in the same column of the periodic table which shows any relationship to uranium in crystal structure is neodymium, which crystallizes hexagonal close-packed, whereas uranium has a distorted hexagonal close-packed structure.

The directions of the four bonds to closest neighbors are very curious. Two bonds go to the north and south poles and the other two point toward the equator making an angle of 127° with one another. Dr. R. Hultgren has pointed out that the curious directions in which the uranium atom has chosen to form four bonds to closest neighbors are such that the four neighboring atoms chosen are not closest neighbors of one another.

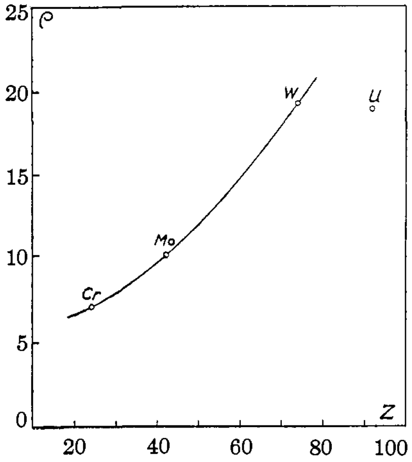

Fig. 2.—Relation between density and atomic number for Cr, Mo, W and U.

Summary

X-ray powder patterns of uranium lead to an orthorhombic unit cell with axes a = 2.852 Å., b = 5.865 Å., c = 4.945 Å. The space group is V_h^{17} $Cmcm$. and there are four atoms in the position 4c. The parameter is determined from the intensities as $y = 0.105 \pm 0.005$. The X-ray density is 18.97. The structure can be considered as a deformed hexagonal close-packed structure with four neighbors closer than the other eight. The structure suggests that uranium is only pseudo-metallic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Rare Earth Metals and their Compounds. III. The Ternary Systems Cerium Group Nitrates–Nitric Acid–Water at 25 and 50°

BY LAURENCE L. QUILL AND RICHARD F. ROBEY[1]

Introduction

This study is part of a systematic investigation of the isothermal phase equilibria existing between rare earth salts and their saturated solutions.

The nitrates of the rare earth elements have played an important part in the separation of the rare earth elements by the process of fractional crystallization. The use of the simple nitrates in this process with solutions of nitric acid as the solvent is especially efficient for the elements of atomic numbers 66 (dysprosium) to 71 (lutecium) inclusive. Attempts to apply the method to the cerium group elements, atomic numbers 57 (lanthanum) to 62 (samarium) inclusive, have not met with success.[2]

For separating the cerium group elements the fractional crystallization of the double magnesium nitrates is particularly advantageous. A conclusive proof of the existence of the double magnesium nitrates has been set forth just recently.[3] A comparison of Jantsch's[4] solubility values of these double salts in nitric acid, with those of Prandtl and Ducrue[5] and of Friend and co-workers[6] in pure water, reveals the general tendency for the introduction of nitric acid to increase the slight differences of solubility between various corresponding salts. In order to take advantage of this effect, it has been the custom for many years to introduce nitric acid in certain rare earth fractional crystallization series.

In a recent investigation Friend[2] determined the solubilities of certain of the cerium group simple nitrates in water and discovered that the trend of the solubility values is complicated by the effects of polymorphism of the nitrates and evidently other factors not clearly understood.

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[1] Present address: Chemical Laboratories, Standard Oil Development Co., Elizabeth, N. J.

[2] J. N. Friend, *J. Chem. Soc.*, 824, 1430 (1935).

[3] L. L. Quill and R. F. Robey, THIS JOURNAL, **59**, 1071 (1937).

[4] G. Jantsch, *Z. anorg. Chem.*, **76**, 303 (1912).

[5] W. Prandtl and H. Ducrue, *ibid.*, **150**, 105 (1926).

[6] J. N. Friend, *J. Chem. Soc.*, 1903 (1930); 356 (1935).

