	Pressure, mm.	Density, g./liter at 20.0°	Relative density (air = 1)
I	753.5	6.091_7	5.10_1
II	753.5	6.094_9	5.10_3
III	760.5	6.164_6	5.11_4
			5.10_6 (mean)

Summary

1. In the preparation of fluorine, monel metal has been found entirely satisfactory for the cathode vessel and diaphragm in the electrolysis of fused potassium bifluoride. Graphite as the anode material is slightly attacked. Details concerning structural features and operation of the fluorine generator are given.

2. The synthesis and purification of sulfur hexafluoride are described; the method of purification is more complete than hitherto has been described.

3. The vapor pressure of solid and liquid sulfur hexafluoride has been measured up to three atmospheres, the temperature interval covered being from -72 to -45°. The pressure becomes 760 mm. at -63.8°.

4. The density of the gas at 20°, 753.5 mm., is found to be 6.093 g. per liter. From this the relative density (air = 1) is calculated to be 5.10_6; theoretical, 5.04.

5. The melting point of pure sulfur hexafluoride is found to be -50.8 ± 0.2°. This is more than 4° higher than the earlier values of Moissan and of Prideaux.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

DEFORMATION OF ELECTRON SHELLS. II. ABSORPTION SPECTRUM, MOLECULAR VOLUME AND REFRACTION OF CERTAIN RARE EARTH SALTS

BY P. W. SELWOOD

RECEIVED AUGUST 25, 1930 PUBLISHED NOVEMBER 5, 1930

In the first paper of this series[1] it was pointed out that there is a relation between the absorption spectrum and other properties of neodymium perchlorate. The object of the present work was to extend the observations to the nitrate and chloride of neodymium and, so far as possible, to other members of the rare earth group.

Experimental

The experimental procedure involved in the measurements described here will be given only wherein it differs from that already reported.

The quantitative analysis of neodymium nitrate solutions presented a

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[1] Selwood, THIS JOURNAL, 52, 3112 (1930).

much simpler problem than either the perchlorate or the chloride. Weighed samples of the solutions were evaporated to dryness and ignited directly to the oxide. The whole analysis took less than an hour, and the results are believed to be accurate to 0.05%.

In the case of the neodymium chloride it was necessary to use the oxalate–oxide method as described for the perchlorate determination. In every case the filtrate from the neodymium oxalate was tested spectroscopically for neodymium, and the oxide, after being weighed, was dissolved in nitric acid and tested for chloride. The absence of chloride in any of the samples indicates that neodymium oxalo-chloride does not form in noticeable amounts if the rare earth is precipitated slowly from the hot, dilute solution, with fairly dilute oxalic acid. The chloride results are believed to be accurate to 0.1%.

The determinations of density and of refractive index were as described before. All the data on molecular refraction refer to the hydrogen C line. The molecular volumes were calculated as shown by Geffcken[2] from the relation

$$V = \frac{M}{d_0} - \frac{3000\ (d - d_0)}{N}$$

where V is molecular volume, M is molecular weight, d is density of the solution, d_0 is density of water and N is concentration in equivalents per 1000 cc. of solution.

In addition to the absorption bands of neodymium nitrate and chloride, an examination was also made of the spectrum of praseodymium, samarium, europium, gadolinium, holmium and erbium. In all cases the spectrum of a 10 N solution through a 3-mm. layer was compared with that of a 0.2 N solution through the equivalent thickness of 150 mm.

In the case of the gadolinium, which has no absorption bands in the visible region of the spectrum, the procedure was modified in that uranium salts placed in the positive crater of a carbon arc formed the source of ultraviolet illumination. The very large number of emission lines from uranium served in place of a continuous spectrum. It has recently been reported by Freed and Spedding[3] that gadolinium has some faint absorption lines in the visible region. In an effort to verify these results, the writer examined the spectrum of a 150-mm. layer of 10 N gadolinium nitrate, but no trace of selective absorption could be detected. The spectrum was photographed on a Hilger E 1 quartz prism spectrograph.

