Wheeler's experiments on the catalytic combination of hydrogen and oxygen in presence of metallic oxides, from which they drew the conclusion that this process does not depend on alternate reduction and reoxidation, are considered from the standpoint of the previous paragraph, and are shown to favor strongly, rather than discredit, this view of the mechanism.

PRINCETON, NEW JERSEY

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

OBSERVATIONS ON THE RARE EARTHS. XIII. STUDIES IN THE ABSORPTION SPECTRA

BY L. F. YNTEMA[1]

Received August 3, 1922

Introduction and Procedure

The data hitherto available on the absorption spectra of the rare earths are, for the most part, the products of various investigators using different methods and different conditions of experiment. In only a few instances have the absorption curves been plotted. The present investigation was undertaken to secure data obtained under uniform conditions, with the object of eliminating as many factors as possible that might affect the bands.

The solutions, slightly acid chlorides, were contained in a Baly absorption tube and a nitrogen-filled tungsten lamp was used as a source of light. The light was very satisfactory, being extremely constant in intensity and furnishing a continuous spectrum. If it should be desired to extend the investigation into the ultraviolet, it is practicable to insert a quartz window into the side of the bulb and refill with nitrogen. A commercial autocollimating quartz-prism spectrograph was used.

The first photograph of a series for an element was taken through a 10-cm. layer of solution and then, as the depth of solution was decreased by steps, 7 photographs were usually taken between 10 and 1 cm., the distances chosen being in a reverse geometric ratio, in order that the logarithms of the distances might be equally spaced on the graphs. At 1 cm. the solution was diluted to $^1/_{10}$ its strength and another series of photographs were taken. The dilution was continued until all bands had disappeared. It was assumed that Beer's law holds true.

All exposures were made for 5 minutes on "Spectrum Process Plates." The iron arc was used as standard of reference.[2] The wave lengths tabulated below are in International Ångstrom units.

The accompanying graphs represent the edges of absorption bands, the wave lengths plotted as abscissas and the logarithms of the equivalent

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[1] National Research Fellow in Chemistry.

[2] Kayser, "Handbuch der Spectroscopie," S. Hirzel, Liepzig, 1912, vol. 6.

thickness of the solutions as ordinates. Where the edges of bands have become indistinct, the curves are dotted.

The tables contain the wave lengths of the maximum of each band, the depth of layer, the normality at which the band last appears, and the equivalent thickness of the last appearance.[3] The sensitivity of the photographic plates to light of different wave lengths may be expected to be constant for the investigation because plates of a single emulsion number were used. No attempt was made to compare their sensitivity to different portions of the spectrum with the sensitivity of the eye.

The solutions were also examined visually in order to check the results obtained by the photographic method. A constant deviation spectrometer was used with a tungsten lamp as the source of light. A number of very faint bands were found in the spectra of neodymium, samarium, dysprosium and erbium that were not registered on the photographic plate. No attempt was made to determine the last appearance of these bands with reference to the stronger bands. It may be noted that the wave lengths found for the stronger bands by the visual and the photographic methods agreed very closely.

Praseodymium

The absorption spectrum of praseodymium in aqueous solution has been investigated by Forsling,[4] Bettendorf,[5] Schottländer,[6] Brauner,[7] Böhm,[8] Aufrecht,[9] Rech,[10] Stahl,[11] Jones and Guy,[12] Ball,[13] Baxter and Stewart,[14] and Uhler and Wood.[14a] The praseodymium used was prepared

Table I

Praseodymium

Maxima	Last appearance N	Last appearance Cm.	Equivalent thickness of last appearance	Maxima	Last appearance N	Last appearance Cm.	Equivalent thickness of last appearance
4441	0.01	7.32	7.32	5890	0.1	3.90	39
4690	0.01	9.76	9.76	5974	0.1	7.00	70
4819	0.01	4.88	4.88	..	...	..	...

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[3] Baly, "Spectroscopy," Longmans, Green and Co., London, **1918**, p. 414.

[4] Forsling, *Bih. svenska. Vet. Akad. Handl.*, **23**, Afd. 1, No. 5, 20 (1898); **18**, Afd. 1, No. 10, 23 (1893).

[5] Bettendorf, *Ann.*, **256**, 159 (1890).

[6] Schottländer, *Ber.*, **25**, 569 (1892).

[7] Brauner, *Proc. Chem. Soc.*, **14**, 71 (1898).

[8] Böhm, *Ber.*, **33**, 42 (1900).

[9] Aufrecht, *Dissertation*, Berlin, **1904**.

