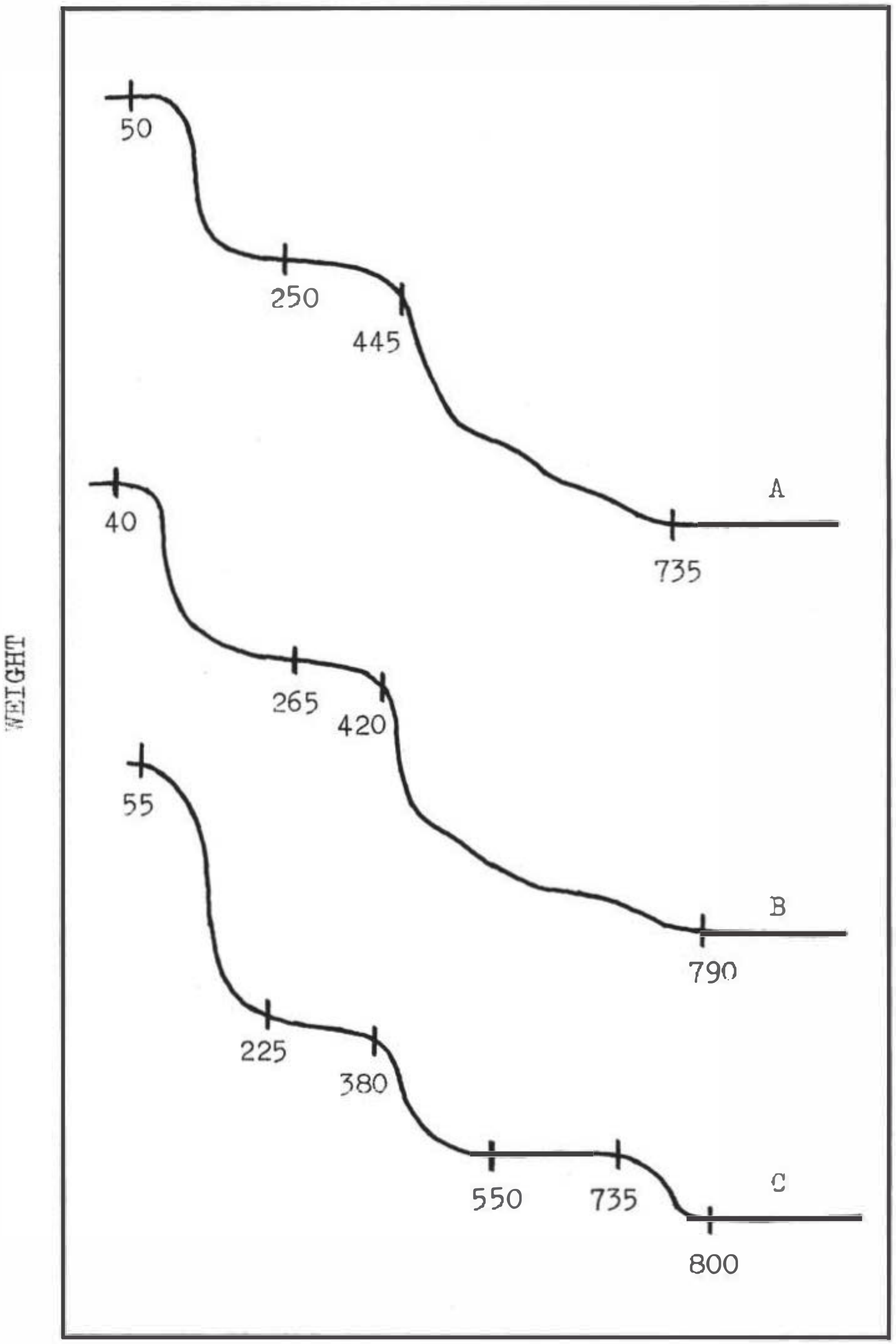
s = high intensity

ms = moderate to high intensity

m = moderate intensity

mw = moderate to low intensity

w = low intensity



TEMP. °C.

Figure 1.

Thermal decomposition curves of rare earth metal oxalates

A. Neodymium oxalate decahydrate

B. Praseodymium oxalate decahydrate

C. Lanthanum oxalate decahydrate

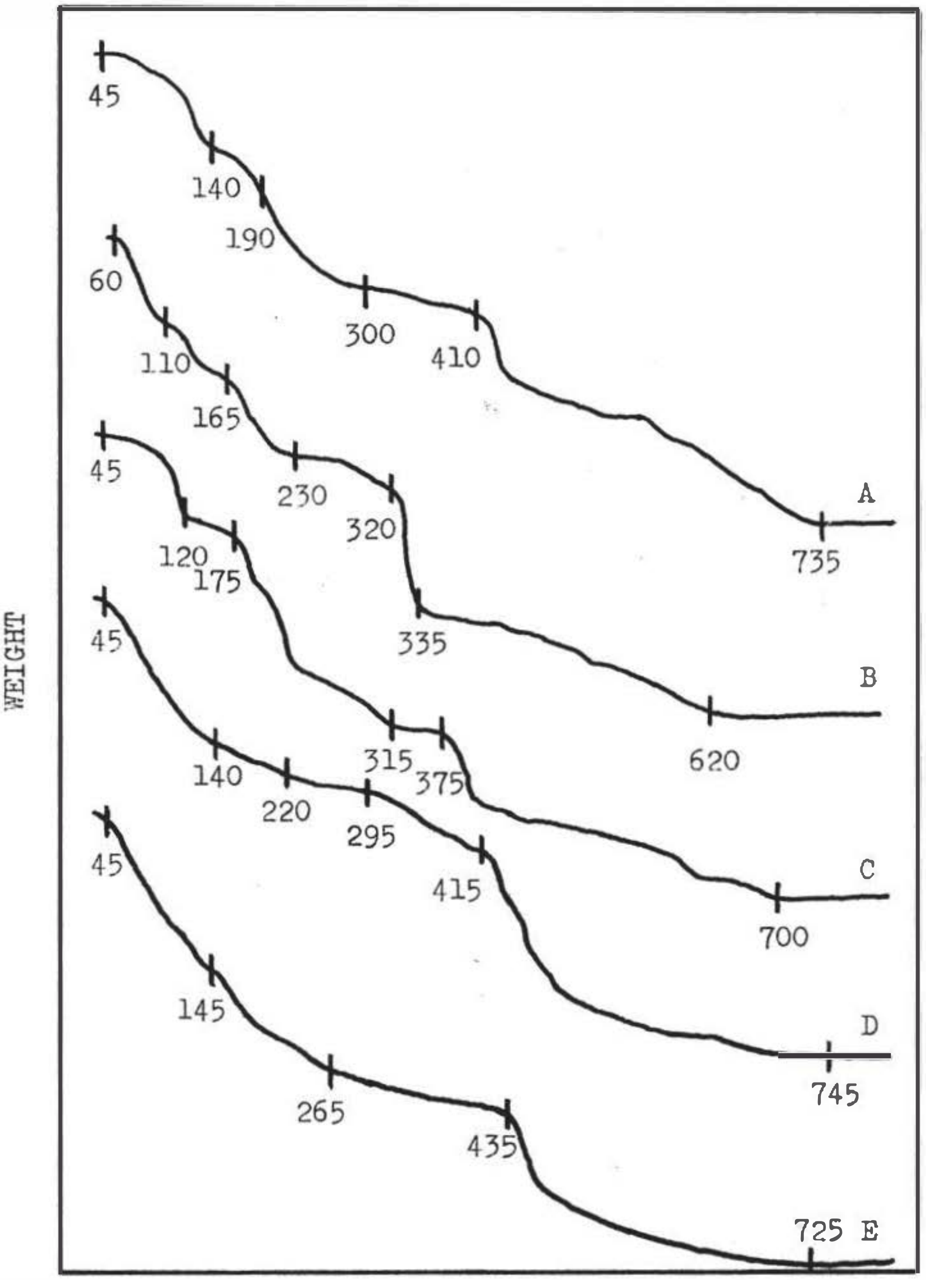
rapidly to yield the oxides. However, in the case of lanthanum, a basic carbonate ($La_2O_3 \cdot CO_2$) is observed in the temperature range of 550° to 735°C.

Group II consists of the oxalate hydrates of samarium, europium, gadolinium, dysprosium, and terbium. Figure 2 shows the TGA curves for group II. In this group, the formation of intermediate hydrates is observed. Breaks in the TGA curves are found for the hexa- and dihydrates, but they yield no horizontal weight levels. The rare earth oxides are reached at slightly lower temperatures than those of the first group.

The oxalate hydrates of yttrium, holmium, erbium, ytterbium, thulium, and lutetium comprise group III. The TGA curves for group III are given in Figures 3 and 4. The dihydrates of this group appear to be quite stable, giving a horizontal weight level over a temperature interval of 40° to 150° C. Breaks in the TGA curves are observed for the anhydrous oxalates, but they immediately decompose to yield the oxides.

The TGA curves for the hexa- and dihydrates of scandium oxalate appear to resemble those of group III, in that breaks in the curves are observed for the anhydrous oxalates, but rapid decomposition to the oxides follow. Figure 5 gives the TGA curves of scandium oxalate hexa- and dihydrate.

The thermal gravimetric analysis curve of cerium oxalate decahydrate, $Ce_2(C_2O_4)_3 \cdot 10H_2O$, appeared unique in that it did not resemble the TGA curves of the other three groups. Loss of water of hydration began to occur near 30° C, with a break in the curve appearing at 205° C. The decomposition became rapid above 300° C, giving the ceric oxide level at 360° C. As expected, the metal oxide temperature level found was the lowest for any of the rare earth metal oxalates.

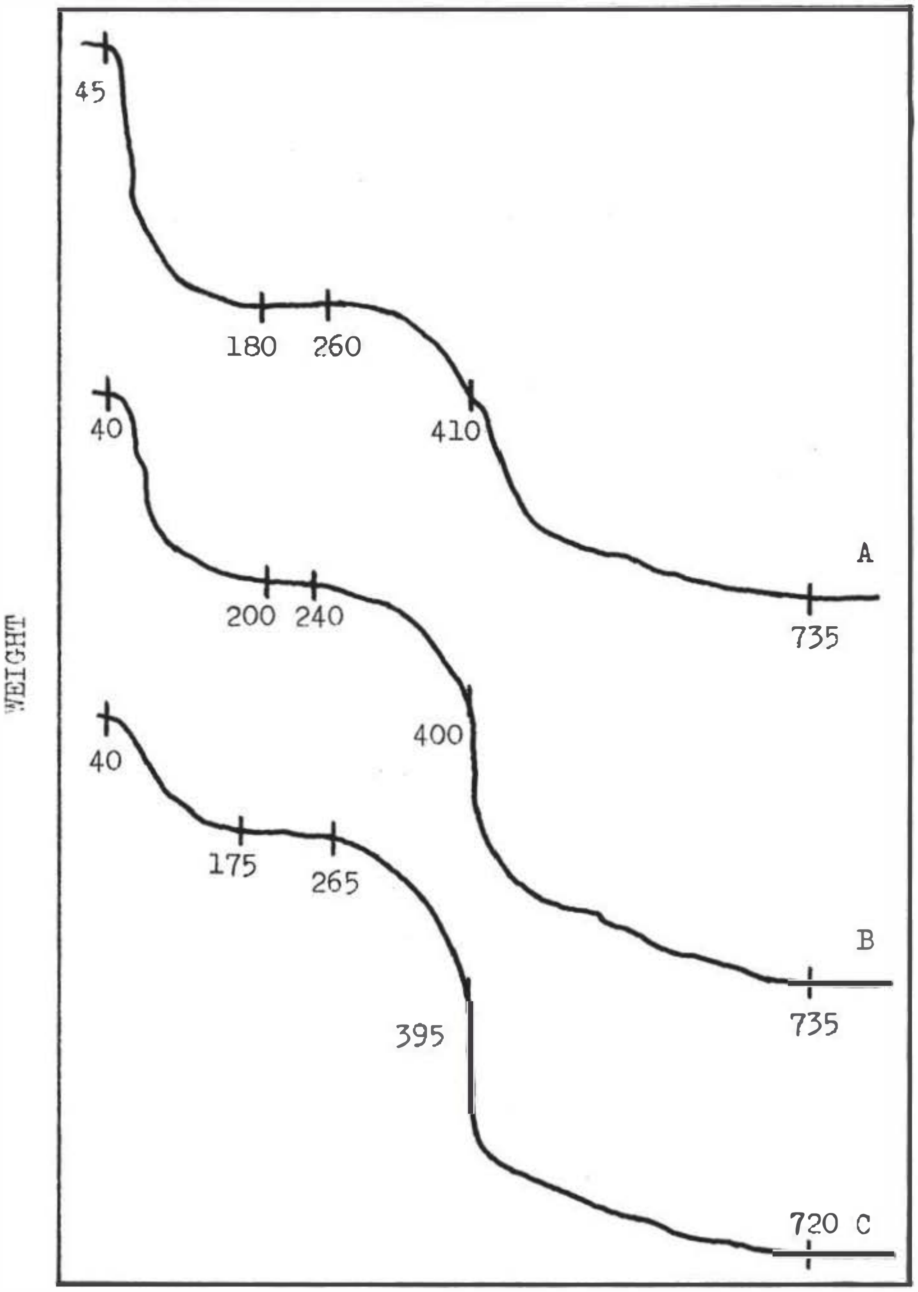


TEMP. °C.

Figure 2.

Thermal decomposition curves of rare earth metal oxalates

A. Samarium oxalate decahydrate
B. Europium oxalate decahydrate
C. Gadolinium oxalate decahydrate
D. Dysprosium oxalate decahydrate
E. Terbium oxalate decahydrate



TEMP. °C.