During the course of the work on neodymium nitrate solutions it seemed desirable to examine the absorption spectrum of a crystal of the same salt. Well-formed crystals were prepared from a saturated solution which was slowly evaporated. They were soft and easily broken, but several pieces

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[2] Geffcken, *Z. physik. Chem.*, **5B**, 81 (1929).

[3] Freed and Spedding, *Phys. Rev.*, **34**, 945 (1929).

with smooth surfaces were obtained by rubbing the crystal down with the moist finger tip. In order to prepare a dilute solution of equivalent thickness with which to compare the spectrum of the crystal it was necessary to determine the concentration of neodymium nitrate in equivalents per 1000 cc. of crystal. This was done by analyzing a crystal for neodymium content by ignition to the oxide, and by finding the density through the loss of weight in benzene, in which neodymium nitrate is insoluble. Two such determinations gave 15.13 and 15.11 as the normality of $Nd(NO_3)_3$ in the crystals. The crystal finally used for the spectroscopic work had a thickness of 1.70 mm. This was equivalent to 100 mm. of 0.257 *N* solution with which it was compared.

The purity of the neodymium used has already been discussed. All the other rare earths except the praseodymium and the erbium had been prepared by the writer, some expressly for this work and some in connection with other work. The praseodymium contained 1% of lanthanum. The samarium showed no absorption bands of neodymium and no arc lines of europium. The europium, of which only a gram or two was available, was free from all other rare earths. The gadolinium contained only a spectroscopic trace of europium. The holmium and erbium material consisted largely of the colorless rare earth yttria. The first contained 26% holmium, and the second 20% erbium.

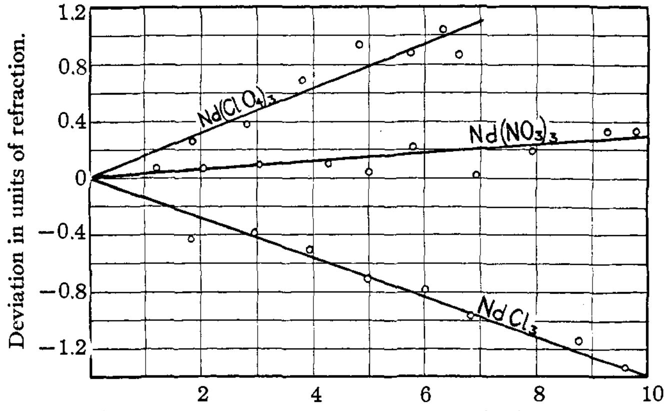


Fig. 1.—Deviations from additivity in the molecular refraction of neodymium perchlorate, nitrate and chloride in aqueous solution.

Results

The values for the molecular volume and refraction of neodymium nitrate and chloride are shown in Tables I and II. Figure 1 shows the deviations from additivity when the molecular refractions of the nitrate and chloride are plotted against concentration. For the sake of complete-

Table I

Molecular Volume and Refraction of Neodymium Nitrate in Aqueous Solution

% $Nd(NO_3)_3$ by weight	Normality	Temp., °C.	Density	Refr. index 6563 Å.	Mol. volume	Mol. refraction
11.92	1.197	24.6	1.1054	1.34858	59.88	36.07
19.14	2.050	24.8	1.1792	1.35966	64.71	36.07
26.50	3.046	24.3	1.2652	1.37268	67.24	36.09
34.49	4.292	24.2	1.3698	1.38800	70.76	36.10
38.56	5.006	25.2	1.4290	1.39637	72.35	36.04
42.95	5.825	25.2	1.4930	1.40530	75.79	36.21
48.32	6.965	25.7	1.5867	1.41812	77.23	36.02
52.76	7.966	25.8	1.6620	1.42815	80.80	36.19
58.02	9.279	26.0	1.7604	1.44115	84.44	36.33
60.10	9.820	25.8	1.7986	1.44604	86.36	36.34