[10] Rech, *Z. wiss. Phot.*, **3**, 411 (1906).

[11] Stahl, *Le Radium*, **6**, 215 (1909).

[12] Jones and Guy, *Physik. Z.*, **13**, 649 (1912).

[13] Ball, *Proc. Roy. Soc.*, **87A**, 121 (1912).

[14] Baxter and Stewart, This Journal, **37**, 523 (1915).

[14a] Uhler and Wood, "Atlas of Absorption Spectra," Carnegie Institution of Washington, **1907**.

in this Laboratory by fractionation of the double magnesium nitrates. It still contained small amounts of lanthanum and neodymium.[15] The first photograph was of a 10cm. layer of a 10 N solution.

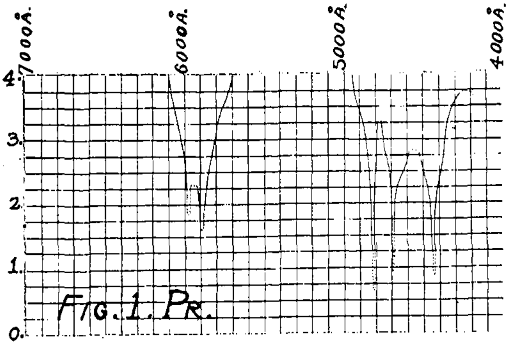

FIG. 1. PR.

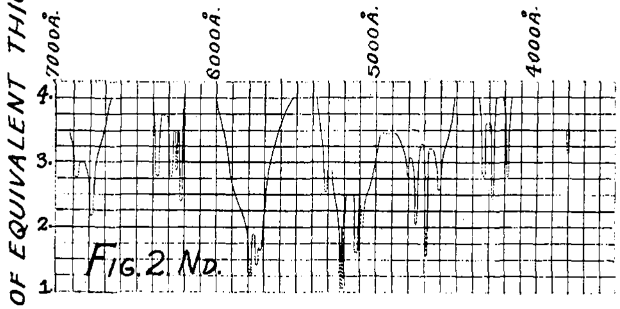

FIG. 2 ND.

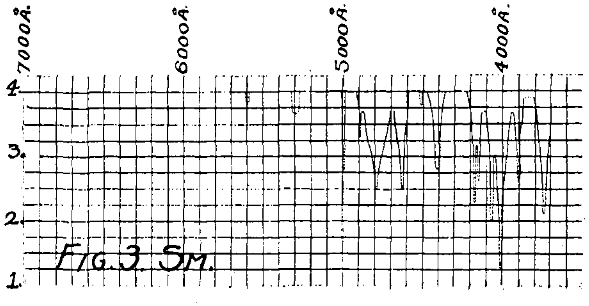

FIG. 3 SM.

Neodymium

The following investigators have studied the absorption spectrum of neodymium in aqueous solution: Demarçay,[16] Forsling,[17] Welsbach,[18]

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[15] Kiess, Hopkins and Kremers, *Bur. Standards Sci. Paper*, **421** (1922).

[16] Demarçay, *Compt. rend.*, **126**, 1039 (1898).

[17] Forsling, *Bih. svenska. Vet. Akad. Handl.*, **18**, I, No. 4, 32 (1892).

[18] Welsbach, *Sitzber., Akad. Wiss. Wien*, **92**, II, 317 (1885).

Brauner,[7] Boudonard,[19] Stahl,[11] Exner,[20] Dimmer,[21] Drossbach,[22] Stutzel,[23] Rech,[10] Baxter and Chapin,[24] Baxter and Woodward,[25] and Uhler and Wood.[14a]

The neodymium used in the present investigation was prepared by fractionation of the double magnesium nitrates.[15] It was of a very high degree of purity. The first photograph was of a 10cm. layer of a 10 *N* solution.

TABLE II

NEODYMIUM

Maxima	Last appearance *N*	Cm.	Equivalent thickness of last appearance	Maxima	Last appearance *N*	Cm.	Equivalent thickness of last appearance
3803	10	1.5	1500	5222	0.1	1.16	11.6
4185	1	6.25	625	5319	1	3.75	375
4273	0.1	1.8	18	5726	0.1	4.6	46
4331	1	6.25	625	5748	0.1	2.7	27
4612	1	3.75	375	5782	0.1	1.8	18
4691	0.1	3.75	37.5	6228	1	2.8	280
4755	1	1.17	117	6251	1	7.5	750
4803	1	6.25	625	6286	1	6.25	625
5091	0.1	7.8	78	6374	1	6.25	625
5123	0.1	4.6	46	6786	1	1.56	156
5205	0.1	1.16	11.6	6877	1	6.25	625

In addition, there were faint bands observed by visual methods at 4293 (very faint), 4869, 5253, 5731, 5816, 5823, 5888 and 6720.