In an endeavor to make at least a step forward in the clarification of this question and to study the effect of nitric acid on the solubilities of the cerium group nitrates, an investigation of these ternary systems was undertaken.

Experimental

Materials.—The nitric acid used in this investigation was prepared by distilling Grasselli C. P. concentrated acid in a Pyrex all-glass apparatus equipped with an efficient spray trap. The middle fraction only was collected. For very high nitric acid concentrations Merck reagent fuming nitric acid was used.

Water was specially distilled and had a conductivity of about 2×10^{-6} mho.

The hexahydrated nitrates of lanthanum, neodymium, and samarium were prepared from the respective oxides by dissolution in the pure nitric acid and evaporating the solution to a sirup. The sirup was taken up in water, twice recrystallized, and finally dried over 55% sulfuric acid in a desiccator. The purity of the original oxides was attested by the arc emission spectra with a Hilger (E-185) spectrograph. No trace of any foreign rare earth elements was found in the individual oxides.

Pure cerium nitrate was prepared from the analytical ceric sulfate reagent produced by the G. Frederick Smith Chemical Company. The cerium was separated and purified by three successive precipitations following the well-known basic bromate method. The washed ceric basic bromate, mixed with nitric acid, was taken into solution by the addition of 3% hydrogen peroxide solution. The cerium was precipitated from this solution as the oxalate in acid solution, washed with hot water, and the oxalate digested in nitric acid on the steam-bath.

The nitric acid solution of cerium was evaporated to a sirup and the hexahydrated nitrate crystallized and dried as the other nitrates.

The fact that these salts are hexahydrates is certified by the analytical results given later in this paper.

The Tetrahydrated Nitrate.—It has been thought in the past that the hexahydrated cerium group nitrates yield the penta-, the tri-, and monohydrates upon desiccation. Loewenstein,[7] however, found only the tetra- and the monohydrates.

In an endeavor to obtain further data of this nature, weighed watch glasses containing small weighed amounts of finely ground hexahydrated cerium and lanthanum nitrates were placed in a small desiccator over phosphorus pentoxide and were weighed periodically. The containing vessels had been brought to constant weight over the desiccant before the introduction of the nitrate. Table I shows the loss of weight with time.

TABLE I

THE RATE OF DEHYDRATION OF RARE EARTH NITRATES OVER PHOSPHORUS PENTOXIDE

Lanthanum nitrate hexahydrate		Cerium nitrate hexahydrate	
Time, hours	Moles of water lost	Time, days	Moles of water lost
0	0.00	0	0.00
6	1.90	3	2.06
22	2.03	8	2.57
72	2.03	9	2.59
		14	2.63
		54	3.27

This information clearly demonstrates that the tetrahydrate is formed by the dehydration of the hexahydrate over phosphorus pentoxide for a period of one to three days in a small desiccator. Further but less rapid dehydration takes place in longer periods.

Procedure for Ternary System.—Briefly the isothermal phase equilibria between the hydrated rare earth nitrates and their saturated solutions in various concentrations of nitric acid were established by shaking appropriate quantities of the solute and the solvent in Pyrex tubes at constant temperature.

In detail the first step consisted of bringing the nitrate into complete solution by warming and then causing the solution to supersaturate by partially immersing the tube in an appropriate thermostatic bath. Two thermostats were employed, one maintained at 25.00 ± 0.03° and the other at 50.0 ± 0.1° as determined by Bureau of Standards thermometers.

An extremely small crystal of bismuth nitrate pentahydrate was added in every case as a "seed" to induce crystallization at the temperature of the isotherm from the supersaturated solution. Bismuth nitrate has long been known to be isomorphous with at least one form of the hexahydrated cerium group nitrates[2] and also with a lower hydrate which crystallizes from the more concentrated nitric acid solutions.