Figure 3.

Thermal decomposition curves of yttrium and rare earth metal oxalates

A. Yttrium oxalate nonahydrate

B. Holmium oxalate decahydrate

C. Erbium oxalate hexahydrate

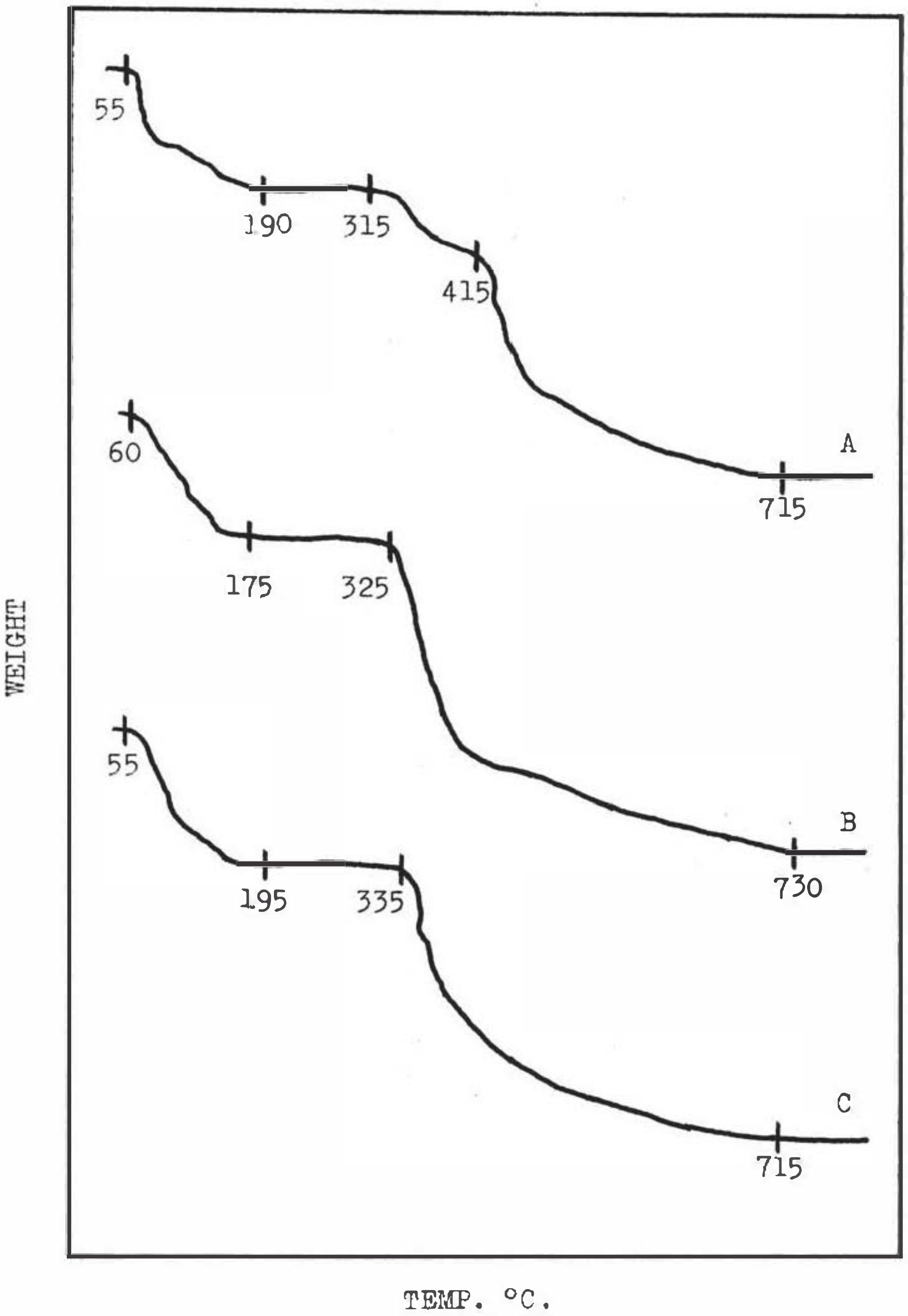
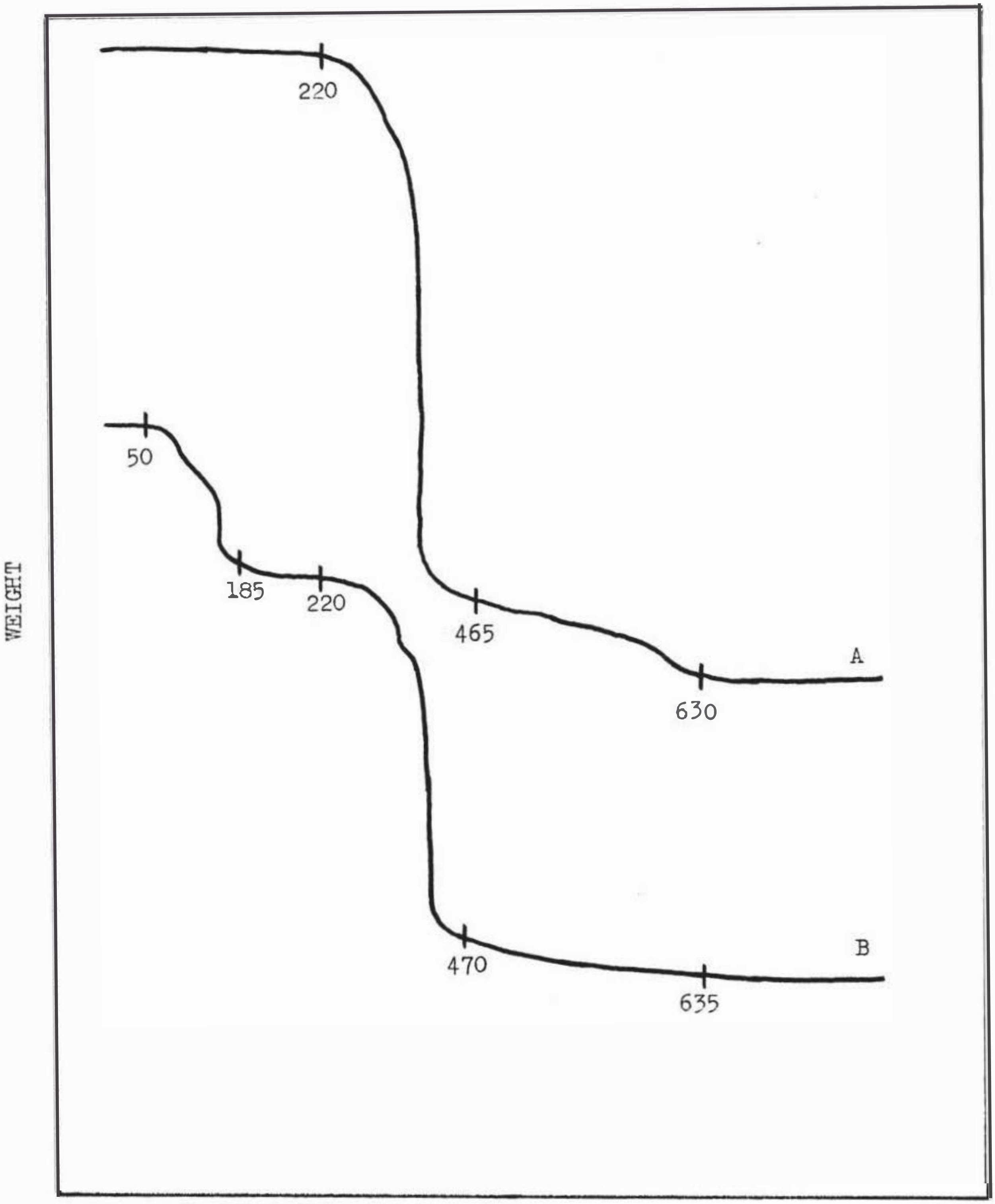


Figure 4.
Thermal decomposition curves of
rare earth metal oxalates
A. Lutetium oxalate hexahydrate
B. Ytterbium oxalate pentahydrate
C. Thulium oxalate pentahydrate



TEMP. °C.

Figure 5.

Thermal decomposition curves of scandium oxalate

A. Scandium oxalate dihydrate

B. Scandium oxalate hexahydrate

Barrett and co-workers also analyzed the TGA behavior of the rare earth oxalate hydrates and obtained results which were in good agreement with the data of Wendlandt.(3)

The TGA curves for the light rare earth oxalate hydrates obtained by Duval differ slightly in the temperatures at which the intermediate products are formed.(38) Table 10 compares the decomposition temperatures as reported by Wendlandt and Duval.

Möbius and Matthes have studied the thermal decomposition of the rare earth oxalate hydrates under various conditions, and have found that the form of the TGA curves obtained and the range of existence of intermediary products depends markedly on the heating velocity of the samples.(39,40) They found for all of the rare earth oxalate hydrates that the slower the heating rate, the lower the temperature at which decomposition occurs.

Differential thermal analysis studies by Wendlandt support his findings on the TGA behavior of the rare earth oxalate hydrates.(41) Mooseth and co-workers also obtained DTA results which agreed with the data of Wendlandt.(42,43)

TABLE 10. DECOMPOSITION TEMPERATURES OF RARE EARTH METAL OXALATES

Rare Earth Metal Oxalate	Temperature, °C.		Transition
	Wendlandt	Duval	
Lanthanum	55-380	35-300	decahydrate → anhydrous
	380-550	300-700	anhydrous → $La_2O_3 \cdot CO_2$
	735-800	800-876	$La_2O_3 \cdot CO_2$ → oxide
Cerium	50-360	58-450	decahydrate → oxide
Praseodymium	40-420	78-346	decahydrate → anhydrous
	420-790	346-746	anhydrous → oxide
Neodymium	50-445	90-290	decahydrate → anhydrous
	445-735	350-813	anhydrous → oxide
Samarium	45-300	69-344	decahydrate → anhydrous
	410-735	360-800	anhydrous → oxide
Europium	60-320	65-280	decahydrate → anhydrous
	320-620	315-695	anhydrous → oxide
Gadolinium	45-120	60-92	decahydrate → hexahydrate
	120-315	92-300	hexahydrate → anhydrous
	375-700	350-813	anhydrous → oxide
Terbium	45-140	—	decahydrate → pentahydrate
	140-265	—	pentahydrate → monohydrate
	265-435	—	monohydrate → anhydrous
	435-725	—	anhydrous → oxide
Dysprosium	45-140	—	decahydrate → tetrahydrate
	140-22	—	tetrahydrate → dihydrate
	295-415	—	dihydrate → anhydrous
	415-745	—	anhydrous → oxide
Holmium	40-200	—	decahydrate → dihydrate
	240-400	—	dihydrate → anhydrous
	400-735	—	anhydrous → oxide
Erbium	40-175	—	hexahydrate → dihydrate
	265-395	—	dihydrate → anhydrous
	395-720	—	anhydrous → oxide

TABLE 10. (CONTINUED)

Rare Earth	Temperature, °C.		
Metal Oxalate	**Wendlandt**	**Duval**	**Transition**
Thulium	55-195	—	pentahydrate → dihydrate
	335-730	—	dihydrate → oxide
Ytterbium	60-175	—	pentahydrate → dihydrate
	325-730	—	dihydrate → oxide
Lutetium	55-190	—	hexahydrate → dihydrate
	315-715	—	dihydrate → oxide
Yttrium	45-180	—	nonahydrate → dihydrate
	260-410	—	dihydrate → anhydrous
	410-735	—	anhydrous → oxide
Scandium	50-185	—	hexahydrate → dihydrate
	220-635	—	dihydrate → oxide

C. Rare Earth Acid Oxalates

1. Preparation

Möbius and Matthes have published data in which they describe the preparation of the acid oxalates, $HRE(C_2O_4)_2 \cdot 3H_2O$, of the heavy rare earth elements.(6) They attempted to prepare the acid oxalates of all the rare earth elements by dissolving the normal oxalates in concentrated hydrochloric acid at 80° C. The solutions were placed in vacuo and after a short time crystals were obtained. The crystals were suction filtered and washed with alcohol and ether.

The normal oxalate hydrates of lanthanum through gadolinium failed to produce the acid oxalates. Instead, an oxalate chloride, $RE(C_2O_4)Cl \cdot 3H_2O$, was obtained. The reaction occurring is given in equation (1).

$$\begin{aligned} & RE_2(C_2O_4)_3 \cdot 10H_2O + 2HCl \longrightarrow \\ & 2RE(C_2O_4)Cl \cdot 3H_2O + C_2O_4^{=} + 6H^+ + 4OH^- \end{aligned} \qquad (1)$$

The acid oxalates were obtained for yttrium and for the elements terbium through lutetium. No attempts were made to prepare the scandium analogue. Equation (2) gives the reaction for this group.

$$\begin{aligned} & 2RE_2(C_2O_4)_3 \cdot xH_2O + 3HCl \longrightarrow \\ & 3HRE(C_2O_4)_2 \cdot 3H_2O + RE^{3+} + 3Cl^- \end{aligned} \qquad (2)$$

No explanation for the failure of the light rare earth oxalates to form the acid oxalates was given.

The break which occurs between gadolinium and terbium in forming the acid oxalates appears in other chemical properties of the rare earths. In the ion exchange separation of the rare earths, there is a break in the regularity of the separations between gadolinium and terbium, and in the extraction of the rare earths from strong nitric acid solutions by tributyl phosphate in carbon tetrachloride, there are changes in the distribution constants at gadolinium.

