uranyl tricarbonate to reach the ratio of 0.5:1) does appear to rule out bicarbonate or hydroxy–bicarbonate complexes unless there is higher polymerization. It should be noted that the calculations which follow concerning the tricarbonate and dicarbonate complexes do not depend on this formulation nor even on the existence of a complex at this ratio.

The region around $2CO_3$:U was also re-examined using series at constant *p*H, here at *p*H 8.0 and 7.5. These absorptions match the former series at 1:1 (which was also at *p*H~8) and at $3CO_3$:U. With the effect of changing *p*H eliminated, these series show an appreciable break near $2CO_3$:U. However, the breaks are still not well defined, since at this uranium concentration level the absorption is still dominated by the highly colored hydrolytic species. The third series shown on this figure was made at uranium concentrations an order of magnitude higher,[24] with *p*H 6.5–7.5. These were prepared by equilibrating sodium carbonate solutions of uranyl carbonate with carbon dioxide at various known partial pressures. Here the higher concentration suppressed hydrolysis of the uranium, so that the break near $2CO_3$:U was well developed. From the optical densities of the solutions above $2.2CO_3$:U, which can be considered essentially free from the hydrolytic species, in combination with the coefficient already evaluated for the tricarbonate ion, the molar extinction coefficient of the dicarbonate ion was found to be 23.4 at 438 mμ. This has been confirmed by Bullwinkel[8] with a value of about 22.[23]

The chemical analyses of the solutions shown to be free of hydrolysis, together with the carbon dioxide pressure, were sufficient for evaluation of the approximate equilibrium concentration quotient for the dissociation of tricarbonate to dicarbonate

$$UO_2(CO_3)_3^{-4} \rightleftarrows UO_2(CO_3)_2^{-2} + CO_3^{-2} \qquad (6)$$

$$K_{3(\mathrm{conc})} = C_D C_{CO_3}/C_T \approx 3 \times 10^{-4}\ (\mu \approx 2)$$

The amount of hydrolyzed uranium in the two solutions showing the highest optical density in this series was estimated by material balance, and the molar extinction coefficient of the hydrolyzed species was estimated to be in the order of 125 at 438 mμ in terms of monomeric uranium (*i.e.*, 250 for $U_2O_5OHCO_3^-$, if that formulation be correct). With the aid of the three extinction coefficients, concentrations were calculated for the solutions at low carbonate ratios. The estimate of $K_{3\text{-}(\mathrm{conc})}$ which results was in good agreement with that from solutions at the higher carbonate levels: 2.3×10^{-4} (μ = 1–3.6) average from the four solutions at $2CO_3$:U and lower, 3.6×10^{-4} (μ = 1.6–2.6) average from the six solutions at $2.2CO_3$:U and higher. Bullwinkel[8] has reported a constant of 6×10^3 for the reverse reaction, corresponding to about 1.7×10^{-4} for the reaction as written here, calculated presumably for infinite dilution.

Acknowledgment.—Most of the chemical analyses were made by the ORNL Analytical Division under the supervision of Dr. M. T. Kelley and Mr. C. D. Susano.

OAK RIDGE, TENN.

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[24] The actual uranium concentrations varied from 0.22 to 1.3 *M*. The corresponding optical densities at 0.35 *M* were calculated after establishing conformation to Beer's law.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Anhydrous Reduced Halides of Zirconium and Hafnium[1]

BY EDWIN M. LARSEN AND JAMES J. LEDDY

RECEIVED JULY 9, 1956

A study was made of reactions of the type $M(s) + 3MX_4(g) = 4MX_3(s)$, where M refers to zirconium or hafnium, and X refers to F, Cl, Br or I. A pseudo-equilibrium position, found by plotting the extent of reaction *versus* reaction time, occurred after the reaction had proceeded for 36 to 48 hours. It shifted in favor of the reaction product with increasing temperature, in the range 200 to 700°, and/or increasing pressure, in the range 5 to 15 atm. The ease of reduction of MX_4 increased considerably from chloride to iodide, and very slightly from hafnium to zirconium. No reaction was found to occur under the above conditions between MF_4 and M. The disproportionation reactions were followed both macroscopically and by an X-ray method. The rates of disproportionation appeared to be appreciable only at temperatures above 450°.