It may be noticed that the 5816 band, recorded by Baxter and Chapin as present only in a nitrate solution, was found in a chloride solution. Their 5470 band, described as present only in a nitrate solution, was not found in a chloride solution.

Samarium

Prandtl[26] has published a complete study of the absorption spectrum of samarium. Using the nitrate, he lists the edges of the bands at various concentrations and plots absorption curves. He gives as the maxima, 345.5, 355, 363, 375, 390, 401, 407, 417, 442, 451.6, 464, 479.5, 500.7, 529 and 560. The results of the present investigation are in close agreement with those of Prandtl. Determinations have also been published by

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[19] Boudonard, *Bull. soc. chim.*, **19**, 382 (1898).

[20] Exner, *Sitzber. Akad. Wiss. Wien*, **108**, IIA, 1259 (1899).

[21] Dimmer, *ibid.*, **106**, IIA, 1087 (1897).

[22] Drossbach, *Ber.*, **35**, 1486 (1902).

[23] Stutzel, *ibid.*, **32**, 2653 (1899).

[24] Baxter and Chapin, THIS JOURNAL, **33**, 13 (1911).

[25] Baxter and Woodward, *ibid.*, **33**, 270 (1911).

[26] Prandtl, *Z. anorg. allgem. Chem.*, **116**, 96 (1921).

Demarçay,[27] Böhm,[28] Soret,[29] de Boisbaudran,[30] Bettendorf,[31] Forsling,[4] Krüss and Nilson,[32] Muthmann, Weiss and Heramhof,[33] and Becquerel.[34] Samarium material, purified in this Laboratory[15,35] for atomic-weight determinations, was used. The first photograph was of a 10cm. layer of a 10 N solution.

TABLE III

SAMARIUM

Maxima	Last appearance N	Cm.	Equivalent thickness of last appearance	Maxima	Last appearance N	Cm.	Equivalent thickness of last appearance
3740	1	1.33	133	4636	1	3.16	316
3905	1	4.64	464	4794	1	3.16	316
4013	0.1	1.78	17.8	4893	10	2.16	2160
4071	0.1	10	100	4995	1	6.81	681
4154	1	4.64	464	5297	10	4.64	4640
4177	1	2.16	216	5594	10	6.9	6900
4411	1	6.81	681	..	...	..	...

Visual methods gave, in addition, bands at 4509, 4744, 5277 and 5572.

Europium

An attempt was made to plot the absorption of europium using the best fraction of series of crystallizations of europium-samarium nitrate but only 2 lines were visible. These were reported as a single line by Prandtl.[26] Their maxima are at 5257 and 5253. The determinations of Demarçay[36] agree with those of Prandtl.

Dysprosium

The absorption spectrum of dysprosium has been measured by Urbain[37] and de Boisbaudran.[38] The results reported herewith agree very closely with theirs.

The dysprosium used was that purified in this Laboratory for the determination of the atomic weight that has been accepted by the International Committee on Atomic Weights.[39] It contained, as shown by the absorption, a small percentage of holmium. The first photograph was of a 10-cm. layer of a 2 N solution.

[27] Demarçay, *Compt. rend.*, **130,** 1185 (1900).

[28] Böhm, *Z. angew. Chem.*, **15,** 372, 1282 (1902).

[29] Soret, *Compt. rend.*, **91,** 378 (1880).

[30] de Boisbaudran, *ibid.*, **88,** 322 (1879); **89,** 521 (1879).

[31] Bettendorf, *Ann.*, **263,** 164 (1891).

[32] Krüss and Nilson, *Ber.*, **20,** 2134 (1887).

[33] Muthmann, Weiss and Heramhof, *Ann.*, **355,** 165 (1907).

[34] Becquerel, *Compt. rend.*, **145,** 1150 (1907).

[35] THIS JOURNAL, **42,** 515 (1920).

[36] Demarçay, *Compt. rend.*, **130,** 1469 (1900).

[37] Urbain, *ibid.*, **142,** 785 (1906).

[38] de Boisbaudran, *ibid.*, **102,** 1003 (1886).

[39] THIS JOURNAL, **40,** 598 (1918).

TABLE IV

DYSPROSIUM

Maxima	Last appearance N	Last appearance Cm.	Equivalent thickness of last appearance	Maxima	Last appearance N	Last appearance Cm.	Equivalent thickness of last appearance
3800	1	4.22	422	4502	1	3.16	316
3873	0.1	4.22	42.2	4534	1	2.37	237
3990	1	4.22	422	4754	1	5.62	562
4275	1	4.22	422	..	...	..	...