The sealed tubes were shaken in the thermostatic baths for a period of at least eight hours. Preliminary experiments indicated that equilibrium was reached in four hours. The approach to equilibrium from an undersaturated solution shaken in contact with an excess of finely divided solute for eight hours also results in values for the composition of the liquid phase identical with those obtained by approach from supersaturation within the limit of ordinary analytical error. The approach from supersaturation was used throughout this investigation, however, because it makes certain the nature of the solid phase.

After equilibrium had been reached the tubes were opened while still partially immersed in the bath and a glass filtering pipet employed to withdraw a filtered sample of the liquid phase. The pipet was constructed in such a manner that its temperature could be maintained at a value slightly higher than that at which the solution was saturated. This precaution prevented crystallization of the solution during withdrawal and transfer. The filter medium in the stem of the pipet was composed of Pyrex "High Stability" very fine glass wool. Glass-stoppered weighing bottles received the samples from the pipet.

The residual solid phase, moist with saturated solution, was also placed in weighing bottles for analysis by Schreinemakers' method. In case a dry or nearly dry sample was desired a Jena glass crucible fitted with a fritted glass filter plate was used. The filtering assembly was encased in a protective jacket immersed in the thermostat so that filtration of the residue was accomplished at the equilibrium temperature.

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[7] E. Loewenstein, *Z. anorg. Chem.*, **63**, 69 (1909).

Analysis.—The weighed samples of the liquid and solid phases were analyzed for nitric acid using 0.1 normal sodium hydroxide solution with methyl red as indicator.

The rare earth oxalates were precipitated by dilute oxalic acid of a purity to pass the specifications of the American Chemical Society. The oxalates of lanthanum and samarium were much less granular than those of cerium and neodymium and it was necessary to digest them with the mother liquor for several hours before filtering. The oxalates were filtered while cold on ashless paper of very fine texture and washed well with hot dilute oxalic acid solution.

The ignition of the oxalates to constant weight as the oxides was accomplished in platinum crucibles over Fisher burners. All oxides except that of cerium were weighed and calculated to the anhydrous nitrates as the normal trivalent oxides. Cerium, however, forms the dioxide, CeO_2.

Ceric cerium was determined in the presence of cerous cerium by adding an excess of standard ferrous salt solution to the sample in sulfuric acid solution and titrating the excess ferrous solution with standard ceric ammonium sulfate. Orthophenanthroline-ferrous complex indicator was used.

Densities.—Carefully calibrated Reischauer pycnometer tubes of 10-ml. capacity were used to determine the densities of the saturated solutions. The tubes were immersed in a thermostat for several hours prior to and after adjusting the liquid level. The dry tubes were permitted to stand in the balance case until they attained room temperature before weighing.

TABLE II

System: $La(NO_3)_3$–HNO_3–H_2O

Solution			Moist residue		
$La(NO_3)_3$, %	HNO_3, %	Density, g./ml.	$La(NO_3)_3$, %	HNO_3, %	Solid phase
		25°			
59.0[a]	None	...	75.00[b]	None	VI
56.42	3.06	1.771	73.14	0.381	VI
46.42	11.95	...	...	...	VI
29.10	34.69	...	65.45	7.31	VI
29.62	40.17	...	65.74	12.45	IV
28.73	41.14	...	61.98	14.63	IV
25.18	54.41	...	35.80	45.26	IV
21.61	58.36	...	51.79	29.61	IV
2.79	70.70	1.489	26.01	50.54	III
0.56	87.85	...	5.07	84.12	0
None	90	1.483	...	...	None
		50°			
66.65	None	1.929	74.98[b]	None	VI
64.21	2.59	1.912	73.67	0.404	VI
61.85	5.29	1.892	73.36	0.642	VI
56.70	12.05	1.852	73.75	1.02	VI
56.34	14.93	1.880	77.52	1.81	VI + IV
44.23	27.73	1.755	80.33	1.14	IV
30.31	44.48	1.645	77.78	3.08	IV
29.58	50.53	...	...	...	IV
5.48	78.31	...	...	...	0 ?
1.38	85.51	...	10.15	78.35	0 ?
0.41	91.15	1.419	...	...	0 ?
None	90	1.440	...	...	None

VI = $La(NO_3)_3 \cdot 6H_2O$; calcd. % $La(NO_3)_3$ = 75.03. IV = $La(NO_3)_3 \cdot 4H_2O$. III = $La(NO_3)_3 \cdot 3H_2O$. 0 = $La(NO_3)_3$.