One aspect of the chemistry of zirconium and hafnium that has received little attention is the chemistry of the lower oxidation states. Earlier work on the reduction of zirconium tetrachloride with aluminum metal in liquid aluminum chloride[2] yielded a zirconium trichloride that was contaminated with aluminum oxide and zirconium oxide. Zirconium tribromide was prepared in a higher state of purity by reducing zirconium tetrabromide with aluminum wire in a hydrogen atmosphere at 650° in a "hot-cold" tube.[3] The only work on the hafnium trihalides was done by Schumb and Morehouse[4] who repeated the experiments of Young and Schumb[3] with hafnium tetrabromide. Although zirconium triiodide has been observed to form,[5] no samples were analyzed or studies made with this compound inasmuch as metal production was the object of the investigation. No significant difference between the behavior of the zirconium and hafnium bromides was reported. No work has been reported on the lower fluorides.

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[1] Based on a thesis submitted by James J. Leddy in partial fulfillment of the requirements for the degree of Doctor of Philosophy. General Electric Co. Fellow, 1954–1955. Work carried out in part under Task Order 4 of Contract N7-onr-28504 between the Office of Naval Research and the University of Wisconsin. Presented at the September, 1955, Minneapolis Meeting of the American Chemical Society before the Division of Physical and Inorganic Chemistry.

[2] O. Ruff and R. Wallstein, *Z. anorg. Chem.*, **128**, 96 (1923).

[3] R. C. Young and W. C. Schumb, THIS JOURNAL, **53**, 2148 (1931).

[4] W. C. Schumb and C. K. Morehouse, *ibid.*, **69**, 2696 (1947).

[5] J. D. Fast, *Z. anorg. allgem. Chem.*, **239**, 145 (1938).

It was the purpose of this work to obtain more definitive information regarding these reduced compounds. To this end, a convenient preparative method was devised which involved treating M with MX_4 at high temperatures and pressures. Metallic zirconium and hafnium were chosen as the reductants in order to least complicate the analytical and X-ray procedures.

Experimental

Completely anhydrous conditions were maintained by carrying out all preparations, transfers and samplings either *in vacuo* or in a dry nitrogen atmosphere. The latter was pro vided by a dry-box of the type described by Tyree.[6]

Preparation of Starting Materials.—The MX_4 species were produced by the following three methods: (1) thermal decomposition of $(NH_4)_3MF_7$ at 350° to prepare MF_4; (2) reaction of a 2:1 sugar-charcoal MO_2 mixture with chlorine or bromine in a carrier gas, such as nitrogen, at 650° to prepare MCl_4 and MBr_4; and (3) reaction of near stoichiometric amounts of MH_2 or M and iodine at 500° to prepare MI_4. Successive sublimations yielded one to two gram amounts of these tetrahalides sealed in small glass ampules which were stored in the dry-box.

The original zirconium and hafnium starting materials were supplied by the Atomic Energy Commission both in the form of the oxides and sponge metals. The zirconium had a hafnium impurity of 125 p.p.m. and the hafnium contained 1.7% zirconium. The atomic weight of hafnium was corrected accordingly.

Finely divided zirconium and hafnium metals were prepared from the sponge material by successively (1) breaking the sponge lumps in a steel mortar to a less than 200 mesh powder; (2) heating in a Vycor hydrogenation line at 1000° in a hydrogen atmosphere for six hours; and (3) heating in the same apparatus *in vacuo* for 18 hours. If the hydride were desired, step (3) was omitted and the metal allowed to cool slowly in the hydrogen atmosphere. Zirconium hydride and some powdered zirconium, each containing a 1.8% hafnium impurity, were obtained from Metal Hydrides, Inc.

