[CONTRIBUTIONS FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PRASEODYMIUM.

THE ANALYSIS OF PRASEODYMIUM CHLORIDE.

BY GREGORY PAUL BAXTER AND OLUS JESSE STEWART.

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Introduction.

Not many years ago the atomic weight of neodymium was investigated in this laboratory by the analysis of the anhydrous chloride.[1] Since considerable success was met both in preparing pure material and with the analytical method employed, the twin element praseodymium was investigated in a similar fashion; for, from the results of the earlier investigations upon praseodymium, it can readily be seen that the value of its atomic weight is far from certain.

After Auer von Welsbach[2] first separated the old didymium, he determined the atomic weights of the constituents by Bunsen's method of converting oxide to sulfate. Apparently the results were interchanged in publication, as Brauner has suggested, for the lower value 140.8 was assigned to neodymium.

Next Brauner,[3] in 1898, starting with material purified by Shapleigh by crystallization of the double ammonium nitrate, continued the process of crystallizing this salt until neodymium was completely eliminated, then removed a trace of lanthanum by fusion with potassium nitrate, extraction of the praseodymium oxide with ammonium nitrate, and fractionation with ammonia and oxalic acid. By both the analysis of the oxalate and synthesis of the sulfate thirteen results were obtained between 140.84 and 141.19, with an average of 140.95.

Jones,[4] in the same year, further purified double ammonium nitrate furnished by the Welsbach Light Company by crystallization until the neodymium content was about 0.06%, as determined by comparison with neodymium solutions of known concentration. Cerium was removed by the basic nitrate process, and traces of lanthanum by further crystallization of the double ammonium nitrate. Spectroscopically only a trace of lanthanum and no cerium could be detected. The oxalate was converted

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[1] *Proc. Amer. Acad.*, **46**, 213 (1911); THIS JOURNAL, **33**, 1; *Z. anorg. Chem.*, **70**, 1.

[2] *Sitzungsb. Akad. Wiss. Wien*, **92**, 317 (1885).

[3] *Proc. Chem. Soc.*, **1898**, 70.

[4] *Am. Chem. J.*, **20**, 345 (1898).

to trioxide by ignition in air and then in hydrogen, and after being weighed the oxide was converted to sulfate. Twelve determinations between 140.38 and 140.54 gave an average of 140.46.

Schéele[1] also purified material first by crystallization of the double ammonium nitrate, next by extracting the black oxide with ammonium nitrate, and then by precipitation of the oxalate. In a final series of determinations oxalate was converted to trioxide in a current of hydrogen, and the oxide in turn to sulfate. From the ratio of trioxide to sulfate five values between 140.48 and 140.61 resulted.

In 1901, Brauner[2] confirmed his earlier work by four different methods, using similarly purified material. By igniting weighed quantities of octahydrated sulfate to the black oxide and correcting for the oxidizing power of the oxide as determined iodimetrically, he obtained from the ratio $Pr_2O_3 : Pr_2(SO_4)_3.8H_2O$ two results, 141.13 and 141.04. Weighed amounts of carefully dehydrated sulfate were then converted to oxide in the same way, yielding the values 140.96 and 140.94. Air-dried oxalate was weighed and ignited, and the oxidizing power of the oxide was determined. Other weighed portions of oxalate were oxidized with permanganate. The ratio $Pr_2O_3 : 3C_2O_3$ gave the average result 140.98. Finally, weighed amounts of oxalate, the praseodymium content of which had been found as above, were ignited to black oxide and this in turn to trioxide in hydrogen. The trioxide was changed to sulfate by solution in nitric acid and evaporation with sulfuric acid. Excess of acid retained by the salt was found by titration. In eight experiments the ratio $Pr_2O_3 : Pr_2(SO_4)_3$ yielded an average value 140.96. The mean of the four methods is 140.97, which is essentially identical with the result of Brauner's earlier work.

Auer von Welsbach[3] next published the results of three determinations by the Bunsen method, without details, 140.64, 140.50, 140.56, average 140.57.

Finally, Feit and Przibylla[4] purified praseodymium material from neodymium by crystallization of the double magnesium nitrate, and from lanthanum by crystallization of the nitrate from nitric acid solution. The higher oxide, prepared by ignition of the oxalate, was dissolved in standard sulfuric acid and the oxygen evolved was measured, as well as the excess of sulfuric acid. The oxygen evolved was subtracted from the weight of the black oxide before computing the atomic weight from the relation of trioxide to sulfuric acid used. The average result of three experiments is 140.54.

