Rideal[7] has already pointed out that a modification of reaction velocity should take place at these low pressures if simple collision, quantum chain or chain theories of molecular activation are applicable to the decomposition of nitrogen pentoxide.

The author takes this opportunity to express his appreciation of the assistance given by Professor Hugh S. Taylor.

Summary

The decomposition of nitrous oxide has been studied at low pressure. The reaction changes from bimolecular to unimolecular. The most probable explanation seems to be that the reaction is entirely heterogeneous when the pressure is at a few hundredths of a millimeter.

The decomposition of nitrogen pentoxide was studied between the total pressure limits of 0.18 and 0.0018 mm. of mercury. The velocity constant remained essentially constant throughout this hundred-fold variation of initial pressure and was in excellent agreement with the values found by Daniels and Johnston at high pressures. This was in contradiction of the observations of Hirst and Rideal.

No evidence of a transition from a unimolecular to a bimolecular reaction as predicted from Lindemann's theory was present. Not even the assumption of 30 degrees of freedom in the nitrogen pentoxide molecules would account for the rate of activation found at low pressures.

An undisturbed life for active molecules of approximately 10^{-5} seconds seems to be without effect.

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

OBSERVATIONS ON THE RARE EARTHS. XXVII. I. FRACTIONAL PRECIPITATION OF THE CERIUM GROUP EARTHS BY ELECTROLYSIS. II. SOLUBILITY OF RARE EARTH OXALATES IN NITRIC ACID[1]

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I. Fractional Precipitation of the Cerium Group Earths by Electrolysis

Electrolysis of neutral salt solutions of the rare earths will cause the formation of hydroxide at the cathode. Due to difference in basicities of the rare earth elements, a fractionation may be effected in this manner. Dennis and his co-workers[2] electrolyzed solutions of the rare earths using

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[1] Part of a thesis submitted by J. W. Neckers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

[2] Dennis and others, THIS JOURNAL, 37, 131 (1915); 37, 1963 (1915); 40, 174 (1918).

a platinum anode and a mercury cathode. They effected separations of lanthanum from praseodymium and erbium from yttrium. Both nitrate and chloride solutions were used.

Brinton[3] has recently determined the *P*H values of several of the rare earth solutions at the point at which the hydroxide began to precipitate. The values of 6.83, 7.00, 7.05 and 8.35 are given for samarium, neodymium, praseodymium and lanthanum hydroxides, respectively. A confirmation of Brinton's values is shown in the electrolytic fractionation here described. Approximately 8% solutions were used.

A potential of 6 to 7 volts was found to give the best results.

The anode was made of platinum and was isolated by means of a porous porcelain cup.

A mercury cathode was always employed. Glass containers were used for cells. The electrolyte was stirred during electrolysis. The hydroxide fractions formed in most cases filtered fairly well although at times their gelatinous nature caused trouble. The following series of fractionations are reported.

Series I

Fifteen liters of 8% solution of lanthanum and praseodymium chlorides were used. Tabulated results are given in Table I.

TABLE I

LANTHANUM-PRASEODYMIUM

No.	Time, hrs.	Voltage, v.	Current, amp.	Wt. of oxide, g.	Color of oxide	Remarks
1	7	6	3.5	..	....	Manganese impurity
2	5	6	3.0	25	Chocolate brown	High % of Pr
3	1.5	5.8	4.8	17	Chocolate brown	High % of Pr
4	1.3	6.2	5.0	15	Chocolate brown	High % of Pr
5	1.5	6	3.8	18	Chocolate brown	High % of Pr
6	3	6.2	1.4	14	Medium brown	50% Pr 50% La
7	4	6.0	1.2	17	Light brown	20% Pr 80% La
8	6	6.2	1.4	22	Buff brown	5% Pr 95% La
9	6	6.5	1.0	18	Light buff	3% Pr 97% La
10	5	7.0	0.9	14	Light buff	1% Pr 99% La
11	5	6.2	.9	10	Light buff	1% Pr 99% La
12	4.5	7.2	1.1	15	Light buff	1% Pr 99% La
		Residue		457	Light buff	99% La

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[3] Brinton, *J. Chem. Soc.*, 127, 2110 (1925).

Series II

The process was next applied to a mixture of all of the metals of the cerium group with a very small percentage of the yttrium group metals also present. An approximately 8% solution of 11.5 liters' volume was used under the same conditions as in Series I. A tabulation of the data follows.

Table II

Cerium Group

No.	Time, hrs.	Voltage, v.	Current, amp.	Wt. of oxide, g.	Color of oxide	Remarks
1	7.5	6.8	0.9	14	Medium brown	Nd, Yt group, Sa, 5% Pr
2	23	7.0	1.3	49	Medium brown	Nd, Yt group, Sa, 5% Pr
3	10	7.0	3.0	41	Dark brown	50% Nd, 40% Pr, 10% Sa
4	9	7.0	3.3	23	Chocolate brown	50% Nd, 45% Pr, 5% Sa
5	14	7.0	2.7	36	Chocolate brown	50% Nd, 50% Pr
6	18	6.3	2.2	32	Chocolate brown	50% Nd, 50% Pr
7	17	6.5	2.3	36	Chocolate brown	50% Nd, 50% Pr
8	22	6.4	2.1	26	Chocolate brown	50% Nd, 50% Pr
9	18	7.0	2.3	27	Chocolate brown	50% Nd, 50% Pr
10	23	6.9	1.9	22	Chocolate brown	50% Nd, 50% Pr
11	24	7.4	1.7	29	Medium brown	35% Nd, 35% Pr, 30% La
12	27	7.0	1.7	30	Light brown	50% La, 25% Pr, 25% Nd
13	36	7.0	0.9	22	Buff	80% La, 10% Pr, 10% Nd
14	39	7.0	1.0	20	Buff	90% La, 5% Pr, 5% Nd
15	40	7.0	1.0	21	Light buff	98% La, 1% Pr, 1% Nd
16	39	7.0	1.1	15	Light buff	99% La, 1% Pr
17	35	7.2	1.2	12	Light buff	99% La, 1% Pr
18	40	7.0	1.1	11	White	100% La
19	36	7.2	1.1	10	White	100% La
20	59	7.0	1.1	12	White	100% La

Although samarium and the yttrium group metals concentrate in the first fractions, it appears possible to obtain only an efficient concentration of lanthanum.