Reductions.—Some initial experiments at 200° indicated that the rate of the solid-solid reaction between MX_4 and reductant was quite slow. It was decided to carry out the reductions using gaseous MX_4. The problem, however, was that unless the entire apparatus were maintained at or above 350° the undesirable condensation of MX_4 occurred. A flow system such as that used by Young[3] was tried without much success. Hence, there had to be devised a means of carrying out the reductions by which the reductant and gaseous MX_4 could be contained in a sealed glass ampule at higher temperatures. However, with the quantities and size ampule used, the pressures inside the ampule were greater than the Pyrex could stand. To offset this pressure effect the evacuated, sealed ampule containing stoichiometric amounts of MX_4 and reductant was placed inside a stainless steel bomb in a furnace (Fig. 1). The bomb was connected *via* a metal trap and flexible copper tubing to a cylinder of nitrogen. A 300 p.s.i. gage on the trap indicated the pressure which could be exerted on the outside wall of the reaction ampule by admitting nitrogen from the cylinder into the bomb. The initial pressure against the inside wall of the ampule was calculated from a knowledge of the furnace temperature and the amount of MX_4 present. An apparent difficulty was the change in inside pressure as the reaction ensued. Fortunately, it was not difficult for the Pyrex ampules to stand a pressure differential of three or four atmospheres. Thus, as the reaction proceeded its extent was approximated, and using this estimate of the amount of MX_4 remaining, the inside pressure was recalculated and matched by adjusting the nitrogen pressure. Larger scale reductions were carried out directly in evacuated stainless steel bombs.

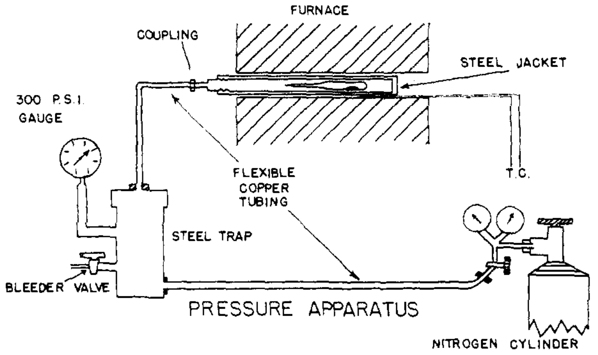

Fig. 1.—Pressure apparatus.

The procedure used throughout was to add approximately one gram of MX_4 to a weighed 15 × 80 mm. Pyrex ampule having an 8 cm. long neck of 10 mm. tubing to which a $^{14}/_{35}$ standard-tapered outer joint was sealed. Vycor ampules were constructed for the 700° work. The amount of reductant required by the stoichiometry $M(s) + 3MX_4(g) = 4MX_3(s)$ was weighed and added to the ampule in the dry-box. The ampule was then capped with a matching standard-tapered joint terminating in a stopcock, attached to the vacuum line, evacuated and sealed about four cm. below the joint with a hand torch. It was heated to temperature in the pressure apparatus described above. The temperature was controlled to within five degrees by a Leeds and Northrup Speedomax Type G Model S recording-controller, using a chromel-alumel thermocouple. When the reaction time was completed the furnace was shut off and a cold air blast directed at that portion of the jacket which contained the 10 mm. section of the ampule. In this way, rapid cooling was assured and in all cases the unreacted MX_4 condensed in the 10 mm. tip. The ampule was removed from the jacket and the residue and sublimate portions separated by sealing the ampule in two with the hand torch. The colors of the residues were brown for the chloride to reddish brown for the iodides. The colors of the zirconium and hafnium compounds were indistinguishable.