Thus it can be seen that while the investigations of Jones, Schéele,

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[1] *Zeit. anorg. Chem.*, **17**, 310 (1898).

[2] *Proc. Chem. Soc.*, **1901**, 65; Abegg, *Handb. d. anorg. Chem.*, **3**, [1] 263 (1906).

[3] *Sitsungsb. Akad. Wiss. Wien*, **112**, 1037 (1903).

[4] *Zeit. anorg. Chem.*, **50**, 258 (1906).

von Welsbach, and Feit and Przibylla indicate a value for the atomic weight of praseodymium between 140.5 and 140.6, that of Brauner, which was carried out with equal or greater care, and with material of undoubted purity, points to a value at least as high as 140.9. The International Committee upon Atomic Weights has chosen the lower figure, and recommends the value 140.6.

The various difficulties likely to be met in carrying out the methods used in the earlier determinations have been many times discussed, and a résumé of the situation is given in the paper by Baxter and Chapin on the atomic weight of neodymium.[1] It is worth pointing out that in addition to the dangers there mentioned, methods involving the use of praseodymium oxide are subject to error from the tendency of this substance to form a higher oxide of somewhat uncertain composition. While ignition in hydrogen causes reduction to the trioxide, yet it is not easy to make certain that no higher oxide is retained in the lower one. On the other hand, the analysis of the anhydrous chloride served so satisfactorily with neodymium that it seemed worth while to apply the same method to praseodymium. The results amply justified our expectations.

The Purification of the Praseodymium Material.

Through the great kindness of Dr. H. S. Miner, of the Welsbach Light Co., Gloucester City, N. J., we were fortunate enough to secure as a starting point about 10 kg. of praseodymium ammonium nitrate containing about 50% of the corresponding lanthanum and cerium salts as well as a small proportion of neodymium. Since one of the most rapid and effective methods of freeing praseodymium from the closely related elements, lanthanum, cerium, neodymium, and samarium, is the fractional crystallization of the above salt, this method of purification was chosen. According to Auer von Welsbach,[2] the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium and yttrium earths. The salt was crystallized in the usual way, that is, a concentrated, hot solution containing a small amount of nitric acid was allowed to cool and deposit the excess of salt, a period of 24 hours being allowed to secure equilibrium between the crystals and liquid. The separation of crystals and liquid was not completed by centrifugal drainage, because the labor and time involved in this operation are not repaid by any considerable increased speed of purification. The details of the crystallization are shown in the diagrams. In any given series of crystallizations a lower number always indicates a less soluble fraction. A line not connecting an end fraction with any fraction in a subsequent series indicates rejection. This crystallization was begun by Mr. W. H. Whitcomb,

