TABLE II (*continued*).

Formula weights per liter at $t°$.	Temperature.	Times of flow.	Mean time of flow.	Density at $t°/t°$.	Relative viscosity.	Relative viscosity at round temperatures.
0.102297	24.94°	659.87 .80 .83 .84	659.84	1.01179	1.16268	1.16262
0.131202	0.00°	1415.08 .00 .55 .36	1415.25	1.02752	1.25233	1.25233
0.130727	24.96°	687.39 .25 .10	687.25	1.02378	1.21719	1.21713
0.129787	50.12°	417.59 .34 .56 .45	417.49	1.01407	1.19261	1.19272
0.176625	0.00°	1524.40 .00 .25	1524.22	1.03645	1.36048	1.36048
0.175818	25.00°	734.50 .75 .74	734.66	1.03172	1.31230	1.31230
0.174336	49.84°	443.06 .00 .13	443.06	1.02302	1.27083	1.27057

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

NEODYMIUM OXALATE AND SOME NEW COMPOUNDS OF EUROPIUM.

BY C. JAMES AND J. E. ROBINSON.

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The first part of this research was to determin the solubility of neodymium oxalate in solutions of neodymium nitrate of various concentrations; for the curve obtained would then show whether hydrates of neodymium oxalate other than $Nd_2(C_2O_4)_3.11H_2O$ existed in contact with neodymium nitrate at 25°, and whether it was possible for an oxalonitrate to be formed under similar conditions.

In the second portion of the work, some new compounds of europium were prepared in the endeavor to find some salt or salts suitable for an equivalent determination or else useful for the purification of this element.

Neodymium Oxalate.—Pure neodymium magnesium nitrate was dissolved in water, making a fairly dilute solution, and precipitated while boiling, by the addition of hot oxalic acid solution. The oxalate was filtered off upon a Buchner funnel, washed and dried. The oxalate was ignited to the oxide, and the latter dissolved in hydrochloric acid.

A portion of the chloride solution was diluted considerably and precipitated in the cold with pure oxalic acid solution. This gave a precipitate of very finely divided neodymium oxalate, which was filtered off washed thoroughly with pure water, and then dried at room temperature in a large shallow dish. After it was dry, it was bottled up. This oxalate was used for the solubility determinations.

The remaining chloride was precipitated in boiling solution with pure oxalic acid. The washed oxalate, after drying, was ignited to the oxide in platinum dishes. The resulting pure oxide was carefully dissolved in pure nitric acid. The slight excess of nitric acid was eliminated by adding just enough oxide to render the solution neutral. The nitrate solution was evaporated until it began to crystallize when cold.

Twenty-one glass stoppered bottles were carefully cleaned and numbered. With the exception of the last three, all contained six grams of neodymium oxalate together with varying concentrations of neodymium nitrate solution. Bottle 21 contained no oxalate. There was, however, an excess of the nitrate, and it was employed for the determination of the solubility of this substance.

The bottles were sealed with paraffin, wired and rotated in a large electrically controlled thermostat at a temperature of 25° for a period of twelve weeks, at the end of which time it was supposed that equilibrium had been attained.

The analysis of the liquid phase was carried out in the following manner: A sample was removed, by means of a pipet, and weighed. It was then washed into a 150 cc. beaker, diluted and an excess of standard oxalic acid solution run in. After the precipitate had settled, it was filtered off and washed. The filtrate, after the addition of some 10% sulfuric acid, was titrated with potassium permanganate solution. The precipitate of neodymium oxalate was ignited and weighed as the oxide.

The potassium permanganate solution was standardized by means of sodium oxalate and ammonium oxalate. Approximately 0.5 *N* oxalic acid solution was made up and titrated against the permanganate.