The MX_3 residue and MX_4 sublimate samples were opened in the dry-box and weighed samples were taken for analysis. The samples in weighing bottles were quickly dumped into glass stoppered erlenmeyer flasks which contained about 50 g. of ice. As the ice melted a vigorous reaction occurred. With the non-sublimable residue, hydrogen was given off and a yellow-brown colloidal solution resulted. This eventually cleared and some brown MX_3 settled to the bottom. It was apparently insoluble in the water but continued to react

TABLE I

TYPICAL ANALYSES OF REACTION PRODUCTS—500°

Sample	M,[a] %	X,[a] %	X/M[b]
Residue	46.37, 46.30	53.82, 53.91	2.99
$ZrCl_4$	(46.48)	(53.52)	
Sublimate	39.35, 39.29	62.08, 62.15	4.06
	(39.44)	(62.56)	
Residue	27.56, 27.71	72.43, 72.39	2.98
$ZrBr_4$	(27.81)	(72.19)	
Sublimate	22.59, 22.47	77.81, 77.65	3.94
	(22.42)	(77.58)	
Residue	19.45, 19.48	80.63, 80.40	3.10
ZrI_4	(19.52)	(80.48)	
Sublimate	15.25, 15.40	85.01, 84.45	3.94
	(15.39)	(84.61)	
Residue	62.51, 62.21	38.11, 37.98	3.03
$HfCl_4$	(62.16)	(37.84)	
Sublimate	55.01, 55.08	45.12, 45.01	4.05
	(55.19)	(44.81)	
Residue	42.47, 42.33	58.11, 58.82	3.04
$HfBr_4$	(42.29)	(57.71)	
Sublimate	35.21, 35.43	64.50, 64.62	4.06
	(35.47)	(64.53)	
Residue	31.62, 31.85	68.50, 68.45	3.01
HfI_4	(31.58)	(68.42)	
Sublimate	25.75, 25.58	74.18, 74.23	4.03
	(25.71)	(74.29)	

[a] Values in parentheses are the theoretical values for MX_3 and MX_4. [b] Atomic ratio.

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(6) S. Y. Tyree, Jr., *J. Chem. Ed.*, **31**, 603 (1954).

with it, although more slowly. After an hour or so all reaction had ceased, a clear slightly brown acidic solution resulted and a small amount of gray metallic zirconium or hafnium remained at the bottom of the flask. This unreacted metal was passive to water and could be very simply filtered from the hydrolyzed product. In this way the per cent. reaction was found and complete analyses of the hydrolyzable portion of the residue and the sublimate were obtained. Typical analytical data for both residue and sublimate appear in Table I. The sublimate was always found to be MX_4. There seems to be no question but that the residual materials are trivalent zirconium and hafnium compounds.

Mixtures of the metal fluorides and metal were prepared in the same way as the other metal halide-metal systems. However, even after heating to 700° for 72 hours no evidence for any reduction was observed as the metal was recovered almost quantitatively after separation from the metal tetrafluoride by sublimation.

The metals were determined in the usual way as the oxides. The chloride, bromide and iodide were titrated with a 0.05 *M* silver nitrate solution, using the adsorption indicator method, with fluorescein as the chlorine indicator and eosin as the bromide and iodide indicator.

The data representing the extent of reaction as a function of time and temperature are summarized in the accompanying diagrams (Figs. 2, 3, 4). The per cent. reaction was calculated in the basis of the amount of unreacted metal. Fortunately, the stoichiometry in this reaction is very favorable for the production of the reduced state, for even with 40% reaction, the weight per cent. purity of the zirconium trichloride product was about 85%. The effect of pressure on the yield is shown in Table II.