[a] Interpolated from data of Friend.[2] [b] Dry salt analyzed.

TABLE III

System: $Nd(NO_3)_3$–HNO_3–H_2O

Solution			Moist residue		
$Nd(NO_3)_3$, %	HNO_3, %	Density, g./ml.	$Nd(NO_3)_3$, %	HNO_3, %	Solid phase
		25°			
59.0[a]	None	...	75.30[b]	None	VI
53.31	6.20	1.741	73.56	0.59	VI
52.15	6.36	...	...	...	VI
40.79	18.28	...	...	...	VI
23.64	43.95	...	60.21	12.68	VI
24.08	44.63	...	53.32	19.74	VI
23.47	49.20	1.595	70.57	10.14	IV
19.11	56.65	1.572	53.90	25.03	IV
		50°			
66.26	None	1.963	75.62[b]	None	VI
64.62	2.14	1.948	74.28	0.466	VI
60.34	6.92	1.901	72.87	1.34	VI
57.74	10.41	1.885	71.36	2.40	VI
59.47	11.93	1.997	77.47	0.523	VI + IV
51.24	22.67	...	...	...	IV
47.36	26.83	1.819	79.39	2.15	IV
32.49	46.55	...	76.62	4.22	IV
34.97	45.46	...	...	...	IV

VI = $Nd(NO_3)_3 \cdot 6H_2O$; calcd. % $Nd(NO_3)_3$ = 75.34. IV = $Nd(NO_3)_3 \cdot 4H_2O$.

[a] Interpolated from data of Friend.[2] [b] Dry salt analyzed.

TABLE IV

System: $Sm(NO_3)_3$–HNO_3–H_2O

Solution			Moist residue		
$Sm(NO_3)$, %	HNO_3, %	Density, g./ml.	$Sm(NO_3)_3$, %	HNO_3, %	Solid phase
		25°			
58.95	None	1.782	75.90[a]	None	VI
52.08	6.15	...	73.35	1.49	VI
46.52	11.34	...	...	...	VI
16.40	44.38	...	60.26	11.32	VI
14.20	48.40	...	52.02	18.94	VI
13.64	51.58	...	65.30	9.20	VI
		50°			
64.81	None	1.939	...	...	VI
62.97	2.12	1.916	74.50	0.350	VI
57.57	7.53	1.859	...	...	VI
45.05	22.38	...	73.00	1.51	VI
33.20	36.40	1.648	72.90	1.46	VI
30.22	47.52	1.664	75.11	3.25	IV + VI
27.89	46.21	1.638	74.94	7.38	IV ?

VI = $Sm(NO_3)_3 \cdot 6H_2O$; calcd. % $Sm(NO_3)_3$ = 75.68. IV = $Sm(NO_3)_3 \cdot 4H_2O$.

[a] Dry salt analyzed.

Results.—The results on the three systems $La(NO_3)_3$–HNO_3–H_2O, $Nd(NO_3)_3$–HNO_3–H_2O, and $Sm(NO_3)_3$–HNO_3–H_2O are given in Tables II, III, and IV, respectively. Analytical results are given as percentage by weight. These data are plotted for 25° in Fig. 1 and for 50° in Fig. 2. The percentages of water were determined by difference.