The equivalent of the total Nd_2O_3 was calculated in grams of C_2O_3. To this was added the number of grams of C_2O_3 corresponding to the amount of permanganate solution used. From this was subtracted the amount of C_2O_3 in the oxalic acid solution run in. It is evident that the difference gives the quantity of C_2O_3 in solution as neodymium oxalate. Now we can calculate the equivalent of the C_2O_3 in grams of $Nd_2(C_2O_4)_3$, and obtain the percentage of neodymium oxalate. Next, the amount of Nd_2O_3 required to unite with this C_2O_3 was computed, and this result deducted from the total Nd_2O_3. The remaining oxide represented the amount of neodymium present as neodymium nitrate, and the per cent. of the nitrate was thus obtained.

The results of the analyses are given in Table I.

TABLE I.

Serial No.	% $Nd_2(C_2O_4)_3$.	% $Nd_2(NO_3)_6$.	Gms. $Nd_2(C_2O_4)_3$ per 100 H_2O.	Gms. $Nd_2(NO_3)_6$ per 100 H_2O.
1	0.18	6.46	0.19	6.92
2	0.54	12.23	0.61	14.02
3	0.76	17.78	0.93	21.83
4	0.85	22.67	1.11	29.63
5	0.96	27.43	1.34	38.29
6	1.28	31.36	1.90	46.56
7	1.38	35.26	2.17	55.64
8	1.66	38.70	2.79	64.89
9	1.88	42.13	3.36	75.25
10	1.96	44.82	3.68	84.22
11	2.07	47.64	4.11	94.73
12	2.54	50.52	5.41	107.6
13	2.89	52.82	6.53	119.2
14	3.17	54.67	7.52	129.6
15	2.21	56.48	5.34	136.8
16	1.21	59.70	3.08	152.7
17	1.33	59.67	3.40	153.0
18	This bottle was not analyzed.			
19	1.44	59.68	3.71	153.5
20	0.96	59.75	2.43	152.1
21	....	60.46	....	152.9

These results are plotted in Fig. 1.

Fig. 1 shows that the solubility curve of neodymium oxalate is divided into three parts, AB, BC, and CD. From 1 to 14 we simply have the solubility of neodymium oxalate, while along BC it was found to be the oxalonitrate. The solid phase along the first part of the curve resembled neodymium oxalate, while that along the second portion consisted of a highly crystallin material. Some of the solid was removed by means of a platinum spoon and pressed between filter papers to remove as much mother liquor as possible. The sample was placed in a weighing bottle and thoroughly mixed. The portion weighed out for analysis was made into a cream with a little water in an agate mortar. This was then washed into a hot solution of standard oxalic acid, and the remainder of the analysis carried out as in the case of the liquid phase. The figures obtained are given in Table II.

TABLE II.

Serial No.	% $Nd_2(C_2O_4)_3$.	% $Nd_2(NO_3)$.
2	70.46	0.35
4	66.65	2.26
8	62.36	6.16
11	59.10	10.01
13	57.36	12.17
15	21.41	52.20

These results are plotted upon the triangular diagram, Fig. 2.