TABLE II

EFFECT OF PRESSURE ON THE 48 HOUR REACTION $M + 3MBr_4 = 4MBr_3$ at 500°

Initial wt. MBr_4, g.	Initial pressure, atm.	Initial wt. M, g.	% Reaction	
0.5961	4.6	0.0745	54.1	M = Zr
1.0955	8.4	.0730	65.9	
1.4769	11.3	.0751	73.5	
2.0031	15.4	.0735	76.7	
2.4098	18.5	.0772	82.9	
1.1569	7.3	0.1196	64.3	M = Hf
2.7051	17.1	0.1179	79.4	

X-Ray diffraction patterns of most of the residues and some of the sublimates were routinely obtained for identification purposes. Nickel-filtered, copper $K\alpha_{1,2}$ radiation produced in a Norelco diffraction unit was used throughout. A 57.3 mm. diameter powder camera was used with a slit focused beam. Trihalides of greater than 99% purity, prepared by repeatedly regrinding MX_3 residues with a large excess of MX_4 and reheating for 12 hours, were used to obtain diffraction photographs with a 114.6 mm. powder camera and a point focused X-ray beam. The analysis of these data will be presented in full in a forthcoming publication.

Equivalent Weight of MX_3 as a Reducing Agent.—The amount of hydrogen evolved when a weighed MX_3 sample was hydrolyzed in water was used as a measure of the reducing power. The data are presented in Table III. A weighed sample was introduced to a 25-ml. graduated cylinder containing 20 g. of ice. At the top of the cylinder was a standard-tapered outer joint into which an adapter was inserted. The adapter was simply a short length of capillary tubing of known volume which led to a buret. The buret formed one leg of a manometer. After constant pressure was attained, the amount of hydrogen evolved was determined from a knowledge of the total volume and the pressure due to dry hydrogen. The total volume was determined as the sum of the liquid free graduated volumes in the cylinder and manometer plus the volume in the adapter. Equivalent weights were found to agree within 10% of those theoretically required for MX_3. These data further substantiated the stoichiometry of MX_3.

Disproportionations.—In agreement with earlier workers[2-5] the MX_3 species were found to disproportionate into MX_4 and MX_2, the MX_2 disproportionating, in turn, to M and MX_4. However, the rates of disproportionation became appreciable only at temperatures above 450°, somewhat higher than those previously reported. This was determined both by macroscopic experiments and by *in situ* capillary experiments, for which a Buerger type high temperature X-ray camera[7] was used. In the former experiments, a weighed amount of MX_3 was inserted into the tip of an 80 cm. length of 8 mm. Pyrex tubing. This was evacu-

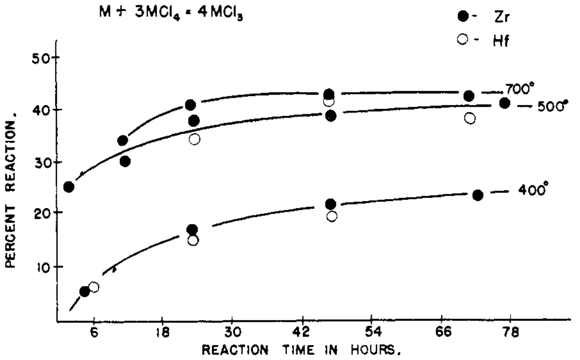

Fig. 2.

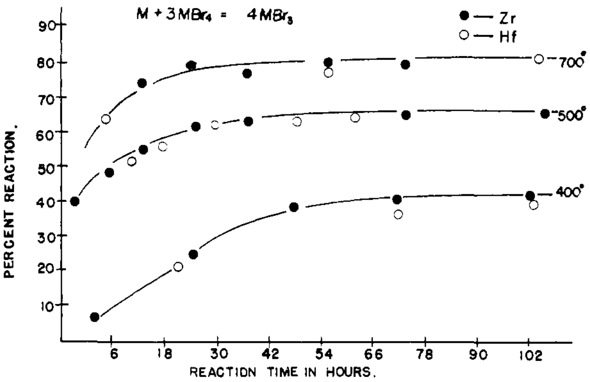

Fig. 3.