Table II

Molecular Volume and Refraction of Neodymium Chloride in Aqueous Solution

% $NdCl_3$ by weight	Normality	Temp., °C.	Density	Refr. index 6563 Å.	Mol. volume	Mol. refraction
13.46	1.830	26.6	1.1357	1.35898	23.49	29.93
20.40	2.978	26.9	1.2198	1.37570	26.51	30.07
25.37	3.914	27.0	1.2890	1.38922	28.01	29.91
30.53	4.993	27.6	1.3664	1.40356	29.23	29.65
35.01	6.031	27.8	1.4393	1.41724	31.22	29.58
38.18	6.855	24.6	1.5001	1.42873	31.26	29.40
44.84	8.739	25.2	1.6283	1.45228	34.69	29.33
47.55	9.639	25.0	1.6936	1.46360	34.72	29.03

ness the values previously reported for the perchlorate are included. While the perchlorate showed a 2% increase with concentration from 0 to 7 *N*, the nitrate shows a 1% increase from 0 to 10 *N*, and the chloride shows nearly a 3% decrease from 0 to 10 *N*. Over the same ranges of concentration the molecular volumes of these salts show a marked increase, the perchlorate 12%, the nitrate 27% and the chloride 36%.

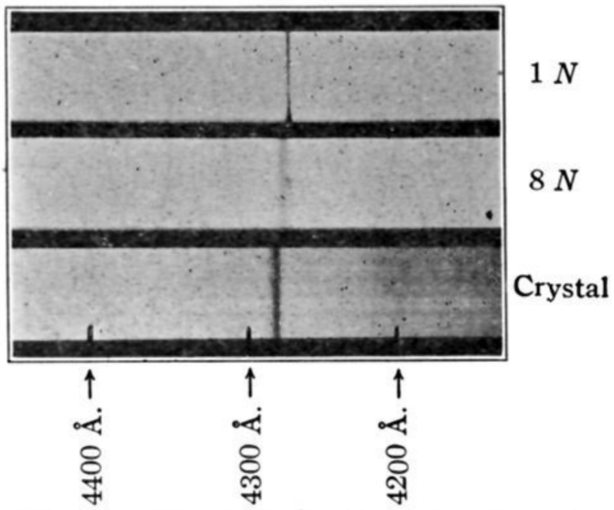


Fig. 2.—The 4272 Å. absorption line of neodymium nitrate.

In general the absorption bands of the neodymium solutions were shifted toward the red end of the spectrum by increasing concentration. In the case of the perchlorate the shifts were small, in most instances of the order of 1 or 2 Å., while both nitrate and chloride concentrated solutions showed marked shifts toward the red, those of the latter salt sometimes approaching 20 Å. The spectra of the dilute solutions of all the salts were practically identical.

As indicated in Figs. 2 and 3, the spectrum of the neodymium nitrate crystal showed a markedly increased shift in the same sense as did that of the more concentrated solution. It is evident that whatever forces were causing the shifts in the solution were acting more intensely in the crystal.

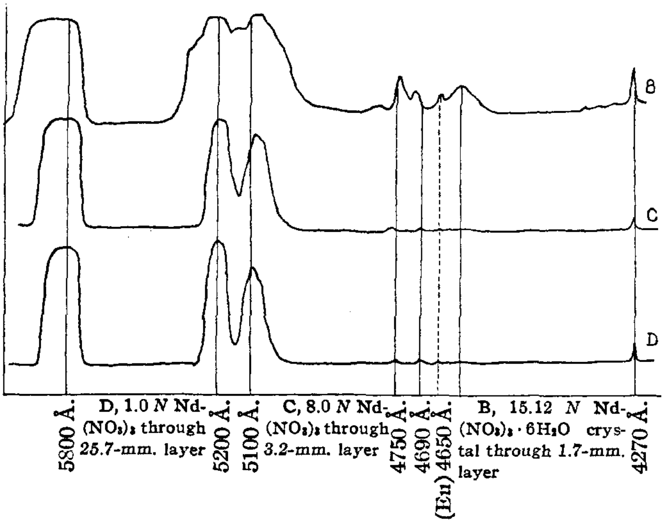
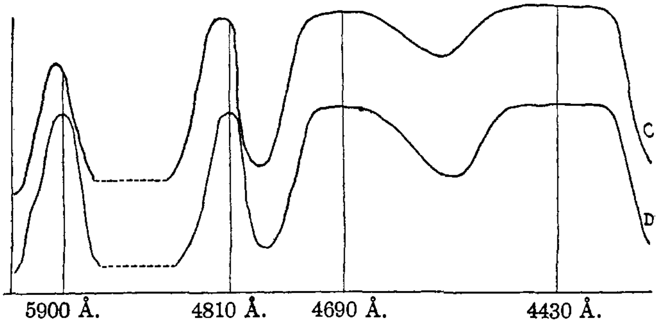