There was also a faint band, found by visual methods, at 4778.

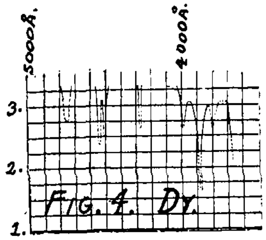

FIG. 4. DY.

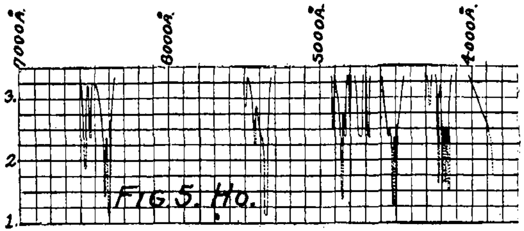

FIG. 5. HO.

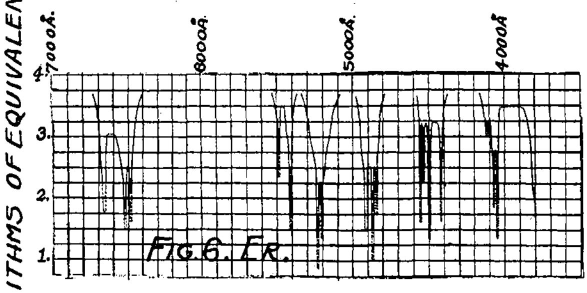

FIG. 6. ER.

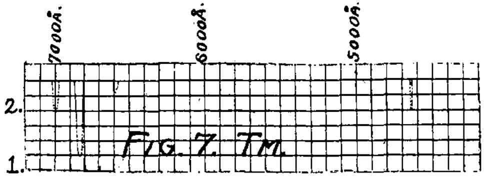

FIG. 7. TM.

Holmium

The absorption of holmium has been determined by Urbain[37] and Holmberg.[40]

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[40] Holmberg, *Z. anorg. Chem.*, **71**, 226 (1911).

The holmium used in the present investigation was a portion of that now in process of purification in this Laboratory. The preliminary separation of the groups and fractionation of the bromates was accomplished by the same method as that used for other members of this group.[15] When examination of the absorption spectrum showed a fraction to be free from all the colored earths except holmium, it was set aside. These fractions were converted into nitrates, and separation from yttrium, the only remaining impurity, was begun by the fusion method.[41] The holmium used had a mean equivalent weight of 157.62 and, therefore, an yttrium content of about 8%. The solution was standardized with respect to holmium, the assumption being made that the yttrium would have little or no effect on the holmium spectrum. The first photograph was of a 10cm. layer of a 2 *N* solution.

TABLE V

HOLMIUM

	Last appearance		Equivalent thickness of last appearance		Last appearance		Equivalent thickness of last appearance
Maxima	*N*	Cm.		Maxima	*N*	Cm.	
3865	0.1	5.62	56.2	4799	1	5.62	562
4159	0.1	3.16	31.6	4831	1	2.37	237
4174	0.1	4.22	42.2	4853	0.1	2.37	23.7
4192	0.1	4.22	42.2	4910	1	3.16	316
4220	0.1	4.22	42.2	5365	0.1	1.33	13.3
4273	1	7.5	750	5435	1	1.78	178
4505	0.1	1.78	17.8	5493	1	7.5	750
4522	0.1	1.78	17.8	6405	0.1	1.33	13.3
4549	1	2.37	237	6433	0.1	2.37	23.7
4678	1	2.37	237	6530	1	2.37	237
4735	1	2.37	237	6567	0.1	7.5	75

These data agree very well with those obtained by Holmberg. The close coincidence of two holmium lines at 4273 and 4505 with dysprosium lines at 4275 and 4502 might be pointed out as being a possible source of confusion in the identification of either element in the presence of the other.

Erbium

The values obtained by different observers of the absorption spectrum of erbium vary greatly, probably because of impurities in many of the materials used. Results are reported by Bunsen,[42] Cleve,[43] Soret,[29] Hofmann and Bugge,[44] Exner,[20] and Uhler and Wood.[14a]

The erbium used in this investigation was prepared in this Laboratory.[45] It had a mean equivalent weight of 161.2 and an yttrium content of about

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[41] Driggs, *Thesis*, Univ. Illinois, 1921.

[42] Bunsen, *Pogg. Ann.*, **155**, 230, 366 (1875).