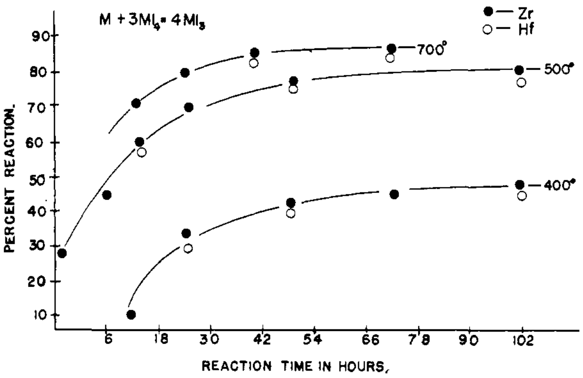

Fig. 4.

TABLE III

EQUIVALENT WEIGHT OF MX_3

Compound	Cor. sample wt., g.	Ambient temp., °C.	Cor. vol. H_2, ml.	Equiv. wt., g.[a]
$ZrCl_3$	0.9183	21.6	50.3	205 (198)
$ZrBr_3$	1.2591	22.8	39.2	361 (331)
ZrI_3	1.3121	22.4	29.7	494 (472)
$HfCl_3$	0.9910	30.5	36.9	301 (282)
$HfBr_3$	1.0633	22.8	25.7	463 (415)
HfI_3	1.2673	30.5	24.0	591 (556)

[a] The values in parentheses are the theoretical values.

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(7) M. J. Buerger, *Am. Mineralogist*, **28**, 285 (1943).

ated, sealed, and the end containing the MX_3 was placed inside a copper block liner in a tube furnace. With the temperature controlled as described previously, sublimate was allowed to collect for a given period of time and then quickly flamed into a short section at the end of the Pyrex tube. This section was sealed from the tube with a hand torch and analyses made. Typical data appear in Table IV. The residues were black in color and pyrophoric. In no cases were pure MX_2 compounds obtained.

MX_3 samples in quartz capillaries were heated and diffraction photographs taken in a 57.3 mm. high temperature X-ray camera. The principal lines from each diffraction photograph were used to identify the predominant species in the sample. No significant changes in the X-ray patterns were noted until temperatures above 450° were reached. Unless the powder patterns of the MX_3 and MX_2 species are alike, this X-ray work suggested that the rate of decomposition of the reduced species was much slower than indicated by previous workers.

TABLE IV

DISPROPORTIONATION REACTIONS

Initial MCl_3, g.	Temp., °C.	Reaction time, hr.	Wt. sublimate, g.	% M Residue Obsd.	% M Calcd. MCl_3	% M Calcd. MCl_2
$ZrCl_3$	250	6	0.0152			
0.6591	300	6	.0271			
	400	8	.1134			
	500	4	.1396	50.27	46.17	56.26
$ZrBr_3$	300	6	0.0085			
0.3460	350	6	Trace			
	400	6	0.0137			
	425	6	.1553			
	450	4	.0052	34.16	27.56	36.34
ZrI_3	300	2	Trace			
0.9382	325	2	Trace			
	350	20	0.0031			
	400	24	.0058			
	450	8	.1797	19.70	19.33	26.44
$HfCl_3$	300	6	0.0319			
0.8753	400	4	.1041			
	450	3	.0089			
	500	14	.1165			
	525	3	.1053			
	550	6	.1394	69.62	62.29	71.25
$HfBr_3$	250	3	Trace			
0.5251	300	8	0.0103			
	325	8	.0191			
	350	4	.0097			
	425	8	.1810			
	450	5	.0076	44.38	42.29	52.36
HfI_3	300	4	0.0019			
1.0090	325	4	.0105			
	350	16	.0083			
	400	24	.0196			
	450	8	.2699	36.91	31.58	40.91