The reason for this chemical divergence from regularity might be attributed to the fact that the 4-f electron shell goes from half filled with gadolinium to greater than half full with terbium.

2. X-Ray Powder Diffraction Patterns

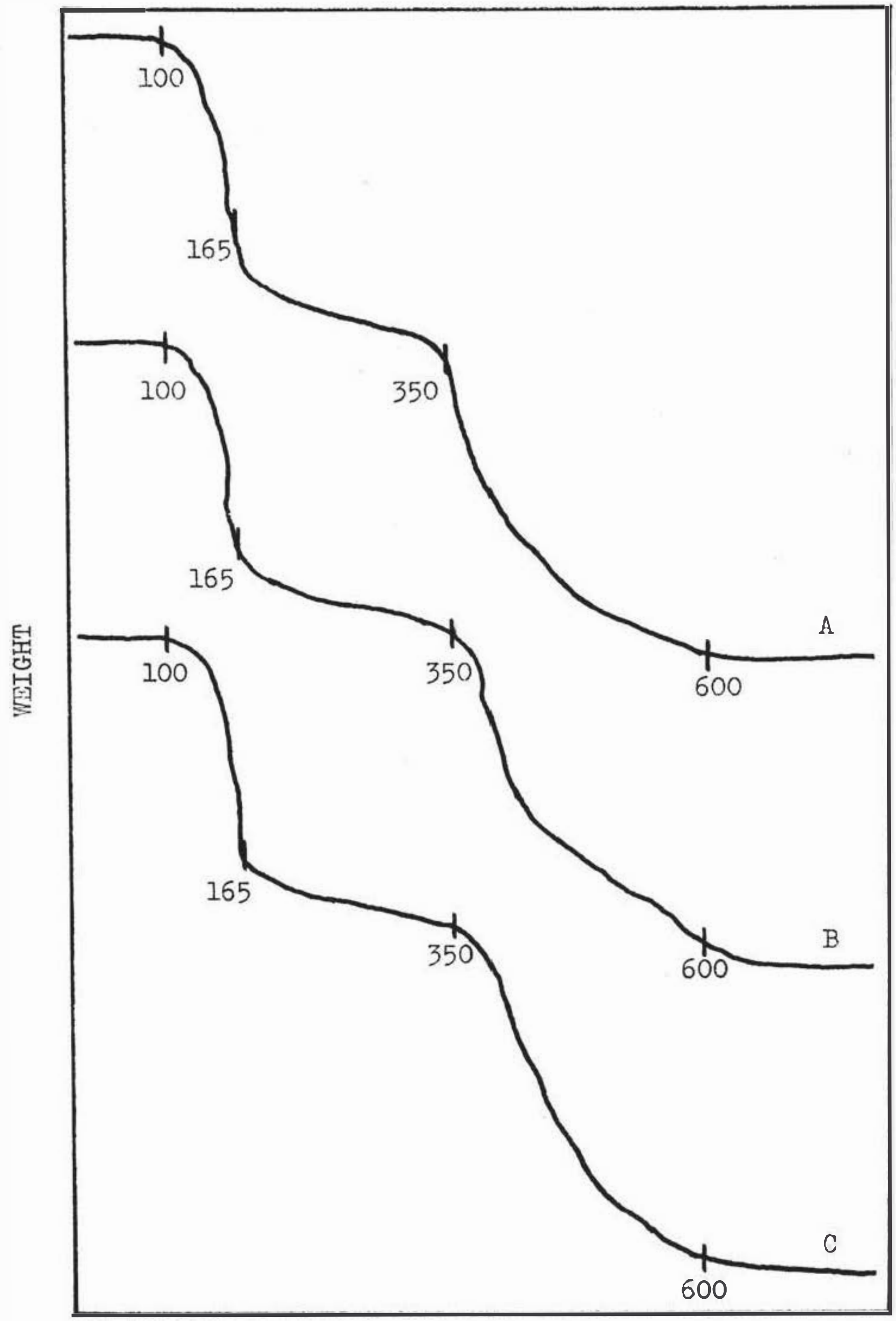
No data has been published on the powder patterns of the acid oxalates, except to show that the patterns differ from those of the normal oxalate hydrates.

Möbius and Matthes have determined the crystal system of erbium acid oxalate trihydrate to be tetragonal and to have lattice parameters of a_o = 12.2 Å and c_o = 6.3 Å.

Brunton and Steinfink have carried out detailed single crystal studies of the erbium compound and have determined the unit cell parameters to be a_o = 8.6664 Å and c_o = 6.4209 Å.(7)

3. Thermal Decomposition Data

Thermal decomposition of the rare earth acid oxalates has been studied by Möbius and Matthes.(5) They found that loss of water began to occur slightly over 100° C. Decomposition continues until the anhydrous acid oxalates, $HRE(C_2O_4)_2$, are reached near 165° C. The anhydrous acid oxalates appear to be unstable and decompose to form the normal oxalates near 350° C. Loss of carbon dioxide and carbon monoxide converts the normal oxalates to the rare earth oxides at a temperature of 600° C. None of the rare earth acid oxalates studied gave any evidence for the formation of any stable lower hydrates or anhydrous compounds. Figures 6 and 7 show the TGA curves of the rare earth acid oxalates.



TEMP. °C.

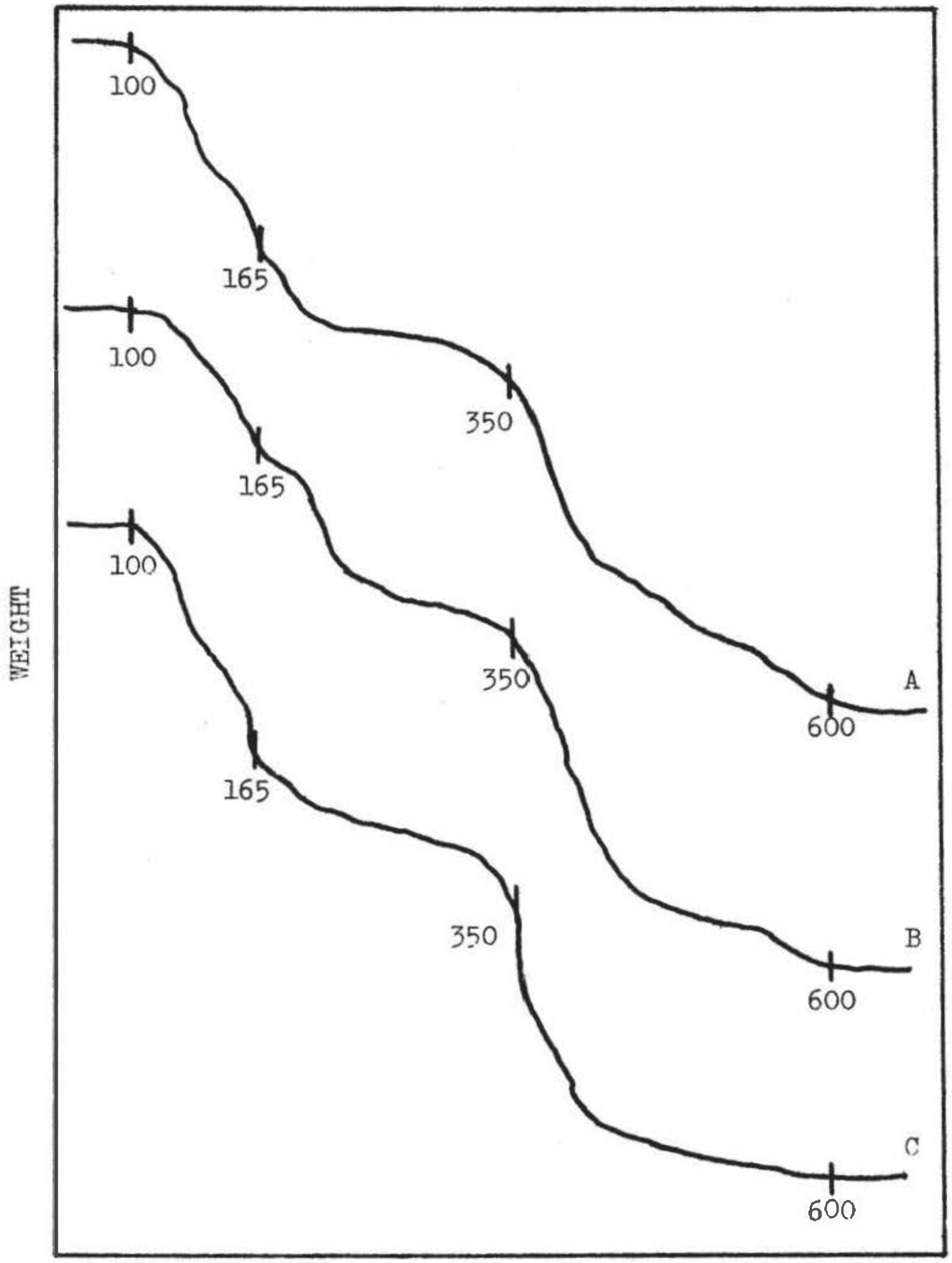
Figure 6.

Thermal decomposition curves of rare earth acid oxalate trihydrates

A. $HTb(C_2O_4)_2 \cdot 3H_2O$

B. $HDy(C_2O_4)_2 \cdot 3H_2O$

C. $HHo(C_2O_4)_2 \cdot 3H_2O$



TEMP. °C.

Figure 7.

Thermal decomposition curves of rare earth acid oxalate trihydrates

A. $HY(C_2O_4)_2 \cdot 3H_2O$

B. $HTm(C_2O_4)_2 \cdot 3H_2O$

C. $HEr(C_2O_4)_2 \cdot 3H_2O$

Chapter II.

EXPERIMENTAL

A. Research Plan

1. Prepare the acid oxalates of the rare earth elements by slow evaporation of an acidic solution of the normal oxalate hydrates.

2. Analyze the X-ray powder patterns of the prepared samples and compare with those of the normal oxalate hydrates.

3. Using the interplanar spacings obtained from the X-ray diffraction patterns, determine which of the reported unit cell parameters for the erbium compound is correct.

4. Index all of the prepared compounds and determine approximate values for their lattice constants.

5. Investigate reasons for the formation of the acid oxalate of terbium, but not that of gadolinium.

6. Study the thermal gravimetric analysis behavior of the acid oxalates and compare with the reported literature data.

B. Chemicals

Lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide, samarium oxide, europium oxide, gadolinium oxide, terbium oxide, dysprosium oxide, holmium oxide, erbium oxide, ytterbium oxide, and yttrium oxide were purchased in 99.9% purity from the Molybdenum Corporation of America, Louviers, Colorado. The oxalic acid dihydrate and hydrochloric acid (6 N and 12 N) were "Fischer Reagent" grade. Potassium permanganate and potassium hydroxide were of U.S.P. grade. Sodium oxalate was "Bakers Analyzed Special" grade. The sodium carbonate was "Fischer Certified Reagent" grade.

C. Apparatus and Measurement

All X-ray diffraction studies were made with a Philips X-ray diffraction generator, type PW 1008, using a Philips Debye-Scherrer powder camera of 114.59 mm diameter, type number 52056-B. Nickel filtered monochromatic copper radiation of wavelength 1.539 Å was employed. Voltage and current applied to the target material were 36.0 KV and 20.0 mA, respectively. Kodak No-Screen Medical X-ray film of 35 mm width was used. The diffraction lines were measured to the nearest 0.05 mm using a Norelco Film Illuminator and Measuring Device, type number 52022/1. All intensity measurements were visually estimated.

Analytical weight measurements were carried out using a Sartarius Model 2743 balance. The infrared spectra were recorded in KBr medium using a Perkin-Elmer 337 grating infrared spectrophotometer.

Thermal gravimetric analysis curves were obtained with an automatic recording precision torque balance similar to that described in the literature.(44,45) Details on the actual construction of the thermobalance were not available.

All index of refraction measurements were made in certified index of refraction liquids obtained from R. P. Cargille Laboratories, Inc., Cedar Grove, New Jersey.

D. Analysis

All of the rare earth acid oxalates were analyzed by ignition to the metal oxides in air at 700° C. The oxalate content of the prepared samples was determined by titration with standard 0.1 N potassium permanganate.(46) The water content of the samples was not determined.

E. Preparations

1. Normal Rare Earth Oxalate Hydrates

All of the normal rare earth oxalate hydrates, $RE_2(C_2O_4)_3\cdot xH_2O$, except cerium oxalate decahydrate, were prepared in the manner described below for erbium oxalate hexahydrate.

One gram (0.0026 mole) of erbium oxide was dissolved in 30 ml of 6 N hydrochloric acid with heating on the steam bath. The solution was allowed to cool to room temperature and then gravity filtered. The solution was placed in an ice bath and stirred while 41.50 ml of a cold saturated solution of oxalic acid dihydrate was added. The precipitate of the rare earth oxalate immediately formed. The precipitate was digested for two hours, after which it was suction filtered. The precipitate of rare earth oxalate hydrate was washed four times with 10 ml portions of ice cold water, twice with 10 ml portions of 95% ethanol, and once with 10 ml of ether. The product obtained was placed in a vacuum desiccator over potassium hydroxide and allowed to dry for 24 hours. The theoretical yield of erbium oxalate hexahydrate was 1.8 grams. Actual yield was 1.7 grams (94%).

2. Cerium Oxalate Decahydrate

Ceric oxide, CeO_2, is not soluble in hot 6 N hydrochloric acid, but can be reduced to the 3+ oxidation state with hydrogen peroxide.