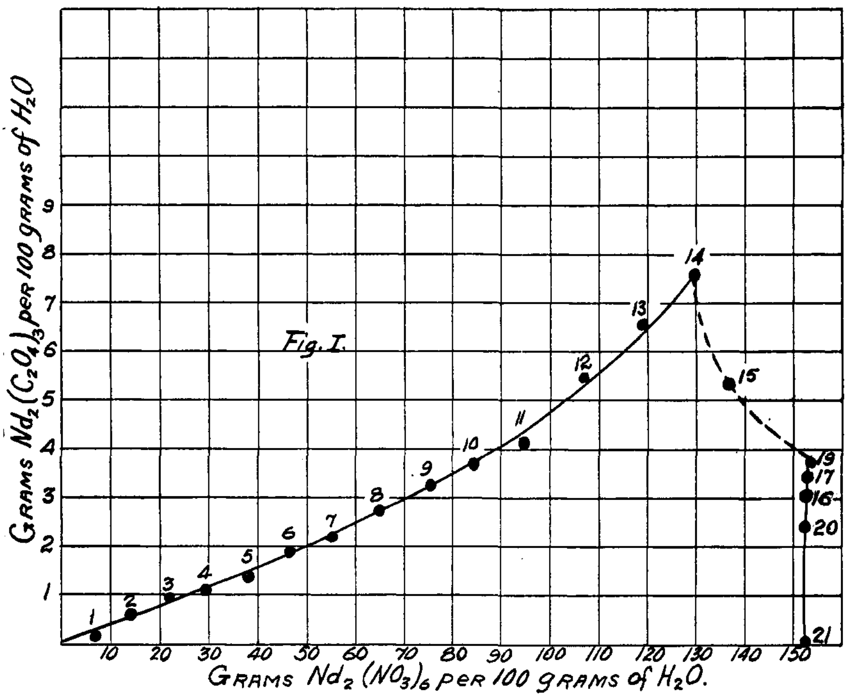

Fig. I.

Grams $Nd_2(C_2O_4)_3$ per 100 grams of H_2O
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Grams $Nd_2(NO_3)_6$ per 100 grams of H_2O.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
19
17
16
20
21

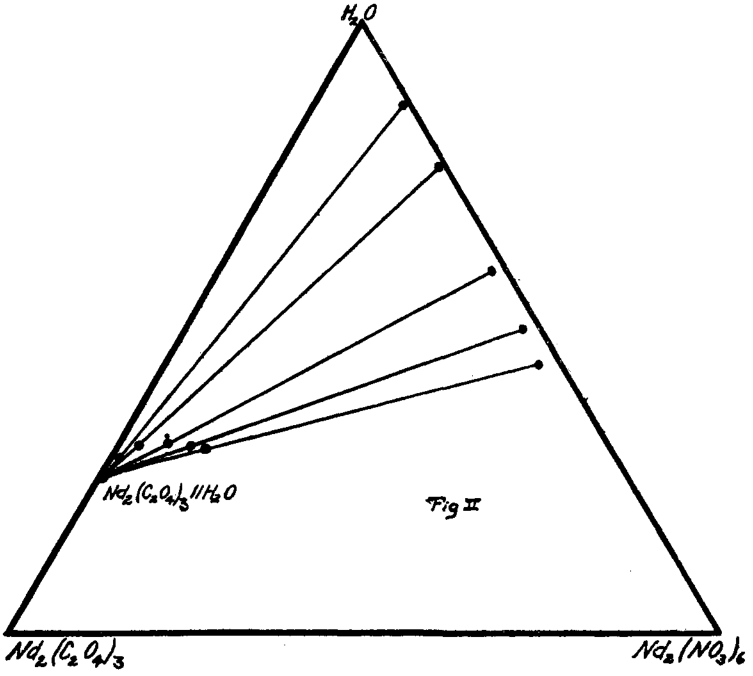

Fig II

H_2O
$Nd_2(C_2O_4)_3 11H_2O$
$Nd_2(C_2O_4)_3$
$Nd_2(NO_3)_6$

From Fig. 2 it is seen that, in the case of bottles 1 to 14, if lines are drawn from the points representing the composition of the liquid phase through points representing the composition of the respective solid phases they all meet at the point X. This point represents the composition of the compound $Nd_2(C_2O_4)_3.11H_2O$.

It was impossible to study the second part of the curve in a similar manner, owing to the fact that there was an insufficient number of bottles lying between the points B and C. No solvent could be found that would remove the neodymium nitrate without decomposing the oxalonitrate. The best prepared material from bottle 15 showed that the probable ratio of oxalate to nitrate was one to two and a half $[Nd_2(C_2O_4)_3.2^1/_2Nd_2(NO_3)_6.24H_2O]$, or else in the ratio of one to two. This point will be taken up at some later date.