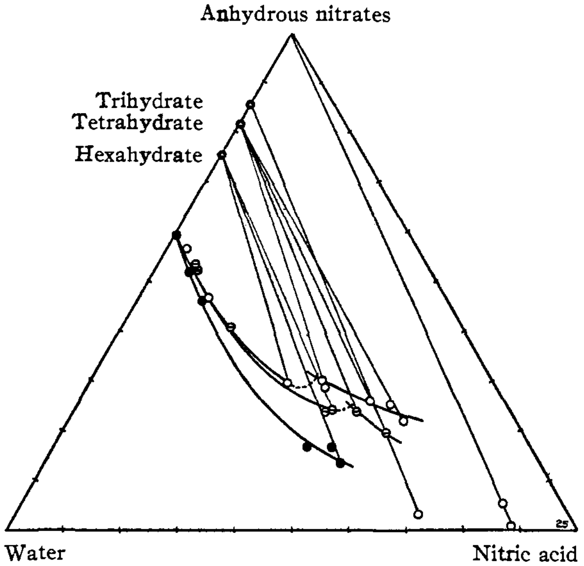

Fig. 1.—The isotherms of the systems cerium group nitrates–nitric acid–water at 25°: ○, lanthanum; ⊖, neodymium; ●, samarium.

Indirect analysis by the method of Schreinemakers reveals that at high acid concentrations a tetrahydrated nitrate is formed and that the early proposed pentahydrated nitrate is either nonexistent or its range of existence is very limited. It is interesting to note that both the tetra- and the hexahydrate crystals grow from the pentahydrated bismuth nitrate employed to induce crystallization from the supersaturated solutions.

The unexplored regions of the systems are those portions in which crystallization is very imperfect and consequently of little value in fractionation. Extensive data have not been obtained because of the limited quantity of the pure material at hand making necessary the frequent working up, purification, and use of residues.

In order to avoid a confusion of lines in Figs. 1 and 2, the tie-lines dependent upon the results of analysis of moist solid residues have been omitted for the most part. The extrapolation of these lines to the proper solid phases has been found to be quite satisfactory. Although the isothermal curves of the three nitrates at both temperatures are almost identical in dilute nitric acid solutions, considerable and possibly useful divergence is noted at higher acid concentrations.

An interesting relationship is found in the 50° (Fig. 2) diagram in which the isothermal curve of neodymium nitrate crosses that of lanthanum. The tetrahydrate of neodymium is more soluble in acid solutions than the corresponding lanthanum compound at this temperature, while for the hexahydrates the opposite is true.

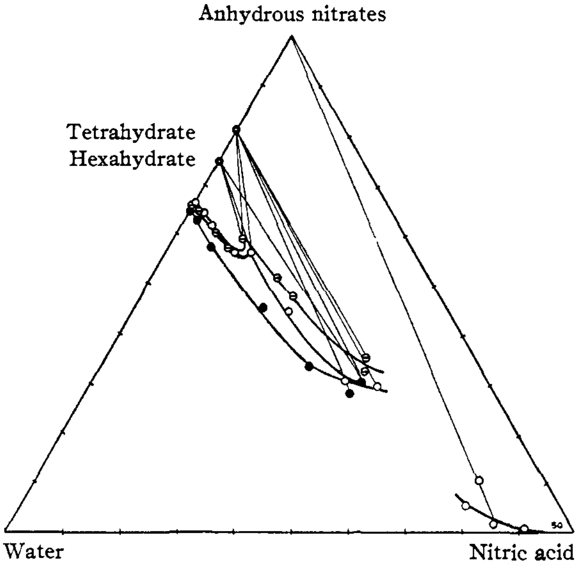

Fig. 2.—The isotherms of the systems cerium group nitrates–nitric acid–water at 50°: ○, lanthanum; ⊖, neodymium; ●, samarium.

The Solubility of Cerium Nitrate.—In order to complete the data for the group of elements the solubility of cerous nitrate in neutral solution at 25 and 50° was determined. At 25° the solubility is 63.71 g. of anhydrous nitrate per 100 g. of solution and the density of the saturated solution 1.88 g. per ml. At 50° the solubility is 73.88 and the density of the saturated solution 2.04. Both solubility values have been corrected for a small concentration of ceric cerium present to the extent of less than 1%. The solid phase present proved to be the hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, at both temperatures; calculated $Ce(NO_3)_3$, 75.10%; found 75.10, 75.00%.