Approximately 1 gram (0.0058 mole) of ceric oxide was placed in a beaker on the steam bath and to this was added 50 ml of 6 N hydrochloric acid. 5 ml of 30% hydrogen peroxide was added dropwise until solution was complete. The solution was cooled to room temperature, gravity filtered, and the cerium oxalate precipitated as described under the preparation of the normal oxalates.

3. Rare Earth Acid Oxalate Trihydrates

The normal oxalate hydrates of yttrium, dysprosium, holmium, terbium, ytterbium, gadolinium, and erbium formed the acid oxalates when dissolved in concentrated (12 N) hydrochloric acid. All of the acid oxalates were prepared by the procedure given for erbium below.

Approximately 1.50 grams (0.0021 mole) of the normal erbium oxalate hexahydrate, $Er_2(C_2O_4)_3{\cdot}6H_2O$, was dissolved in 35 ml of 12 N hydrochloric acid on the steam bath. The solution was allowed to cool to room temperature and gravity filtered into a 100 ml beaker. The solution was then placed in a vacuum desiccator containing a beaker of potassium hydroxide. The vacuum desiccator was connected to a water aspirator, and a vacuum applied for 30-45 minutes. The vacuum desiccator was then shut off and allowed to remain undisturbed for a period of 3-7 days. After this time interval, small crystals of the desired compounds were obtained. The beaker containing the crystals was removed from the vacuum desiccator and the crystals were suction filtered, washed four times with 10 ml portions of ice cold water, twice with 10 ml portions of 95% ethanol, and once with 10 ml of ether. The crystals were dried in a vacuum desiccator for 48 hours. The theoretical yield of the erbium acid oxalate trihydrate was 1.3 grams. Actual yield was 1.1 grams (85%).

Attempts to prepare the acid oxalate of gadolinium by the procedure described for the other acid oxalates always resulted in the normal oxalate precipitating from solution. However, when a solution of the normal oxalate in concentrated hydrochloric acid was allowed to evaporate to dryness in the vacuum desiccator (17 days), crystals of both the normal oxalate and the acid oxalate of gadolinium were obtained.

4. Attempted Preparation of Light Rare Earth Acid Oxalate Trihydrates

The normal rare earth oxalate hydrates of lanthanum, cerium, praseodymium, neodymium, samarium, and europium failed to produce the acid oxalates.

The insolubility of the light rare earth oxalate hydrates in concentrated hydrochloric acid appeared to be a major factor in preventing formation of the acid oxalates.

Approximately one gram each of the light rare earth oxalate hydrates was placed in a 100 ml beaker with 50 ml of concentrated (12 N) hydrochloric acid. The contents of the beaker were heated for an hour on the steam bath, after which the solution was cooled to room temperature and gravity filtered. It appeared as though no noticeable amount of the normal oxalates went into solution. The filtered solution was placed in a vacuum desiccator as previously described. After standing for one week, no crystals of the acid oxalates were detected. A quantitative determination of the residue remaining after filtration indicated a 93% recovery of the starting material.

P. X-Ray Diffraction Patterns

The discovery in 1912 by von Laue that crystals could act as diffraction gratings for X-rays has led to the wide usage of X-ray diffraction techniques as a modern tool for determining the structure of compounds.

Shortly after World War I began, P. Debye and P. Scherrer in Germany and almost simultaneously A. W. Hull in the United States, discovered that there existed a characteristic X-ray diffraction effect from a fine-grained crystalline aggregate. This method required that the individual crystals of the aggregate be in the form of a fine dust or powder. For this reason this method of examining crystals is commonly referred to as the "powder method."

The mathematical relationship between θ, the angle at which X-rays are deflected by the crystalline sample, λ, the wavelength of the incident X-rays, and d, the interplanar distance within the crystal, was put forth by W. L. Bragg.

This relationship may be derived by reference to Figure 8, in which the horizontal lines represent a series of parallel planes within the crystal separated by the interplanar distance d.(47)

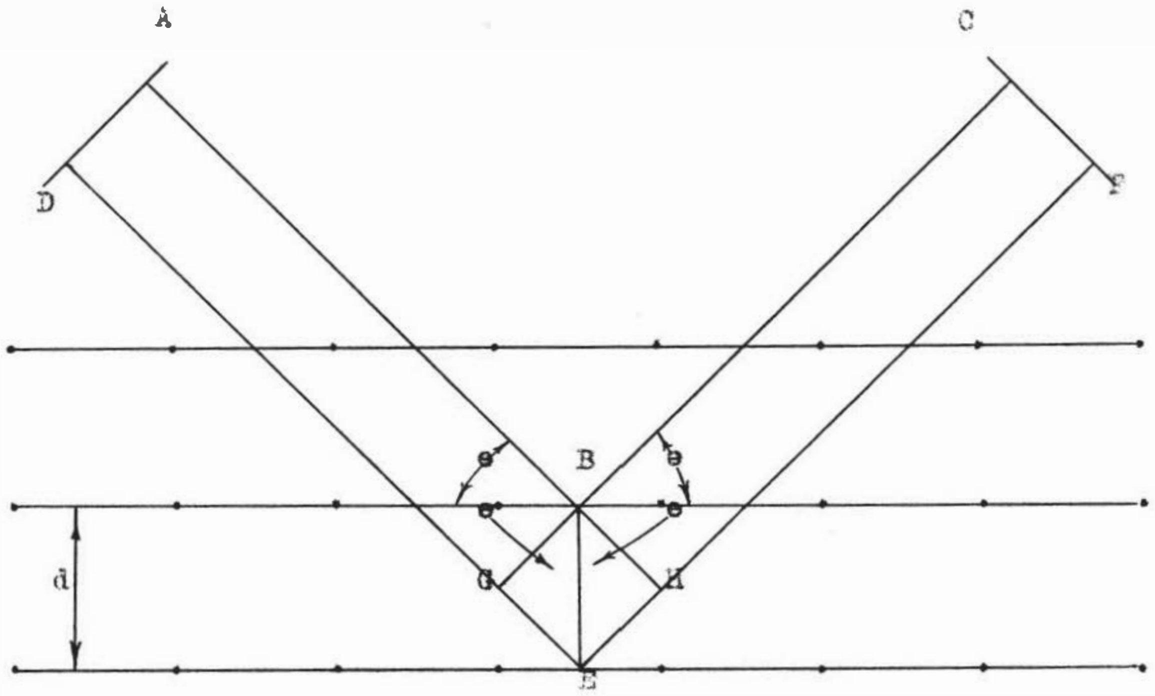


Figure 8.

Derivation of Bragg's Equation

The plane AD is perpendicular to the incident beam of parallel monochromatic X-rays, and the plane CF is perpendicular to the reflected beam of X-rays. As the angle of incidence θ is changed, a reflection will be observed only when the waves are in phase at plane CF, that is, when the difference in distance between planes AD and CF, measured along rays reflected from different planes, is an integral multiple of the wavelength. Since the angle of incidence is equal to the angle of reflection, then the distance travelled by ray DEF must be greater than that travelled by ray ABC by an amount equal to GE + EH. When the difference in distance between planes AD and CF is an integral number of wavelengths, the rays reinforce each other and

$$GE + EH = n\lambda \qquad (3)$$

Furthermore, since

$$\sin\theta = \frac{GE}{BE} = \frac{EH}{BE} \qquad (4)$$

and

$$BE = d \qquad (5)$$

then

$$\sin\theta = \frac{GE}{d} \qquad (6)$$

or

$$GE = d\sin\theta \qquad (7)$$

Substitution into equation (3) gives the desired relationship

$$n\lambda = 2d\sin\theta \qquad (8)$$

Thus, if the wavelength of radiation λ, and the angle θ of diffraction are known, the interplanar spacing d within a crystal can be calculated.

The interplanar spacings d of the prepared acid oxalate trihydrates were calculated by substituting the values of θ obtained from the powder photographs into equation (8). The design of the 114.59 mm powder camera used is such that 2 mm of film length is equivalent to an angle of 1 degree in the Bragg equation. Program I, written in Fortran IV language for the IBM 360 Operating System, was used to make the calculations.

The relationship between the interplanar spacing d and the unit cell dimensions for a crystal belonging to the tetragonal crystal system is given by(48,49)

$$\frac{1}{d^2_{hkl}} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (9)$$

It can be seen from equation (9) that for a given plane (hkl) the value of d is a function only of the cell dimensions a and c.

The lattice constants reported by Möbius and Matthes ($a_o = 12.2$ Å, $c_o = 6.3$ Å) and those of Steinfink and Brunton ($a_o = 9.6664 \pm 0.0003$ Å, $c_o = 6.4209 \pm 0.0003$ Å) for erbium acid oxalate trihydrate were used in equation (9) to calculate all possible d values up to (hkl) values of (888). Program II was used to compute the interplanar spacings from the known lattice constants.

The experimentally obtained values were then compared with the calculated values to ascertain the correct lattice constants and to index the erbium compound.

Since the X-ray powder diffraction patterns indicated all of the prepared rare earth acid oxalate trihydrates were isomorphous, the (130) and (111) planes with their corresponding interplanar distances were selected and used in equation (9) to calculate the lattice constants of the remaining acid oxalates.

G. Thermal Gravimetric Analysis Curves

Interest in the thermogravimetric pyrolysis of inorganic compounds has increased rapidly since the publication of Duval's work in 1953.(38) In recent years, several commercial instruments have become available.

The essential components of a thermobalance are illustrated in Figure 9.(45) The thermobalance consists of a torsion-wire balance, normally 0 to 100-mg capacity, which is connected to a pen recorded cylindrical drum. The furnace of the thermobalance is constructed of approximately 15 feet of Nichrome alloy wire wound around a Vycor glass tube and covered with asbestos insulation. The sample is contained in a platinum pan, 1 cm in diameter and 0.5 cm in height, and suspended in the furnace by means of a platinum wire connected to the balance beam. The heating rate of the furnace can be varied by altering the input voltage to a motor driven powerstat. The null point of the balance is maintained by a beam of light falling between two sensitive cadmium sulfide photocells.

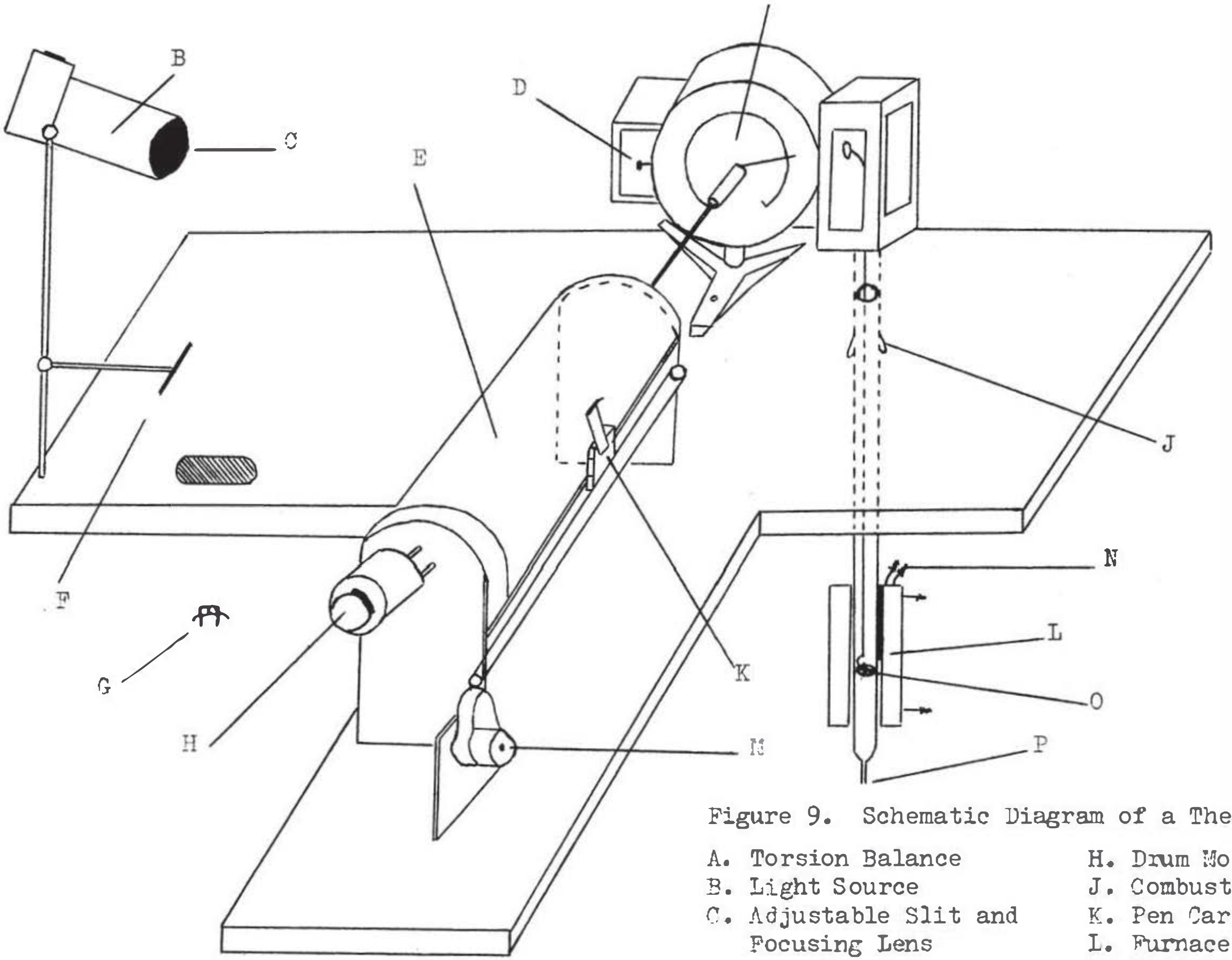


Figure 9. Schematic Diagram of a Thermobalance

A. Torsion Balance
B. Light Source
C. Adjustable Slit and Focusing Lens
D. Beam Mirror
E. Recording Drum
F. Reflecting Mirror
G. Photocells
H. Drum Motor
J. Combustion Tube Joint
K. Pen Carriage
L. Furnace
M. Pen Drive Motor
N. Thermocouple
O. Sample Pan
P. Exhaust Gas Connection

Calibration of the thermobalance is obtained by correlating the temperature rise of the furnace with the horizontal pen travel distance on the recorder.