Fig. 3.—Microphotometric curves of the absorption spectrum of neodymium nitrate, showing the effect of concentration on the positions of the various bands.



D, 0.2 *N* $Pr(NO_3)_3$ through 150-mm. layer; C, 10.0 *N* $Pr(NO_3)_3$ through 3-mm. layer.

Fig. 4.—Part of the absorption spectrum of praseodymium nitrate.

This observation parallels that of Brunetti,[4] who reached the same conclusion in the case of praseodymium salts.

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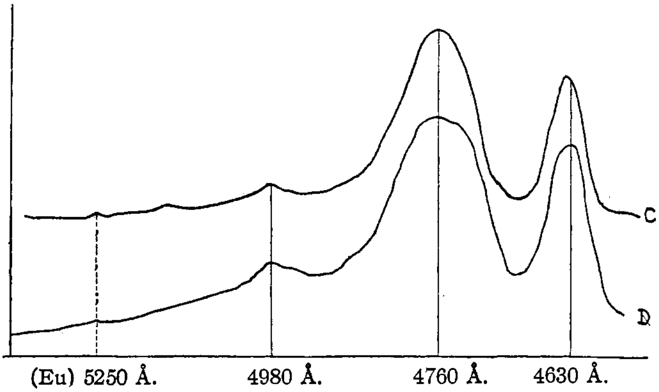
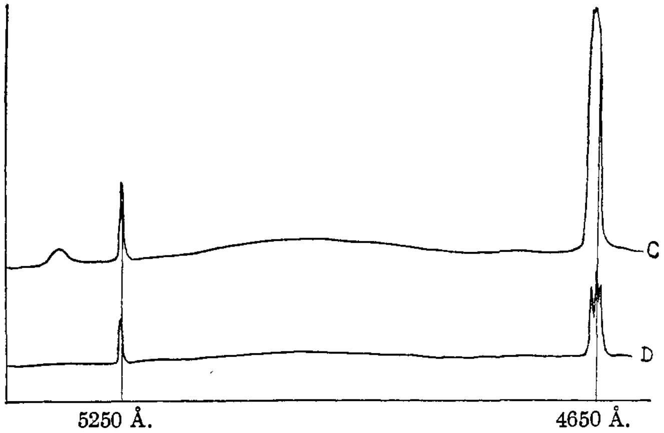
[4] Brunetti, *Nuovo cimento*, [N. S.] 5, 391 (1928).

The spectral bands of praseodymium, samarium and europium also tended to shift toward the red with increasing concentration. The nitrate was investigated in every case. The bands of praseodymium were all shifted slightly toward the red, those of samarium were very slightly if at all shifted except the broad band at 4020 Å., which was noticeably moved toward the red. All the visible bands of europium seemed to be very slightly shifted toward the red. The relative intensities were also much changed. A few bands in the ultraviolet were too hazy to make any definite statement about their positions.



D, 0.2 *N* $Sm(NO_3)_3$ through 150-mm. layer; C, 10.0 *N* $Sm(NO_3)_3$ through 3-mm. layer.

Fig. 5.—Part of the absorption spectrum of samarium nitrate.