It was found that the system $Ce(NO_3)_3$–HNO_3–H_2O is complicated by the formation of considerable amounts of ceric cerium and attempts to investigate it were abandoned for the time.

Discussion

The solubilities of the hexahydrated cerium group nitrates in neutral solution have been plotted as curves *a* for 25° and *b* for 50° in Fig. 3 against the atomic numbers of the rare earth elements. The data for praseodymium are due to Friend.[2] It is observed that the maximum solubility is reached with cerium nitrate and not with lanthanum as was formerly supposed.

The solubilities of the nitrates are thus not simply related to the atomic numbers and the close relationship between the isothermal curves of lanthanum and neodymium nitrates in various concentrations of nitric acid is due to the anomalously low value of the solubility of lanthanum nitrate.

The cerium group arranged in the order of decreasing 25° water solubility of the simple hexahydrated nitrates crystallized in the form which grows on crystals of pentahydrated bismuth nitrate is cerium, praseodymium, lanthanum, neodymium, and samarium.

The congruent melting points of the nitrates which have been studied recently by Quill, Robey, and Seifter[8] are plotted against atomic number as curve *c* also in Fig. 3. The form of the curve also demonstrates the anomalous behavior of lanthanum nitrate.

Acknowledgment.—The authors are deeply indebted to B Smith Hopkins, Professor of Inorganic Chemistry of the University of Illinois, for the loan of valuable and pure rare earth oxides employed in this investigation.

Summary

Investigation of the solubilities of the cerium group nitrates in water and in nitric acid solutions shows that they do not decrease in the order of increasing atomic number but that the solubility of lanthanum nitrate is anomalously low. The order of decreasing solubility is Ce, Pr, La, Nd and Sm.

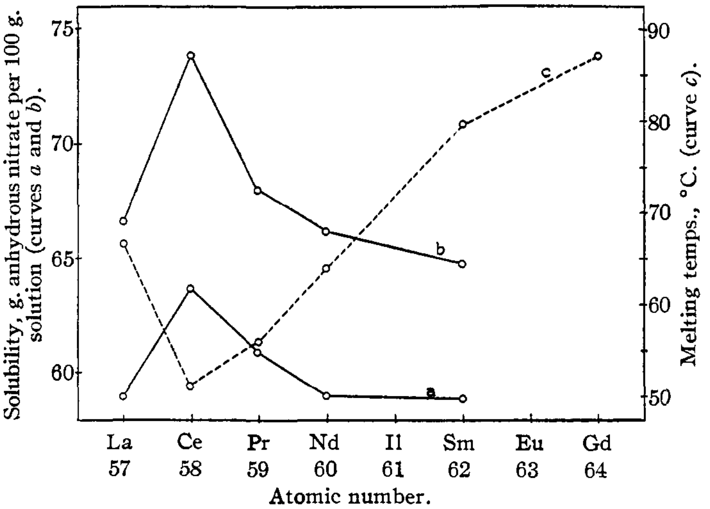

Fig. 3.—The solubilities and melting points: *a*, solubilities at 25°; *b*, solubilities at 50°; *c*, melting points of the hexahydrated nitrates.

In a fractional crystallization series of the hexahydrated nitrates, cerium and praseodymium should separate in the head fractions. The order and the rapidity of the separation of the remaining cerium group elements depends upon the concentration of free nitric acid and the temperature of crystallization.

The hexa-, tetra- and trihydrated nitrates as well as the anhydrous salt have been shown to exist as solid phases crystallizing from nitric acid solutions of the cerium group nitrates. No evidence for the existence of a pentahydrate was found.

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(8) L. L. Quill, R. F. Robey, and S. Seifter, *Ind. Eng. Chem., Anal. Ed.*, **9**, 389 (1937).