Samples of the acid oxalate trihydrates of erbium, terbium, dysprosium, holmium, ytterbium, and yttrium were sent to Ames Laboratory of the Atomic Energy Commission, Iowa State University, for thermal gravimetric analysis. At the time of this writing, only erbium acid oxalate trihydrate has been analyzed. The thermal decomposition of the erbium compound was studied in the temperature range of 25° to 420° C. A heating rate of 0.67° C/minute was employed.

Chapter III.

RESULTS AND DISCUSSION

A. Analysis

Chemical analysis of the prepared acid oxalate trihydrates indicated the formula $HRE(C_2O_4)_2 \cdot 3H_2O$. The calculated and experimental percentages of rare earth metal and oxalate ion content of the acid oxalates are given in Table 11.

B. X-Ray Diffraction Studies

Comparison of the experimentally determined interplanar spacings with the calculated values obtained from the lattice parameters reported by Möbius and Matthes and those of Steinfink and Brunton indicated the unit cell parameters for erbium acid oxalate trihydrate ($a_0 = 8.6664 \pm 0.0003$ Å, $c_0 = 6.4209 \pm 0.0008$ Å) determined by Steinfink and Brunton are correct. Comparison of the experimental and calculated interplanar spacings also permitted indexing of the erbium compound.

Table 12 compares the experimentally obtained interplanar spacings with the calculated values for erbium acid oxalate trihydrate.

The X-ray powder patterns of the acid oxalate trihydrates of erbium, terbium, dysprosium, holmium, ytterbium, gadolinium, and yttrium showed that all of the acid oxalate trihydrates were isomorphous. Thus, all of the diffraction lines observed for the acid oxalates would have indexes identical with those of erbium acid oxalate previously indexed.

TABLE 11. ANALYTICAL RESULTS

Compound	Rare Earth Calc. (%)	Rare Earth Found (%)	Oxalate Calc. (%)	Oxalate Found (%)	Water Calc. (%)	Water Found* (%)
$HTb(C_2O_4)_2 \cdot 3H_2O$	40.75	40.62	45.39	45.35	13.86	14.03
$HDy(C_2O_4)_2 \cdot 3H_2O$	41.29	40.87	44.98	44.97	13.73	14.16
$HHo(C_2O_4)_2 \cdot 3H_2O$	41.65	41.77	44.71	44.58	13.64	13.65
$HEr(C_2O_4)_2 \cdot 3H_2O$	41.99	42.08	44.44	44.54	13.57	13.38
$HYb(C_2O_4)_2 \cdot 3H_2O$	42.82	43.09	43.81	43.53	13.37	13.38
$HY(C_2O_4)_2 \cdot 3H_2O$	27.79	27.77	55.32	55.27	16.89	16.96

* Water By Difference

TABLE 12. COMPARISON OF EXPERIMENTAL AND CALCULATED d VALUES FOR BARIUM ACID OXALATE TRIHYDRATE

Index hkl	d(Calc.)		d(Obs.)
	Möbius and Matthes	Steinfink and Brunton	
001	6.30	6.42	6.51
110	8.63	6.13	6.12
011 101	5.60	5.16	5.14
111	5.09	4.43	4.43
020 200	6.10	4.33	4.32
021 201	4.38	3.59	3.59
121 211	4.12	3.32	3.31
220	4.31	3.06	3.04
012 102	3.05	3.01	2.99
130 310	3.36	2.74	2.74

TABLE 12. (CONTINUED)

Index hkl	d(Calc.) Möbius and Matthes	d(Calc.) Steinfink and Brunton	d(Obs.)
022 202	2.80	2.58	2.57
131 311	3.29	2.52	2.50
122 212	2.73	2.47	2.46
231 321	2.98	2.25	2.24
040 400	3.05	2.17	2.18
003	2.10	2.14	2.14
032	2.49	2.15	
302	2.49	2.15	
041 401	2.75	2.05	2.06
141 411	2.68	2.00	1.99
023 203	2.01	1.92	1.92

TABLE 12. (CONTINUED)

Index hkl	d(Calc.) Möbius and Matthes	d(Calc.) Steinfink and Brunton	d(Obs.)
123	1.96	1.87	1.86
213			
042	2.19	1.80	1.79
402			
223	1.89	1.75	1.75
412	2.16	1.76	
142	2.16	1.76	
150	2.39	1.70	1.70
510			
051	2.28	1.67	1.67
501			
151	2.24	1.64	1.64
511			
233	1.78	1.60	1.60
323			
250	2.27	1.61	
520			
014	1.56	1.58	1.58
104			

TABLE 12. (CONTINUED)

Index hkl	d(Calc.)		d(Obs.)
	Möbius and Matthes	Steinfink and Brunton	
043 403	1.73	1.52	1.52
143 413	1.71	1.50	1.50
124 214	1.51	1.48	1.48
333	1.70	1.48	
060 600	2.03	1.44	1.44
243 423	1.66	1.44	
252 522	1.84	1.44	
261 621	1.84	1.34	1.34

Tables 13, 14, 15, and 16 compare the interplanar spacings for the rare earth acid oxalates obtained from the X-ray powder patterns.

The lattice constants for the acid oxalate trihydrates of terbium, dysprosium, holmium, ytterbium, gadolinium, and yttrium were calculated by substituting the experimentally obtained interplanar spacings for the (130) and (111) planes into equation (9).

The crystal system and unit cell parameters for the acid oxalate trihydrates are given in Table 17.

TABLE 13. X-RAY POWDER DATA FOR GADOLINIUM AND TERBIUM ACID OXALATE TRIHYDRATE

Index	$HGd(C_2O_4)_2 \cdot 3H_2O$		$HTb(C_2O_4)_2 \cdot 3H_2O$	
hkl	d(Obs.)	Intensity	d(Obs.)	Intensity
001	Absent	—	6.53	s
110	6.23	s	6.21	vs
011 101	5.16	vw	5.16	m
111	4.44	s	4.43	vs
020 200	Absent	—	4.36	vw
021 201	Absent	—	3.60	vw
121 211	3.34	w	3.32	m
220	3.10	w	3.08	m
012 102	3.00	vw	2.97	m
130 310	2.79	m	2.76	s
022 202	2.56	w(d)	2.56	m(d)

TABLE 13. (CONTINUED)

Index hkl	$HGd(C_2O_4)_2 \cdot 3H_2O$		$HTb(C_2O_4)_2 \cdot 3H_2O$	
	d(Obs.)	Intensity	d(Obs.)	Intensity
122 212	2.47	w(d)	2.46	m(d)
231 321	2.28	w	2.26	m
040 400	Absent	—	2.21	vw
003 032 302	2.15	vw	2.14	w
041 401	2.07	m(d)	2.09	m(d)
141 411	2.00	w(d)	2.01	vw
331	Absent	—	1.96	w
023 203	1.92	w(d)	1.92	w
123 213	1.87	w	1.86	m

TABLE 13. (CONTINUED)

Index hkl	$HGd(C_2O_4)_2\cdot 3H_2O$ d(Obs.)	 Intensity	$HTb(C_2O_4)_2\cdot 3H_2O$ d(Obs.)	 Intensity
042 402	Absent	—	1.80	vw
223 412 142	Absent	—	1.76	w
150 510	1.72	w	1.71	m
051 501	Absent	—	1.68	vw
151 511	Absent	—	1.65	w
233 323 250 520	Absent	—	1.60	w
014 104	Absent	—	1.56	vw
043 403	1.54	vw	1.53	w

TABLE 13. (CONTINUED)

Index	$HGd(C_2O_4)_2 \cdot 3H_2O$		$HTb(C_2O_4)_2 \cdot 3H_2O$	
hkl	d(Obs.)	Intensity	d(Obs.)	Intensity
143 413	1.51	vw	1.50	m
124 214 333	1.47	vw	1.47	vw
060 600 243 423 252 522	Absent	—	1.45	vw
034 304	Absent	—	1.40	vw
260 620	Absent	—	1.38	vw
261 621	1.36	vw	1.35	m

vs = very high intensity
s = high intensity
m = moderate intensity

w = low intensity
vw = very low intensity
(d) = diffuse

TABLE 14. X-RAY POWDER DATA FOR DYSPROSIUM AND HOLMIUM ACID OXALATE TRIHYDRATE

Index hkl	$HDy(C_2O_4)_2\cdot 3H_2O$ d(Obs.)	Intensity	$HHo(C_2O_4)_2\cdot 3H_2O$ d(Obs.)	Intensity
001	6.35	vs	6.48	s
110	6.13	vs	6.14	vs
011 101	5.15	m	5.16	m
111	4.42	vs	4.42	vs
020 200	4.38	vw	4.35	vw
021 201	3.60	vw	3.60	vw
121 211	3.33	m	3.31	m
220	3.09	m	3.07	m
012 102	2.99	m	2.98	m(d)
130 310	2.77	m	2.75	s

TABLE 14. (CONTINUED)

Index hkl	$HDy(C_2O_4)_2 \cdot 3H_2O$		$HHo(C_2O_4)_2 \cdot 3H_2O$	
	d(Obs.)	Intensity	d(Obs.)	Intensity
022 202	2.55	w	2.57	m
131 311	Absent	—	2.52	w
122 212	2.47	m	2.46	m
231 321	2.26	m	2.25	m
040 400	2.21	w	2.21	w
003 032 302	2.13	w	2.14	m(d)
041 401	2.07	m(d)	2.06	w(d)
141 411	2.01	w	2.00	w
331	1.96	w	Absent	—
023 203	1.92	m	1.93	m

TABLE 14. (CONTINUED)

Index	$HDy(C_2O_4)_2 \cdot 3H_2O$		$HHo(C_2O_4)_2 \cdot 3H_2O$	
hkl	d(Obs.)	Intensity	d(Obs.)	Intensity
123 213	1.37	m	1.86	m
042 402	1.80	vw	1.80	vw
223 412 142	1.76	w	1.76	w
150 510	1.72	m	1.71	w(d)
051 501	Absent	—	1.67	vw
151 511	1.65	vw	1.65	w
233 323 250 520	1.60	w	1.60	vw
014 104	1.57	w	1.57	vw
043 403	1.53	w	1.52	vw

TABLE 14. (CONTINUED)

Index	$HDy(C_2O_4)_2 \cdot 3H_2O$		$HHo(C_2O_4)_2 \cdot 3H_2O$	
hkl	d(Obs.)	Intensity	d(Obs.)	Intensity
143 413	1.50	m	1.50	w(d)
124 214 333	1.48	vw	1.47	w(d)
060 600 243 423 252 522	1.46	vw(d)	1.44	w
034 304	1.40	vw	Absent	—
260 620	1.38	vw	Absent	—
261 621	1.35	w	1.34	w

vs = very high intensity
s = high intensity
m = moderate intensity

w = low intensity
vw = very low intensity
(d) = diffuse

TABLE 15. X-RAY POWDER DATA FOR ERBIUM AND YTTERBIUM ACID OXALATE TRIHYDRATES

Index hkl	$HEr(C_2O_4)_2\cdot 3H_2O$		$HYb(C_2O_4)_2\cdot 3H_2O$	
	d(Obs.)	Intensity	d(Obs.)	Intensity
001	6.51	s	6.36	s
110	6.12	vs	6.06	vs
011 101	5.14	m	5.13	m
111	4.43	vs	4.41	vs
020 200	4.32	vw	4.32	vw
021 201	3.59	vw	3.57	w
121 211	3.31	m	3.30	m
220	3.04	m	3.03	m
012 102	2.99	m	Absent	—
112	Absent	—	2.84	w(d)
130 310	2.74	s	2.73	m

TABLE 15. (CONTINUED)

Index hkl	$HEr(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	Intensity	$HYb(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	Intensity
022 202	2.57	m	2.57	w
131 311	2.50	w(d)	2.52	m
122 212	2.46	w(d)	2.45	m
231 321	2.24	m	2.23	m
040 400	2.18	w	2.19	w
003 032 302	2.14	m	2.14	m
013 103	Absent	—	2.07	w
041 401	2.06	w(d)	2.03	w
141 411	1.99	w	1.98	w

TABLE 15. (CONTINUED)

Index hkl	$HEr(C_2O_4)_2 \cdot 3H_2O$		$HYb(C_2O_4)_2 \cdot 3H_2O$	
	d(Obs.)	Intensity	d(Obs.)	Intensity
023 203	1.92	m	1.92	m
123 213	1.86	m	1.87	m
042 402	1.79	vw	1.78	vw
223 412 142	1.75	w	1.75	w
150 510	1.70	w(d)	1.71	w
051 501	1.67	vw	1.68	w
151 511	1.64	w	1.63	w
233 323 250 520	1.60	w	1.59	w
014 104	1.58	vw	1.57	vw

TABLE 15. (CONTINUED)