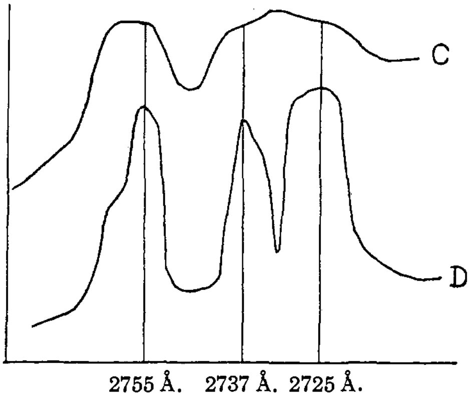


D, 0.2 *N* $Eu(NO_3)_3$ through 150-mm. layer; C, 10.0 *N* $Eu(NO_3)_3$ through 3-mm. layer.

Fig. 6.—Part of the absorption spectrum of europium nitrate.

At the concentrations employed no bands of gadolinium were observed at

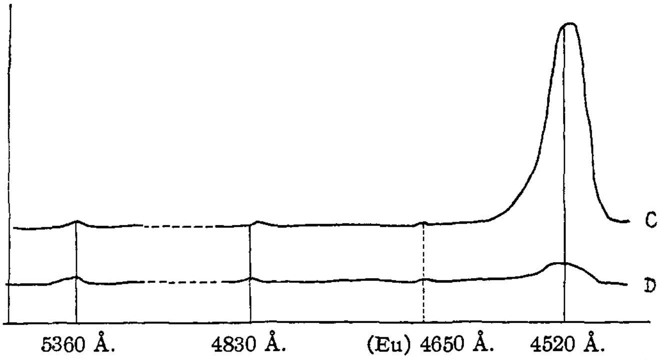
3108, 3059, 3056 or 3052 Å.,[5] where they have previously been reported. Several bands reported by Freed and Spedding, however, were found. Of these, the two at 2730 and 2750 Å. were most intense in the cases of both nitrate and chloride. While the nature of the bands was altered by concentration, it is doubtful whether there was any definite movement one way or another.



D, 0.2 *N* $GdCl_3$ through 150-mm. layer; C, 10.0 *N* $GdCl_3$ through 3-mm. layer.

Fig. 7.—Absorption bands of gadolinium chloride.

The bands, however, of holmium and erbium were generally shifted toward the blue, the change being most noticeable for those at 4530, 4850 and 5350 Å. for holmium, and 4430, 4490 and 6520 Å. for erbium. This peculiar change is so striking as to suggest some radical difference in the atomic structure of these last rare earth elements. Such a change is, in fact, postulated in the current theories of atomic structure, inasmuch as the 4_4 electron shell is believed to complete its first sextet with europium.[6] But the interpretation of the phenomenon is not entirely clear and it seems at the present time to be impossible to generalize further with respect to the effect of increasing concentration so far as direction of shift is concerned.



D, 0.2 *N* $Ho(NO_3)_3$ through 150-mm. layer; C, 10.0 *N*, $Ho(NO_3)_3$ through 3-mm. layer.

Fig. 8.—Part of the absorption spectrum of holmium nitrate.

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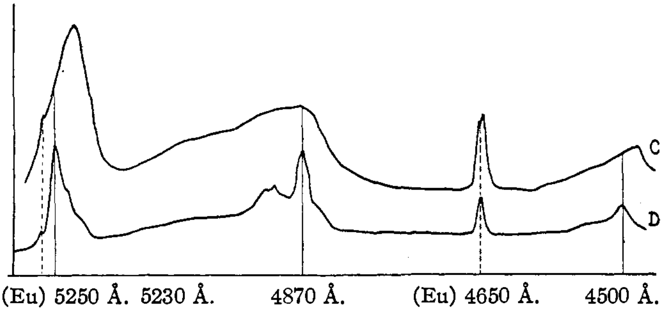
[5] Little, "A Textbook of Inorganic Chemistry" (Friend), London, Vol. IV, **1921**, p. 289.