[43] Cleve, *Compt. rend.*, **89**, 478, 708 (1879); *Chem. News*, **49**, 125 (1879).

[44] Hofmann and Bugge, *Ber.*, **41**, 3783 (1908); **43**, 2631 (1910).

[45] THIS JOURNAL, **40**, 1615 (1918).

7.9%. No impurities except yttrium were present. The first photograph was taken of a solution 10 cm. thick and 5 *N* with respect to erbium.

TABLE VI

ERBIUM

Maxima	Last appearance *N*	Cm.	Equivalent thickness of last appearance	Maxima	Last appearance *N*	Cm.	Equivalent thickness of last appearance
4050	0.1	2.37	23.7	4871	0.01	10	10
4060	1	5.62	562	4913	0.1	3.16	31.6
4072	0.1	7.5	75	5208	0.1	2.37	23.7
4104	1	10	1000	5232	0.01	7.5	7.5
4123	1	10	1000	5416	0.1	4.22	42.2
4422	0.1	4.22	42.2	5490	1	7.5	750
4479	0.1	2.37	23.7	6490	0.1	4.22	42.2
4537	1	1.78	178	6526	0.1	3.16	31.6
4555	0.1	4.22	42.2	6669	0.1	5.62	56.2
4849	0.1	5.62	56.2	..	...	..	..

Erbium has, in addition, two faint bands at 5396 and 5515.

Thulium

The absorption spectrum of thulium has been measured by Cleve[43] and Forsling.[46] For this investigation a thulium-rich fraction from the soluble end of a bromate series[22] was converted into chloride. There were present, as impurities, erbium and all the members of the ytterbium group. Since the strength of the solution with respect to thulium could not be estimated, it was designated as "X.*N*". The first photograph was through a 30cm. layer.

TABLE VII

THULIUM

Maxima	Last appearance *N*	Cm.	Equivalent thickness of last appearance	Maxima	Last appearance *N*	Cm.	Equivalent thickness of last appearance
4643	X	10	100	6835	X	1.78	17.8
6588	X	20	200	6999	X	10	100

Quantitative Estimation of Rare Earths

An approximate determination of the percentage of a colored rare earth in a mixture may be made by diluting a solution of the mixture until the most persistent band has disappeared, and taking the ratio between the equivalent thickness of the last appearance in the mixture and in the pure salt. Using a mixture of yttrium and erbium, the last appearance of the most persistent erbium band, 5232 Å., was at a concentration of 0.1 *N* and a depth of layer of 7.5 cm. From the data on erbium it is seen that the band persists to a concentration of 0.01 *N* and 7.5 cm. depth. Therefore the mixture contained about 10% of erbium. The mean equivalent weight of the material was 95.9, indicating an erbium content of 8.4%.

[46] Forsling, *Bih. svenska. Vet. Akad. Handl.*, **24,** I, No. 7, 35 (1899).

The method would be most useful in the analysis of mixtures of elements of nearly equal atomic weights, such as lanthanum and praseodymium, since the mean equivalent weight, unless determined with extreme accuracy, would give little information as to the composition of the mixture. The accuracy of this method depends on the standardization of working conditions.

Periodicity of Lines

One object of this investigation was to secure data on the absorption spectra of the rare earth elements, obtained under uniform conditions, for postulating a periodic relationship among the spectra, but no very definite relations were found. It is hoped to continue the study of this problem.

The author desires to express his appreciation of the suggestions given by Professor B. S. Hopkins during the progress of this work.

Summary

1. The absorption spectra of praseodymium, neodymium, samarium, dysprosium, holmium, erbium and thulium in the visible portion of the spectra have been measured at various concentrations and thicknesses of solution.
2. Absorption curves have been drawn and the last appearance of each band on dilution has been tabulated.
3. A method for the quantitative estimation of rare earths is outlined.
4. There seems to be no definite periodic arrangement of the absorption bands.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 14]

AN APPARENT DEVIATION FROM HENRY'S LAW FOR THE SYSTEM, AMMONIA-WATER

BY G. CALINGAERT AND F. E. HUGGINS, JR.

Received November 4, 1922

According to Henry's law: "Any chemical substance present in a gaseous phase and in a condensed phase in equilibrium with it has, at any definite temperature, a mole fraction c in the condensed phase which is proportional to its mole fraction C in the gaseous phase: $C = ac$, where a is an equilibrium constant which is determined by the nature of the chemical substance, of the solvent, and by the temperature." The system ammonia-water, is reported by all experimenters as obeying Henry's law up to concentrations of 3.2 g. of ammonia per liter and over a temperature range from 0° to 100°.