Index hkl	$HEr(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	$HEr(C_2O_4)_2 \cdot 3H_2O$ Intensity	$HYb(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	$HYb(C_2O_4)_2 \cdot 3H_2O$ Intensity
043 403	1.52	w	1.52	w
143 413	1.50	w(d)	1.49	m
124 214 333	1.45	vw(d)	Absent	—
060 600 243 423 252 522	1.44	w	1.44	w
034 304	Absent	—	1.40	vw
260 620	Absent	—	1.36	vw
261 621	1.34	w	1.34	w

vs = very high intensity
s = high intensity
m = moderate intensity

w = low intensity
vw = very low intensity
(d)= diffuse

TABLE 16. X-RAY POWDER DATA FOR YTTRIUM ACID OXALATE TRIHYDRATE

Index hkl	$HY(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	Intensity
001	6.45	vs
110	6.14	vs
011 101	5.14	m
111	4.43	vs
020 200	4.35	vw
021 201	3.60	vw
121 211	3.31	m
220	3.07	m
012 102	2.97	m
112	2.85	vw
130 310	2.75	m
022 202	2.58	m
131 311	2.52	vw
122 212	2.47	m
231 321	2.25	m

TABLE 16. (CONTINUED)

Index hkl	$HY(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	Intensity
040 400	2.21	w
003 032 302	2.14	m(d)
013 103	2.08	w(d)
041 401	2.05	w(d)
141 411	2.00	w
023 203	1.93	m(d)
123 213	1.87	m
042 402	1.79	w
223 412 142	1.76	w
150 510	1.71	w(d)
051 501	1.67	vw
151 511	1.64	w
233 323 250 520	1.60	w

TABLE 16. (CONTINUED)

Index hkl	$HY(C_2O_4)_2 \cdot 3H_2O$ d(Obs.)	Intensity
014 104	1.57	vw
043 403	1.52	w
143 413	1.49	m(d)
060 600 243 423 252 522	1.44	w(d)
034 304	1.40	vw
260 620	1.37	vw
261 621	1.34	w

vs = very high intensity
s = high intensity
m = moderate intensity
w = low intensity
vw = very low intensity
(d)= diffuse

TABLE 17. CRYSTAL SYSTEM AND UNIT CELL PARAMETERS FOR RARE EARTH ACID OXALATE TRIHYDRATES

Compound	Crystal System	Unit Cell Parameters	
		a_o (Å)	c_o (Å)
$HGd(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.82 ± 0.02	6.32 ± 0.03
$HTb(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.73 ± 0.02	6.36 ± 0.03
$HDy(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.76 ± 0.02	6.31 ± 0.03
$HHo(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.70 ± 0.02	6.36 ± 0.03
$HEr(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.66 ± 0.02	6.42 ± 0.03
$HYb(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.63 ± 0.02	6.38 ± 0.03
$HY(C_2O_4)_2 \cdot 3H_2O$	Tetragonal	8.70 ± 0.02	6.38 ± 0.03

C. Thermal Gravimetric Analysis Data

The TGA curve obtained for the acid oxalate trihydrate of erbium varied considerably from the data of Möbius and Matthes. Figure 10 shows the TGA curve of erbium acid oxalate trihydrate. Loss of water of hydration was found to begin at 110° C and continue until the monohydrate was reached at 134° C. The monohydrate appeared stable in the temperature range of 134° C to 192° C, as indicated by a constant weight level in this temperature interval. Decomposition of the monohydrate occurred by loss of one mole of CO_2 until the compound corresponding to the formula $HEr(C_2O_4)\cdot CO_2\cdot H_2O$ was reached at 334° C. This compound appeared somewhat stable over a short temperature interval until rapid decomposition occurred.

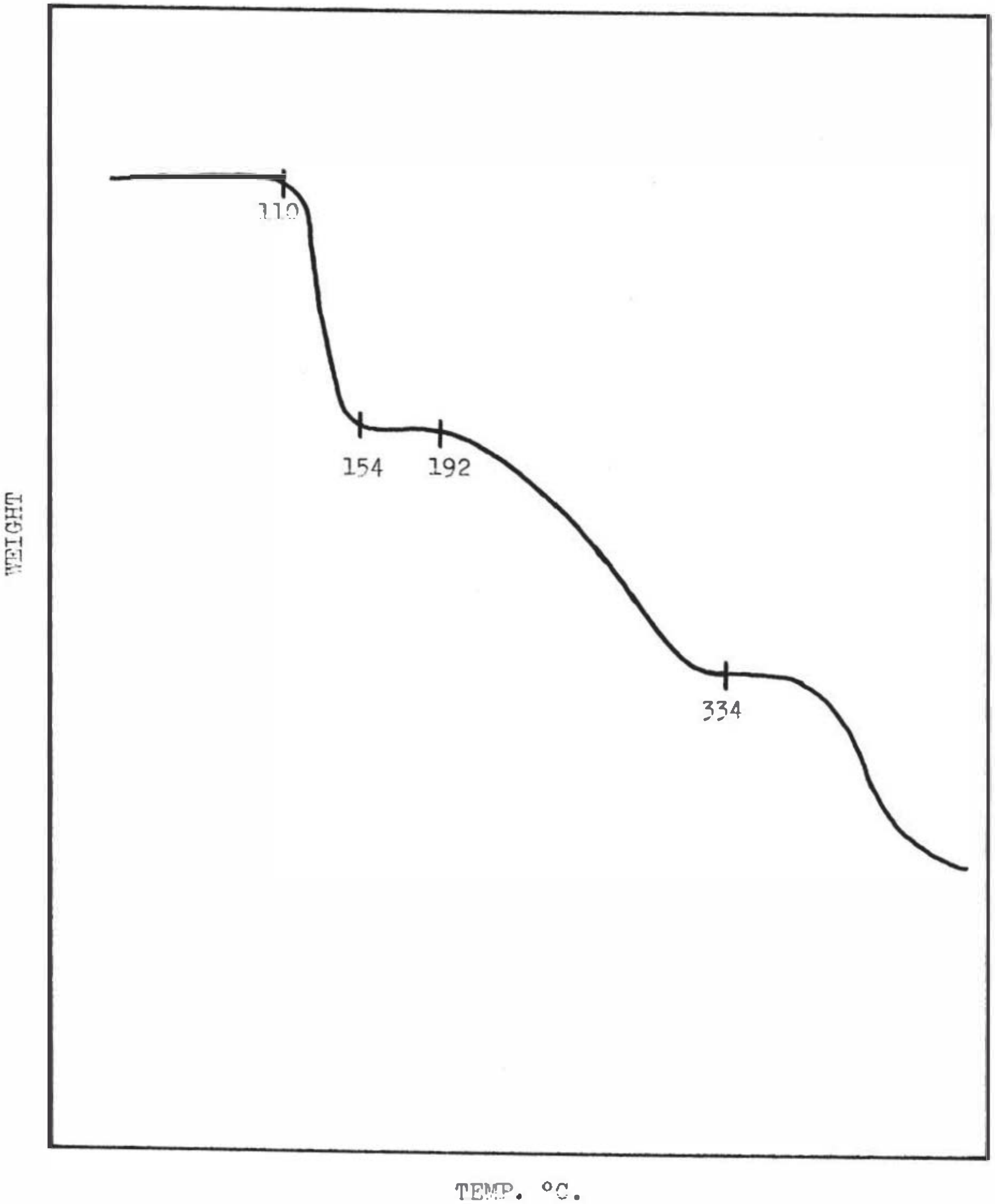


Figure 10.
Thermal Decomposition Curve of
Erbium Acid Oxalate Trihydrate

D. Index of Refraction Measurements

The indices of refraction of the rare earth acid oxalates were measured at 25° C at the D line of sodium (5893 Å) in certified index of refraction liquids by observing the movement of the Becke line under a microscope.(50) Because the crystals of the acid oxalate of gadolinium could not be separated from the normal oxalate, the index of refraction was used to characterize the acid oxalate of gadolinium. Table 18 lists the measured indices of refraction of the rare earth acid oxalates.

E. Infrared Spectra

All of the rare earth acid oxalate trihydrates gave identical infrared absorption spectra when examined in KBr medium. Principal bands appearing in the spectra were located at 1645 cm^{-1} (Vas ) and 1430 cm^{-1} (Vs ). No apparent difference was noticed between the spectra of the acid oxalates and those of the normal oxalates. The observed spectra were identical with the reported literature data.(51) Table 19 summarizes the infrared spectral data. The infrared spectra of erbium acid oxalate trihydrate, erbium oxalate hexahydrate, and oxalic acid dihydrate are given in Figures 11-13.

TABLE 18. RARE EARTH ACID OXALATE INDICES OF REFRACTION

Compound	$n_D^{25°}$
$HGd(C_2O_4)_2 \cdot 3H_2O$	1.580-1.585
$HTb(C_2O_4)_2 \cdot 3H_2O$	1.575-1.580
$HDy(C_2O_4)_2 \cdot 3H_2O$	1.590-1.595
$HHo(C_2O_4)_2 \cdot 3H_2O$	1.585-1.590
$HEr(C_2O_4)_2 \cdot 3H_2O$	1.585-1.590
$HYb(C_2O_4)_2 \cdot 3H_2O$	1.580-1.585
$HY(C_2O_4)_2 \cdot 3H_2O$	1.570-1.575

TABLE 19. INFRARED SPECTRAL DATA FOR RARE EARTH ACID OXALATE TRIHYDRATES, ERBIUM OXALATE HEXAHYDRATE, AND OXALIC ACID DIHYDRATE

Compound	Frequency (cm^{-1})									
$HGd(C_2O_4)_2 \cdot 3H_2O$	482	807	1050	1320	1360	1480	1645	3410	3550	3620
$HTb(C_2O_4)_2 \cdot 3H_2O$	484	805	1047	1318	1360	1475	1645	3410	3545	3620
$HDy(C_2O_4)_2 \cdot 3H_2O$	482	807	1049	1320	1360	1480	1650	3410	3550	3620
$HHo(C_2O_4)_2 \cdot 3H_2O$	483	808	1048	1318	1360	1480	1645	3410	3550	3625
$HEr(C_2O_4)_2 \cdot 3H_2O$	483	810	1048	1315	1360	1480	1645	3410	3550	3620
$HYb(C_2O_4)_2 \cdot 3H_2O$	482	810	1050	1320	1360	1480	1650	3410	3550	3625
$HY(C_2O_4)_2 \cdot 3H_2O$	483	805	1047	1318	1360	1480	1645	3410	3550	3620
$Er_2(C_2O_4)_3 \cdot 6H_2O$	484	810	1045	1322	1360	1480	1645	3420	3540	3615
$H_2C_2O_4 \cdot 2H_2O$	590	722	1118	1255	—	—	1685	3480	—	—