Discussion

From the level portions of the per cent. reaction *versus* reaction time curves, it is tempting to conclude that equilibrium has been attained. However, on the basis of the following reasoning it must be concluded that at the lower temperatures at least, equilibrium was not reached. Since the reaction involves the disappearance of a gas, the system becomes more ordered and the entropy change must be negative to the extent of about −63 e.u., there being three moles of MX_4 involved. The reaction proceeds quite in favor of the products, the favoritism increasing with increasing temperature. However, it is unreasonable to suggest that the reaction is endothermic, because this along with the decrease in entropy would make the free energy change quite positive. It can only be concluded that this pseudo-equilibrium is the result of a rate phenomenon, the change in the extent of reaction with time being eventually quite small due to the necessity for the MX_4 to diffuse through the product MX_3 layer in order to react further with the remaining metal.

At the highest temperatures studied equilibrium was most likely to be attained. Certainly in the cases of the bromide and iodides at 700° the system must be close to equilibrium, since the yields are above 80%. Assuming that equilibrium has been established it can be concluded from the phase rule that only MX_3, and no MX_2, could be produced in the reaction: $M(s)+3MX_4(g) = 4MX_3(s)$; that is, provided no solid solution is formed between MX_3 and MX_2, and that the vapor pressure of MX_3 is negligible. There are two solid phases and one gas phase present at equilibrium. The temperature is held constant and the pressure varies. Thus the phase rule takes the form: $F = C - P + 1$. Since this is a two component system and the total number of phases is three, the system is invariant. Thus, there is only one solid product formed, MX_2 is eliminated, and the reaction proceeds according to the above equation. That solid solution did not occur was suggested by the X-ray data from which no evidence of solid solutions of MX_2 or M in MX_3 could be discerned.

As expected the iodides are the most easily reduced of the three, followed by the bromides and then the chlorides. No reaction was observed with the fluorides. These differences are probably related to the differences in the crystal energies of these compounds.

In each case the hafnium yields were slightly lower than the zirconium yields, although for the chlorides at high temperatures, the differences were within the reproducibility of the experiment. The difference in the ease of reduction does not appear to be great enough to utilize in a separation process.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Preparation, Crystal Structure and Some Properties of SmN, EuN and YbN[1]

BY H. A. EICK,[2] N. C. BAENZIGER AND L. EYRING

RECEIVED MAY 10, 1956

SmN, EuN and YbN were prepared by the direct combination of the metals with nitrogen. All three were found to have a NaCl-type structure with the followng lattice parameters: 5.0481 ± 0.0008, 5.007 ± 0.004 and 4.7852 ± 0.0008 A., respectively. A differential thermal analysis–thermogravimetric analysis of SmN in an atmosphere of moist nitrogen is reported. The decomposition curves showed a plateau indicating a thermally stable compound corresponding to a molecular weight of SmO(OH).

Introduction

The nitrides of samarium, europium and ytterbium have not been reported although the nitrides of some of the lighter rare earths are known. Besides the intrinsic interest in the preparation and investigation of the properties of new compounds, the nitrides of these elements are important because they are isomorphous with the monoxides and hence knowledge of their structure will aid in the identification of the lower oxides.

Experimental Part

Materials.—The samarium, ytterbium and lanthanum metals, greater than 99.9% pure, were obtained from Ames Laboratories, Ames, Iowa. The europium metal was prepared according to the method of Spedding and Daane[3] by the reduction of Eu_2O_3 (99.8% pure, obtained from Research Chemicals, Inc., Burbank, California) with lanthanum metal.

Procedure.—The metal filings were put in a small molybdenum boat which was placed in a Vycor tube along with a large quantity of titanium turnings. The tube was evacuated to better than 10^{-5} mm. pressure and maintained there for 4–6 hours. Tank nitrogen was then passed over the titanium, which had been warmed, and through the system. The system was sealed off and the titanium turnings were heated to a dull red. The sealed system was heated for 12–16 hours at 800° with europium and samarium filings and at 1020° with ytterbium filings.