[6] Hevesy, "Die seltenen Erden von Standpunkte des Atombaues," Springer, Berlin, **1927**.

As pointed out before, the classical dispersion formula shows that a decrease in characteristic frequency (shift toward the red) should be attended with an increase of molecular refraction. Such is what has been observed for the cases of neodymium perchlorate and nitrate.

Fajans and others have shown that while the perchlorate ion is only slightly influenced by its neighbors, the nitrate ion is somewhat deformed and the chloride ion is very highly deformed. While deformation of a cation results in an increase of refraction, deformation of an anion results in a decrease of refraction. It appears then that the increase in refraction of the neodymium ion is partly compensated by the decrease of the nitrate, and it is completely so and more by that of the chloride. The decrease in refraction of neodymium chloride is, therefore, in no way evidence against the conclusion that a shift toward the red of absorption bands is generally attended with an increase of refraction. It appears, then, from both refraction and spectroscopic evidence that the outer electron shell of the neodymium ion must be deformed in concentrated solution, and that this deformation is communicated in part, at least, to the inner electron shells thought to be the source of the characteristic absorption bands.



D, 0.2 *N* $Er(NO_3)_3$ through 150-mm. layer; C, 10.0 *N* $Er(NO_3)_3$ through 3-mm. layer.

Fig. 9.—Part of the absorption spectrum of erbium nitrate.

The writer wishes to thank Professor B. Smith Hopkins, in whose laboratory this work was done, for the invaluable advice and encouragement which he has from time to time supplied.

Summary

The molecular refraction of neodymium nitrate has been found to increase slightly with concentration, while that of the chloride decreases. The molecular volume of both salts is increased. The absorption bands are shifted toward the red. These measurements afford evidence that the neodymium ion is deformed in the more concentrated solutions. The absorption bands of praseodymium and samarium nitrates are also shifted toward the red. The bands of europium and gadolinium are not much

altered in position, while those of holmium and erbium are noticeably shifted toward the blue.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

STUDIES ON COMPLEX IONS. III.[1] THE RELATIVE STABILITIES OF THE HALOGENOPLATINATES

BY H. I. SCHLESINGER AND R. E. PALMATEER[2]

RECEIVED AUGUST 30, 1930 PUBLISHED NOVEMBER 5, 1930

As part of a study of the factors which determine the conditions under which complex ions are formed, a determination of the relative stabilities in solution of a series of complex ions of similar types has become desirable. Schlesinger and Tapley[3] have shown that the halogenoplatinates are mutually and reversibly convertible into each other, and are therefore suitable for such an investigation.

The usual method of determining the "stability" or "instability" constants of such ions is inapplicable to this case, for aqueous solutions of the halogenoplatinates contain no detectable quantities of the free platinic ions. Relative values of the stabilities might, however, be obtained if the amount of transformation of one halogenoplatinate into the other could be determined in the presence of given quantities of halide ions. But even such measurements present difficulties, for the reactions involved probably proceed in many steps, leading through all of the theoretically possible mixed halogenoplatinates. No method available allows a determination of each of the seven possible components of such a system.

It nevertheless has become possible to obtain approximate relative values by the following procedure. When, for example, a chloroplatinate is mixed in aqueous solution with a bromide and a chloride in suitable proportions, a reaction occurs which leads to the formation of a mixture intermediate in color between that of the pure chloroplatinate and the pure bromoplatinate. An identical mixture, at least so far as the color is concerned, is obtained if the starting material is the bromoplatinate, a fact which demonstrates that a state of true equilibrium is attained. By comparing photometrically the color of such solutions with mixtures of chloro and bromoplatinates of known concentration, one could estimate the percentage of transformation of the one platinate into the other were no

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[1] For the preceding papers of this series see THIS JOURNAL, **51**, 3520, 3523 (1929).

[2] This paper is taken from a thesis presented by R. E. Palmateer to the Faculty of the Ogden Graduate School of Sciences of the University of Chicago, in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Schlesinger and Tapley, THIS JOURNAL, **46**, 276 (1924).