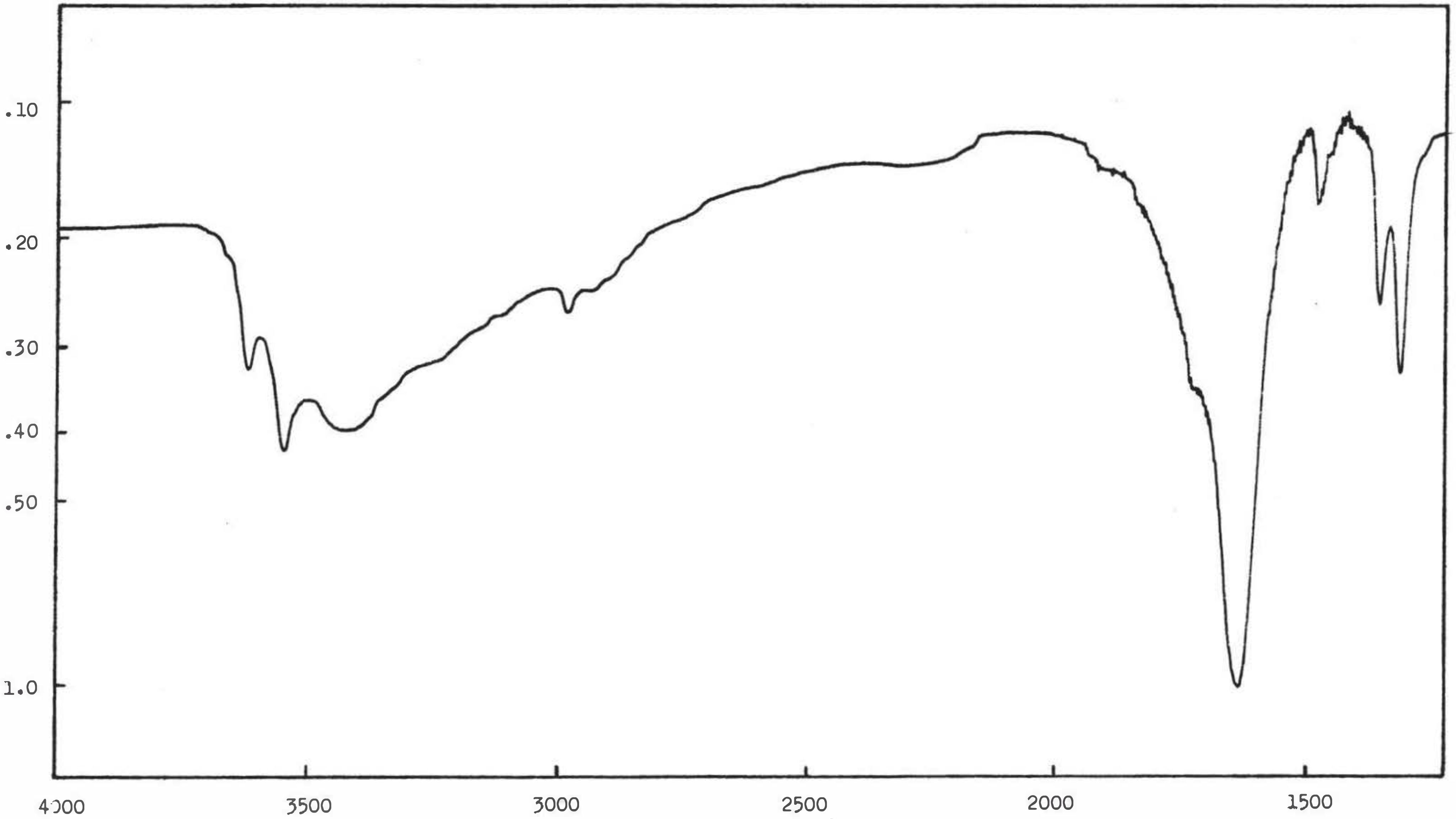


Figure 11(a)
Erbium Acid Oxalate Trihydrate

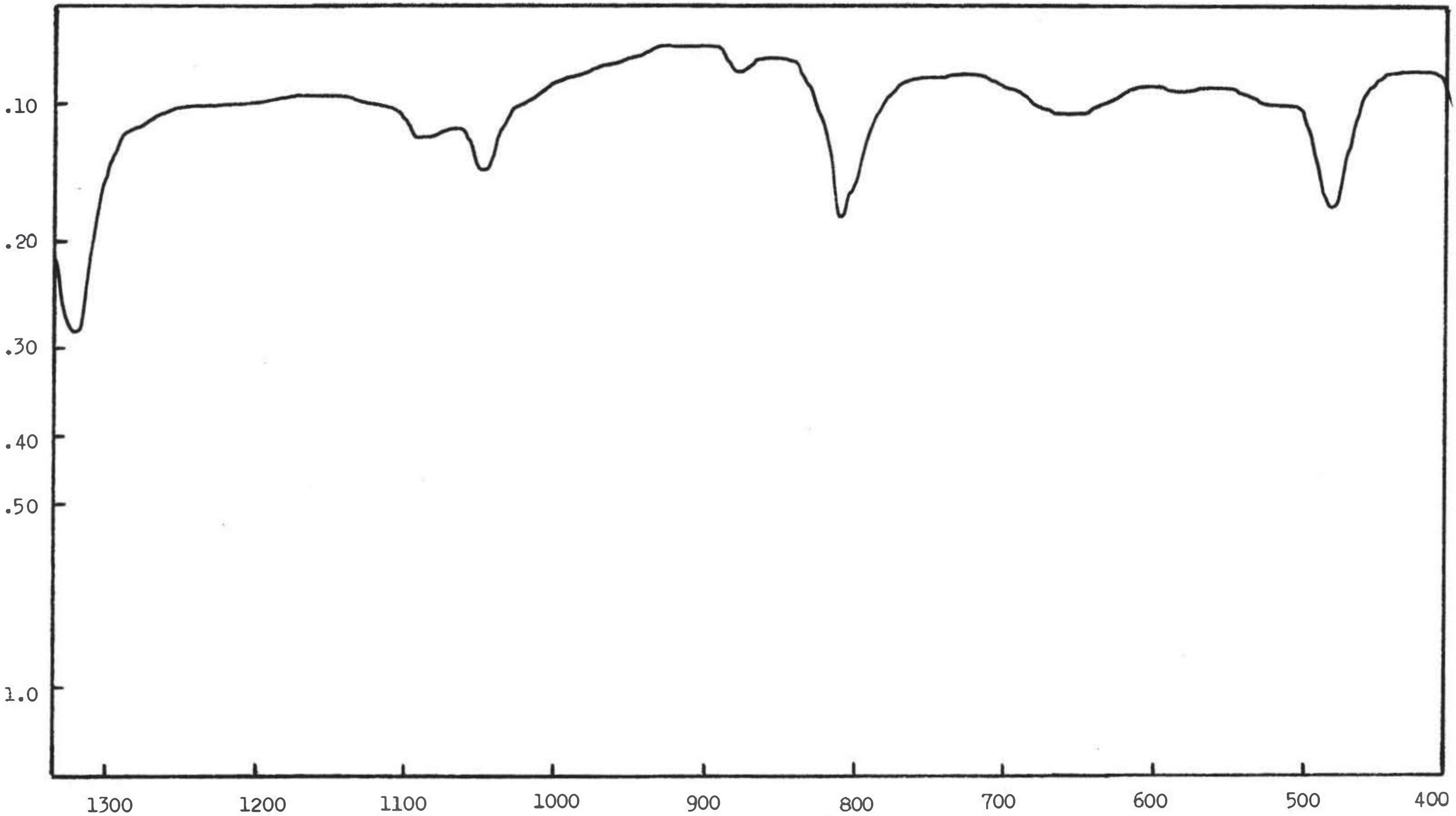


Figure 11(b)
Erbium Acid Oxalate Trihydrate

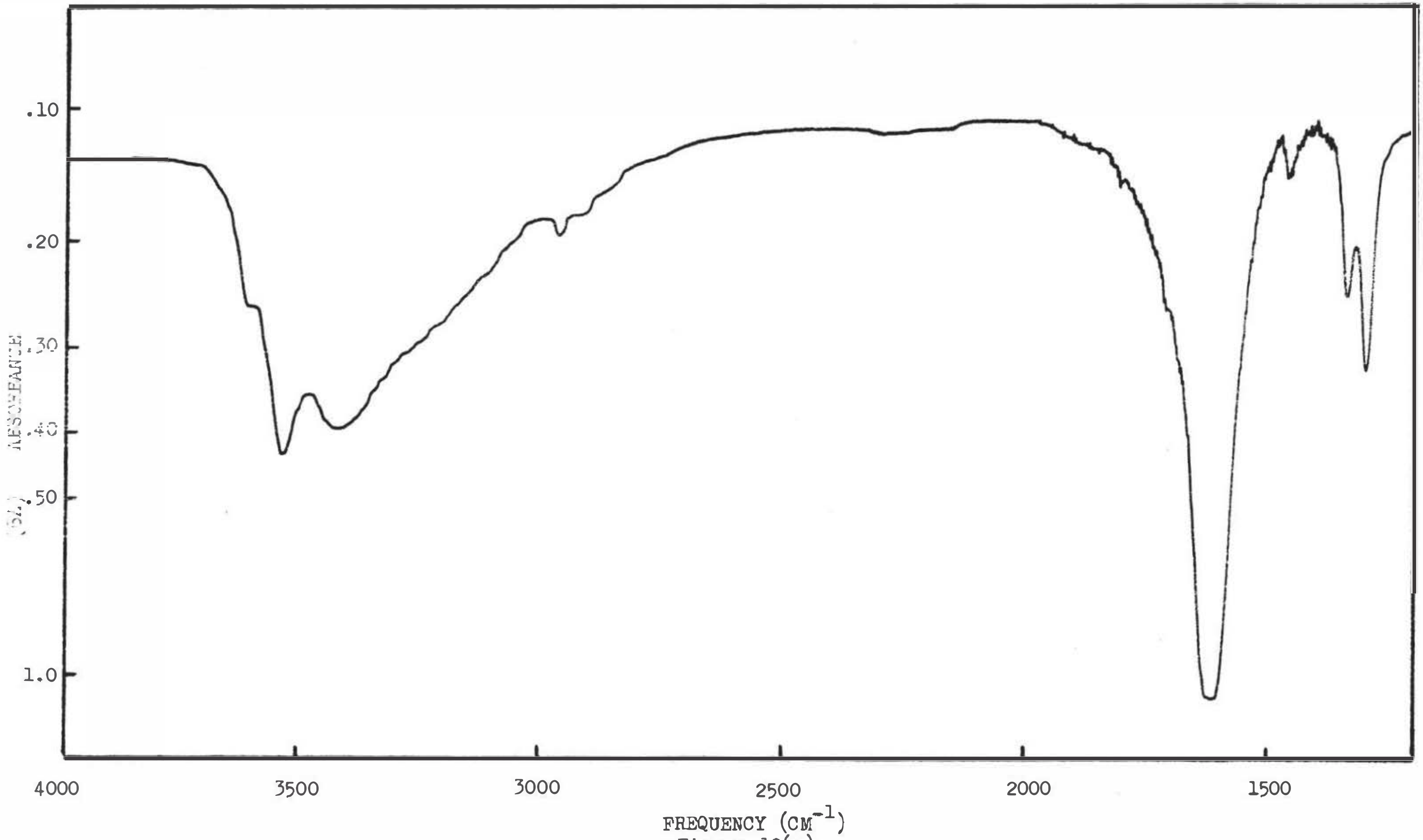


Figure 12(a)
Erbium Oxalate Hexahydrate

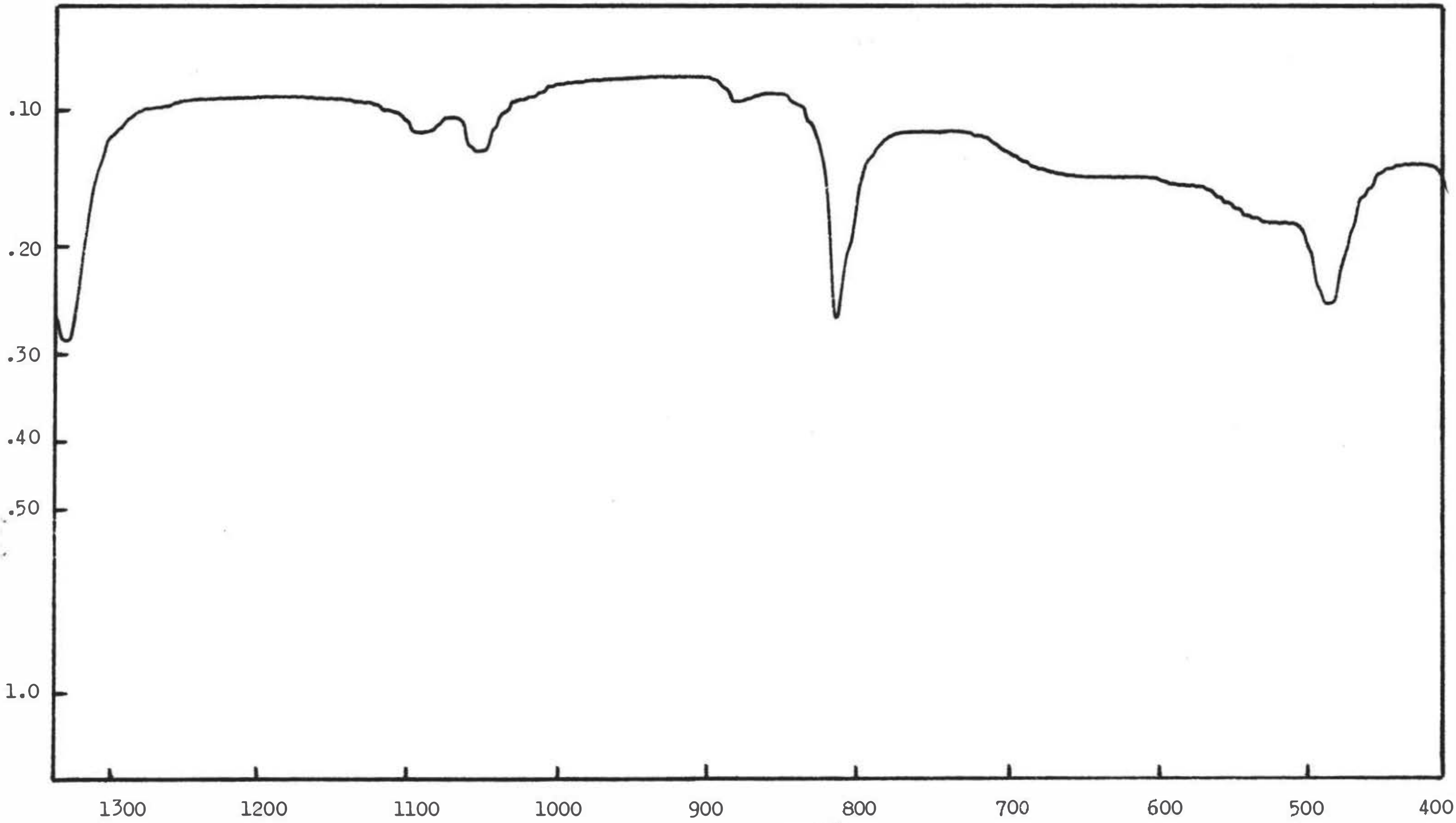
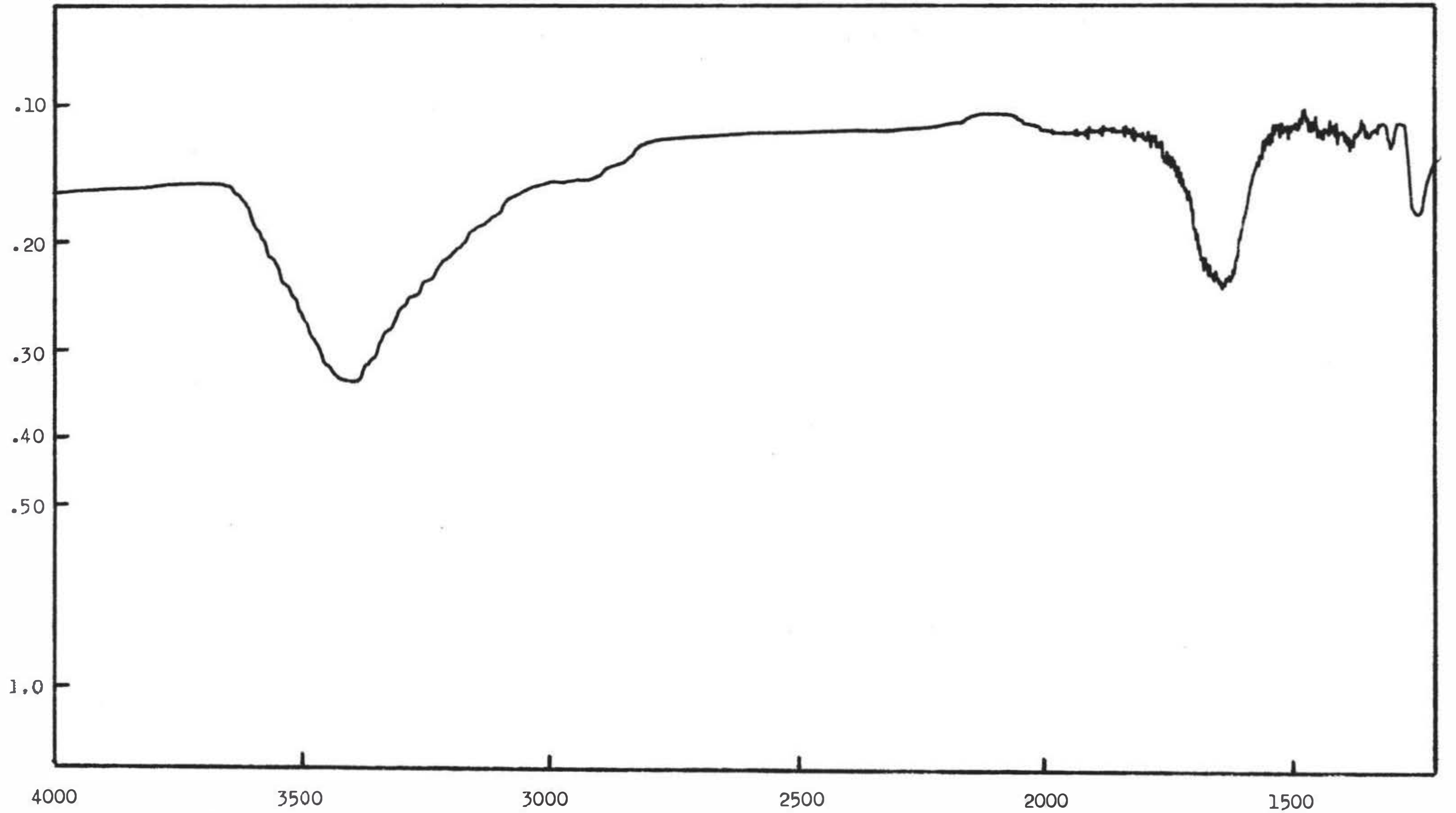
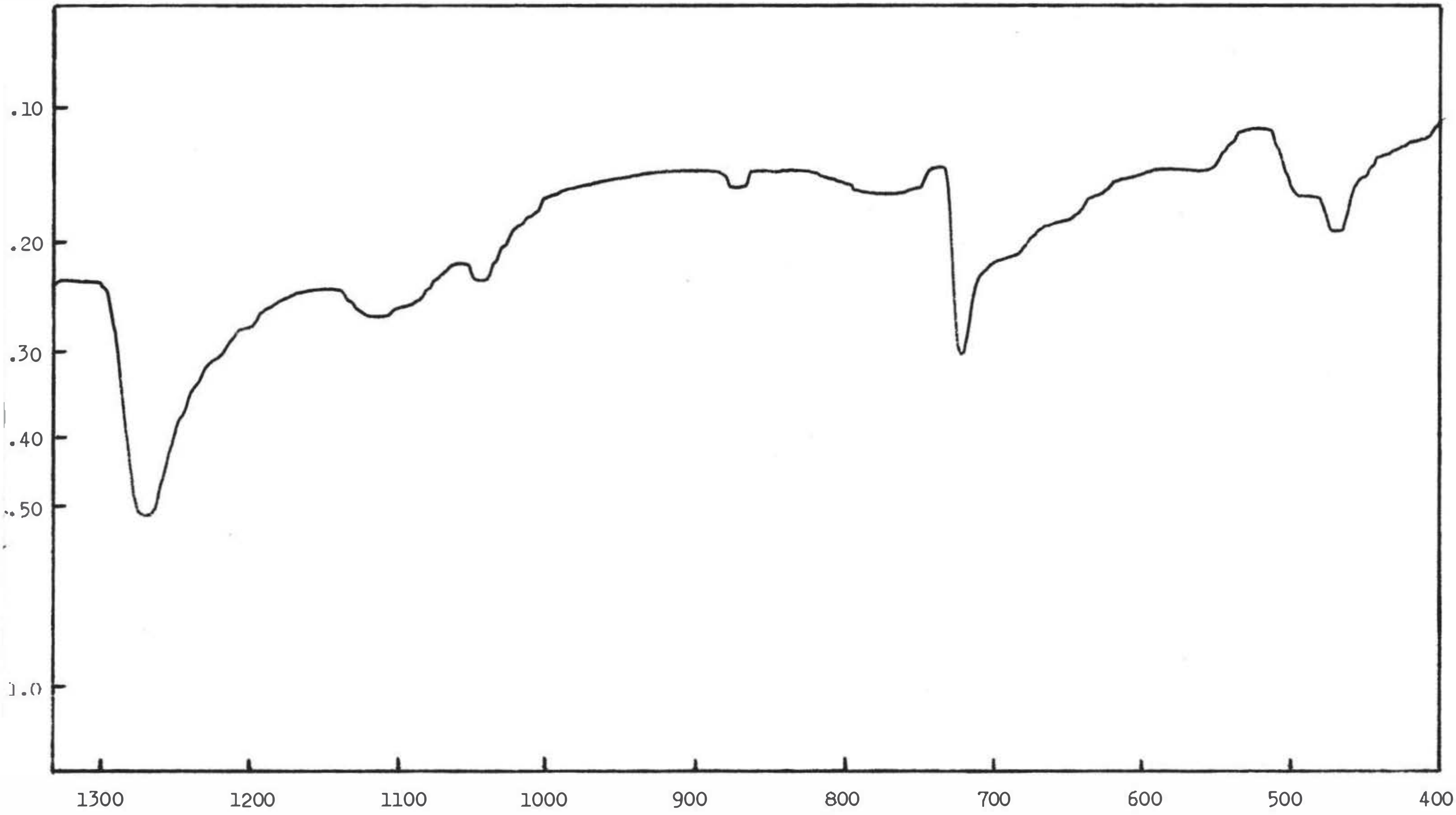


Figure 12(b)
Erbium Oxalate Hexahydrate



FREQUENCY (CM^{-1})
Figure 13(a)
Oxalic Acid Dihydrate



FREQUENCY (CM^{-1})
Figure 13(b)
Oxalic Acid Dihydrate

Chapter IV.

CONCLUSION

A. Summary

The normal oxalate hydrates of erbium, terbium, holmium, dysprosium, ytterbium, gadolinium, and yttrium form acid oxalates of type, $HRE(C_2O_4)_2 \cdot 3H_2O$, when dissolved in concentrated hydrochloric acid. X-ray diffraction studies confirm the lattice parameters reported by Steinfink and Brunton for the erbium analogue ($a_o = 8.6654 \pm 0.0003$ Å, $c_o = 6.4209 \pm 0.0008$ Å). The lattice parameters for the acid oxalate trihydrates of terbium, holmium, dysprosium, ytterbium, gadolinium, and yttrium have been determined. The acid oxalate trihydrates are all isomorphous and belong to the tetragonal crystal system. The indices of refraction of the rare earth acid oxalates have also been measured.

Thermal gravimetric analysis studies of erbium acid oxalate trihydrate indicated that loss of water began at 110° C and continued until a stable monohydrate was reached at 154° C. The monohydrate was stable from 154° C to 192° C, after which loss of one mole of CO_2 converted the monohydrate to the stable compound $HEr(C_2O_4) \cdot CO_2 \cdot H_2O$ at 334° C.

B. Suggestions for Additional Research

1. Examine in detail the solubilities of the normal oxalates of gadolinium and terbium in hydrochloric acid and explain the break in chemical properties between the two elements.

2. Sarver and Brinton report the solubility of the anhydrous light rare earth oxalates to be approximately 1.4 grams per 100 grams of solution in 3.20 N hydrochloric acid. Prepare the anhydrous oxalates of the light rare earths and determine if they will form the acid oxalates.

3. Möbius and Matthes report that the normal oxalates of lanthanum, cerium, praseodymium, and neodymium form oxalate chlorides of the type, $RE(C_2O_4)Cl \cdot 3H_2O$, when dissolved in concentrated hydrochloric acid at room temperature. No structure determinations have been carried out on these compounds. Characterize the oxalate chlorides by X-ray diffraction methods.

PROGRAM 1.

```
FORTRAN    IV    G    LEVEL    18          MAIN          DATE = 70271       13/57/41      PAGE 0001

                C       TABLE OF CALCULATIONS FOR DIFFRACTION PATTERNS FROM X-RAY POWDER
                C       PHOTOGRAPHY
                C
                C       INPUT DATA REQUIREMENTS:
                C       ——FIRST CARD IS EXACTLY REPRODUCED UNDER THE TITLE — "COMPOUND
                C       DESCRIPTION"
                C       ——SECOND CARD IS EXACTLY REPRODUCED UNDER THE TITLE — "FILM
                C       DESCRIPTION"
                C       ——THIRD CARD IS EXACTLY REPRODUCED UNDER THE TITLE — "OPERATOR"
                C       ——FOURTH CARD CONTAINS PATTERN CENTER VALUES AT COLUMNS 1-10
                C       (F10.2) AND COLUMNS 11-20 (F10.2) AS WELL AS CAMERA SIZE IN