When the treatment was completed the samples were removed to an argon-filled dry-box where they were opened. Capillaries were filled with the samples; they were then removed and sealed immediately.

Because the reaction of ytterbium with nitrogen proceeded so slowly, another preparation of YbN was investigated. Ytterbium turnings were placed in a Vycor reaction vessel, which was then set in the Vycor tube and evacuated. Hydrogen obtained from the thermal decomposition of UH_3 was admitted and the system heated at 500° for 12 hours. Powder diagrams of this material indicated it was YbH_2.[4] Nitrogen, purified by passage over activated copper and titanium turnings, was admitted and the Vycor tube was heated for 12 hours at a constant temperature differing among several runs from 600 to 1000°. Because of the apparent stability of both these compounds, it was unnecessary to work in a dry-box.

X-Ray powder diagrams were taken with a 114.7 mm. Debye-Scherrer powder camera. Cu $K\alpha$ ($\alpha_1 = 1.54051 \times 10^{-8}$ cm.) radiation was used for the samarium and ytterbium samples and Fe $K\alpha$ ($\alpha_1 = 1.93597 \times 10^{-8}$ cm.) radiation was used for the europium samples. The intensity was calculated according to the formula $I = LPAjF^2T$ (where $LP = (1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$; A is the absorption factor calculated according to the method of Bradley[5]; T is the temperature factor calculated from an estimated characteristic temperature θ, equal to 350; j is the multiplicity factor which is the same for both lines; F is the structure factor[6] with the atom form factor for samarium corrected for dispersion with iron radiation according to the method of Dauben and Templeton.[7]

The ytterbium sample diagrams obtained from the direct combination of Yb + N_2 could not be indexed precisely because of small particle size. Therefore, to obtain crystal growth these samples were placed in a tantalum crucible which was set inside a tantalum distillation tube. This tube was removed from the dry-box and heated by radiation from inductively heated shields to 1400° in a high vacuum or in an atmosphere of argon. Powder diagrams were taken of both the distillate and the residue.

The samarium samples were analyzed quantitatively with a micro-Kjeldahl apparatus for nitrogen content and were found to be greater than 90% SmN. However, the X-ray diagrams showed no additional phase and it is believed that the Kjeldahl method used gave consistently low results. The intensities of the reflections from planes (331) and (420) were determined with a powder spectrometer using iron radiation. The ytterbium and europium preparations were analyzed qualitatively for nitrogen.

Samples of SmN were placed on a thermal balance and weight uptake was recorded as moist nitrogen was passed over the samples at a constant temperature of 50°. At the end of 20 hours the sample was no longer gaining weight. The temperature was then elevated at about 10°/min. and a differential thermal analysis curve was obtained along with curves for the temperature and weight of the sample. Such data were not obtained for ytterbium and europium nitrides.

Results and Discussion

The black compounds, SmN, EuN and YbN were found to be of the NaCl-type structure with lattice parameters of 5.0481 ± 0.0008, 5.007 ± 0.004 and 4.7852 ± 0.0008 Å., respectively. These lattice parameters were obtained as an average of a series of determinations, with the error listed twice the root-mean-square error.

Figure 1 shows a plot of the lattice parameters of seven rare earth nitrides which have been determined against the crystal radii of their tripositive ions. The value of LaN is from the data of Young and Ziegler,[8] while the values of CeN, PrN and NdN are from the work of Iandelli and Botti[9] (converted from kX. units). This plot shows a linear correlation between the lattice parameters of most of the nitrides so far determined and their crystal radii (from the data of Templeton and Dauben[10]).

The intensities of the reflections from planes (331) and (420) were carefully measured; these planes reveal the type of structure in the face centered cubic system and are most sensitive to chang-

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(1) The data presented here were included in a dissertation submitted by H. A. Eick to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree. This work was partially supported by the Atomic Energy Commission Research Contracts Division.

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