Series III

This series was similar in composition to Series II except that the conductivity was increased threefold by the addition of 5% sodium chloride. The speed of electrolysis was thus increased correspondingly with no decrease in efficiency of separation.

Series IV

To apply this method to a more difficult separation, 12.5 liters of an 8% solution of praseodymium and neodymium chlorides (with 5% of sodium chloride) was electrolyzed. No appreciable separation or concentration occurred although several small fractions were precipitated at both ends of the series.

Discussion of Results

It appears possible to separate rare earths by electrolysis of neutral solutions only when the *P*H values are separated by more than 0.25. The values given by Brinton[3] are thus substantiated.

It is possible that a more efficient separation might be obtained by using more dilute solutions and much smaller amperages. Under such conditions the method would become less practicable.

II. Solubilities of Rare Earth Oxalates in Nitric Acid

Sarver and Brinton[4] have recently determined the solubilities of several rare earth oxalates in nitric, hydrochloric and sulfuric acids at 25°.

Since there is considerable difference in solubility of the oxalates at room and at elevated temperatures, it seemed desirable to have solubility data taken at more elevated temperatures. Such data might be of value in a further study of methods of fractionation. Solubilities were accordingly run in mixtures of nitric and oxalic acids.

The solubility tests were carried out in 500cc. Florence flasks with long necks and covered with close fitting heavy watch glasses. A temperature of 90 ± 2° was maintained by means of a slightly modified steam-bath. Temperatures of 25° were maintained by ordinary methods. Excess oxalate was added to 150 cc. of the nitric acid contained in the flasks as described. Thirty-six hours with frequent shaking was considered long enough to establish equilibrium. For analysis, two 50cc. quantities of the solutions were withdrawn with a pipet, to the tip of which an efficient filter was attached, evaporated to dryness and ignited in porcelain.

TABLE III

SOLUBILITY OF OXALATES AT 90°

Grams of oxide from 100 cc. of solution

Normality of nitric acid	Oxalic acid, %	La	Pr	Nd	Sm	Dy	Yt
0.779	...	0.4421	0.3871	....	....	....	....
1.25	...	....	....	0.8707	....	....	....
1.558	...	1.2377	1.0764	....	....	....	....
2.337	...	....	1.8467	....	....	....	....
2.50	...	....	....	1.9571	1.8779	1.8458	1.3180
3.75	...	4.6670	....	....	....	....	....
5.00	...	10.4160	6.8825	6.7788	5.6750	4.8470	3.0135
0.779	5	0.0302	0.0275	....	....	....	....
1.25	5	....	....	0.0915	....	....	....
1.558	5	0.3083	0.1639	....	....	....	....
2.337	5	.7517	.6932	....	....	....	....
2.50	5	....	....	0.6760	0.5457	0.4215	0.4315
3.75	5	3.5260	....	....	....	....	....
5.00	5	9.3907	5.2339	5.1263	4.1520	3.4135	1.4515

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[4] Sarver and Brinton, THIS JOURNAL, 49, 943 (1927).

The solubility determinations made at 25° were in practical agreement with those published by Sarver and Brinton and hence need not be given here. The determinations made at 90° in nitric acid of various strengths and also in the presence of oxalic acid are given in Table III.

Discussion of Results

The determination of solubilities in 1.25 *N* acid was discontinued after it was found that the solubility was so small that no practical use could be made of such data. At 90°, especially in the 5 *N* acid solutions, it was found that the solution reached no definite saturation point. The solubility of the oxalate seemed to be proportional to the length of time that the excess solid salt was in contact with the solution. This was shown by the fact that neodymium oxalate in contact with the 5 *N* acid for a few hours yielded 5.7060 g. of oxide from 100 cc. of the solution while if it stood for three days the oxide weighed 8.8596 g. This is probably due to the formation of oxalonitrates and the data under the hot, concentrated acid may well be called a comparison of the rate of decomposition rather than of the solubility. (The solubility, however, is a function of the rate of decomposition.) Therefore, to obtain data which would, in a graphic form, show a comparison of the solubilities, the different oxalates were submitted simultaneously to the same solubility treatment, under like conditions for the same length of time. The data resulting from the procedure are those used in the 5 *N*, 90° series.

It is observed that the solubilities of the oxalates at 90° is of the same order as at 25°. From these data it may also be gathered that the separation of lanthanum from praseodymium is feasible by fractionation of the oxalates. Very little separation of the other members of the cerium group might be expected. Both of these facts have been proved by actual trial in this Laboratory. The separation of yttrium from holmium might also be feasible by this method.

Summary

1. It has been found possible to separate lanthanum from praseodymium and the other cerium group earths by fractional electrolytic precipitation. Addition of 5% of sodium chloride increases the conductivity, and thus the rate of precipitation, threefold without impairing the efficiency of the fractionation. Other separations in the cerium group are not feasible by this method.

2. The solubility of the oxalates of lanthanum, praseodymium, neodymium, samarium, dysprosium and yttrium has been determined in 1.25, 2.50 and 5.00 *N* nitric acid at 90°. A corresponding series of determinations has also been made with 5% oxalic acid added to the nitric acid.

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