                C       COLUMNS 21-30 (F10.2).  ALL VALUES ARE ASSUMED TO BE DIMENSIONED
                C       IN MILLIMETERS AND THE FIRST PATTERN CENTER VALUE IS ASSUMED
                C       SMALLER THAN THE SECOND PATTERN CENTER VALUE.
                C       ——ALL REMAINING CARDS (EXCEPT THE LAST CARD) CONTAIN A
                C       DIFFRACTION PATTERN POSITION IN COLUMNS 1-10 (F10.2)9 VALUE IS
                C       ASSUMED TO BE DIMENSIONED IN MILLIMETERS.
                C       ——LAST CARD SHOULD BE A BLANK CARD.
                C
0001                    DOUBLE PRECISION A(10)
0002                    WRITE(6,600)
0003              6000 FORMAT('1 TABLE OF CALCULATIONS FOR DIFFRACTION PATTERNS FROM X-RAY
                     1 POWDER PHOTOGRAPHY',//)
0004                    READ(5,500)(A(I),I=1,10,1)
0005               500 FORMAT(10A8)
0006                    WRITE(6,601)(A(I),I=1,10,1)
0007               601 FORMAT(' COMPOUND DESCRIPTION — ',10A8)
```

PROGRAM 1. (CONTINUED)

```
FORTRAN   IV   G   LEVEL   18          MAIN          DATE = 70271       13/57/41     PAGE 0002

0003              READ(5,500)(A(I),I=1,10,1)
0009              WRITE(6,602)(A(I),I=1,10,1)
0010       602    FORMAT('FILM DESCRIPTION — ',10A8)
0011              READ(5,500)(A(I),I=1,10,1)
0012              WRITE(6,603)(A(I),I=1,10,1)
0013       603    FORMAT(' OPERATOR — ',10A8,//)
0014              READ(5,501) PC1,PC2,CAMERA
0015       501    FORMAT(3F10.2)
0016              WRITE(6,604)PC1,PC2,CAMERA
0017       6040   FORMAT(' PATTERN CENTERS AT ',F7.2,' MM. AND ',F7.2,' MM. USING ',
             1    F7.2,' MM. CAMERA.',//)
0018              WRITE(6,605)
0019       6050   FORMAT(' LINE      S        S UNCORR   S CORR    ANGLE Q     SIN(Q)     2
             1    *SIN(Q)      D'/'   HR       (MM)       (MM)      (MM)      (DEG)',23x,
             2    '(ANGSTROM)',/)
0020              N=0
0021       10     N=N+1
0022              READ(5,502) S
0 23       502    FORMAT(F10.2)
0024              IF(S)12,12,11
0025       12     RETURN
0026       11     SUNCOR=S-PC1
0027              SCORR=SUNCOR*180.0/(PC2-PC1)
0028              Q=SCORR/INT(CAMERA/57.295)
0029              QNIS=SIN(Q*3.14149/180.0)
0030              QNIS2=2.0*QNIS
0031              D=1.539/QNIS2
0032              WRITE(6,606)N,S,SUNCOR,SCORR,Q,QNIS,QNIS2,D
0033       6060   FORMAT(' ',I2,3X,F8.2,2X,F8.2,1X,F9.3,1X,F9.3,2X,F8.6,1X,F9.6,2X,
             1    F8.4)
0034              GO TO 10
0035              END
```

PROGRAM 2.

```
FORTRAN IV G LEVEL 18              MAIN          DATE = 70215        23/20/00      PAGE 0001

       C     INTERPLANAR SPACINGS CALCULATED FROM LATTICE CONSTANTS FOR ERBIUM ACID
       C     OXALATE TRIHYDRATE
       C     KEN PYLES BOX 120
             INTEGER H,HH
             WRITE(6,601)
         601 FORMAT('1  H  K  L     D'/)
             A=8.6664
             C=6.4209
             DO 10 HH=1,9,1
             DO 10 KK=1,9,1
             DO 10 LL=1,9,1
             H=HH-1
             K=KK-1
             L=LL-1
             D=SQRT(1.0/(((H*H+K*K)/(A*A))+(L*L/(C*C))))
          10 WRITE(6,602)H,K,L,D
         602 FORMAT(1X,3I3,1X,F6.2)
             RETURN
             END
```

Chapter V.

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