It is interesting to observe that only one hydrate of neodymium oxalate is stable in contact with varying concentrations of neodymium nitrate solution at 25°. In the case of lanthanum oxalate and lanthanum nitrate, three hydrates were found to exist, *viz.*, 8, 5 and 3 molecules of water. Also in the case of the lanthanum it was found that the mixtures remained in a metastable condition for a very long time (several months). The results that were published show this.[1]

New Compounds of Europium.

The europium used in this study was obtained by the fractional crystallization of the double magnesium nitrates in the presence of bismuth magnesium nitrate.[2]

Europium Formate, $(HCOO)_6Eu_2$, was obtained by dissolving the hydroxide in dilute (1–3) formic acid. The solution was heated in a water bath, when the europium formate separated as a white crystallin mass only slightly soluble in water. The compound was dried at 80° in an electric oven, and the oxide was determined by a simple ignition.

Calculated: Eu_2O_3, 61.32. Found: Eu_2O_3, 61.34.

Europium Quinate, $(C_6H_7(OH)_4COO)_6Eu_2.12H_2O$.—This substance was prepared by boiling europium hydroxide with a solution of quinic acid. Upon evaporation, the liquid became very concentrated before it showed signs of crystallizing. The almost solid product was broken up and digested with absolute alcohol. This quinate is insoluble, while the acid itself is fairly soluble in alcohol. After several digestions, the salt was drained and dried in the air at room temperature. It forms a granular mass, very soluble in hot water.

Calculated: Eu_2O_3, 21.12. Found: Eu_2O_3, 21.19.

Europium Pyromucate, $[C_4H_3OCOO]_6Eu_2.2H_2O$.—This substance was made in a similar manner to those above. However, it was found that

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[1] THIS JOURNAL, **34,** 1168.

[2] *Ibid.*, **33,** 1363.

as soon as the solution became concentrated, it crystallized readily upon cooling. The solid was powdered; washed with alcohol and dried at room temperature. This pyromucate was easily soluble in water.

Europium Meta-nitro-benzenesulfonate, $[C_6H_4(NO_2)SO_3]_6Eu_2.6H_2O$.—An aqueous solution of meta-nitrobenzenesulfonic acid was treated with a slight excess of europium hydroxide. The excess of hydroxide was filtered off and the solution evaporated. The crystals were washed with alcohol and dried at 80° for some time. The salt was slightly yellowish and very soluble in water. By a simple ignition it was found to contain 21.63% Eu_2O_3, while the calculated amount comes to 21.65 Eu_2O_3.

DURHAM, N. H.

RELATION BETWEEN THE MAGNETIC FIELD AND THE PASSIVE STATE OF IRON. III.

BY HORACE G. BYERS AND SETH C. LANGDON.

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Since the discovery of the passivity of iron by James Keir in 1790, a very great number of investigations have been devoted to it and allied phenomena. These investigations have been summarized by one of us in an article published in 1908.[1]

It was there pointed out that none of the numerous suggestions as to the cause of passivity were satisfactory, and an attempt was made to define the term which by reason of extension to similar phenomena has become confused. The term was defined as properly used when applied to an element when it "shows abnormal electrochemical relations and a chemical inactivity not corresponding to its ordinary behavior and not in accord with its position in the electromotive series of the elements."

Using this definition we find that up to the publication of the article mentioned it was recognized that certain metals become "passive," *i. e.*, behave abnormally, when used as an anode provided the electrolyte is of a given type, chiefly oxygen compounds, and provided excessive temperatures are avoided. It was also there shown that in addition to the character of the electrolyte and the temperature another determining factor in the establishment of the passive condition in a given metal as an anode is the density of the current employed. A fourth factor is the time during which the current passes. It is the purpose of the present paper to show that still another factor enters into the establishment of the passive state upon a metal.

In 1910 and 1911 it was shown by one of us, together with Marc Darrin and A. F. Morgan[2] that the establishment of the passive state of iron and

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[1] THIS JOURNAL, 30, 1718.

[2] *Ibid.*, 32, 750; 33, 1757.