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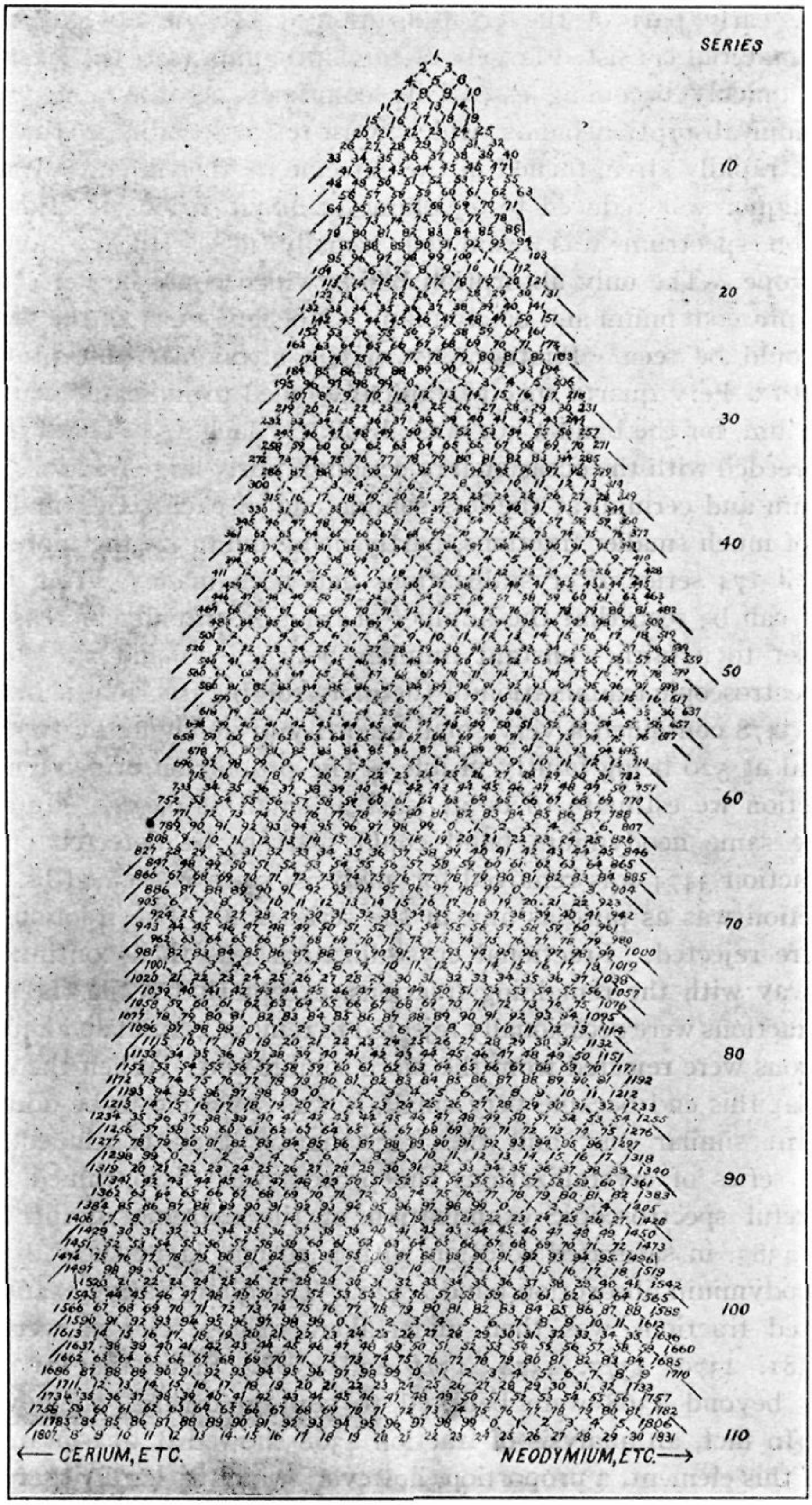
[1] *Loc. cit.*

[2] *Sitzungsb. Akad. Wiss. Wien*, 112, 1043 (1903).

continued by Mr. B. W. Grimes and Mr. C. C. Wallace and completed by Mr. Stewart.

In the early part of the crystallization it became obvious that the original material consisted largely of the lanthanum salt, the least soluble fraction quickly becoming essentially colorless. At the same time the neodymium absorption bands, which were readily visible in the original material, rapidly strengthened in the extreme mother liquor. When this mother liquor was reduced to a volume of about 20 cc., fraction 63, its absorption spectrum was examined visually in a Hilger wave-length spectroscope. The only absorption bands which could be detected were those of praseodymium and neodymium. No sign of any of the samarium bands could be seen. Photography of the ultraviolet absorption spectrum with a Féry quartz spectrograph also failed to indicate even a trace of samarium, for the band λ 401 was absolutely lacking. The crystallization proceeded with the occasional rejection of fairly large fractions, chiefly lanthanum and cerium, at the less soluble end of each series, and the rejection of much smaller fractions, partly neodymium, at the more soluble end, until 174 series of crystallizations had been made. From the diagrams it can be seen that the number of fractions rapidly increased from the outset to a fairly constant number between 20 and 25. In series 174 a spectroscopic examination of the more soluble fractions showed that fraction 3478 contained a very small quantity of neodymium, the absorption band at 520 being faintly visible. The proportion of neodymium in this fraction we estimate to be at least as small as 0.05%. In fraction 3476 the same neodymium band could scarcely be detected. At this point fraction 3474 was removed for analysis, since it seemed likely that this fraction was as pure as any in the series 174. The fractions 3475–3480 were rejected. Fractional crystallization was then continued in a similar way with the remaining fractions, except that while the extreme crystal fractions were occasionally rejected to remove cerium and lanthanum no fractions were rejected from the more soluble end. When the extreme fraction at this end became very small, it was set aside to be added to a subsequent similar one, and the fractionation then continued. After 41 more series of crystallizations the process was discontinued because very careful spectroscopic examination of the extreme mother liquor, fraction 4383, in saturated solution with a 10 cm. layer showed no sign of the neodymium absorption band λ 520. The quantitative examination of selected fractions was then undertaken. Those chosen were 3474, 4383, 4381, 4379, 4377, 4374, 4371 and 4368. Since the less soluble fractions beyond 4368 were believed to contain cerium, they were rejected. In fact, an analysis of fraction 4368 showed it to contain about 0.4% of this element, a proportion, however, which is hardly perceptible in the atomic weight.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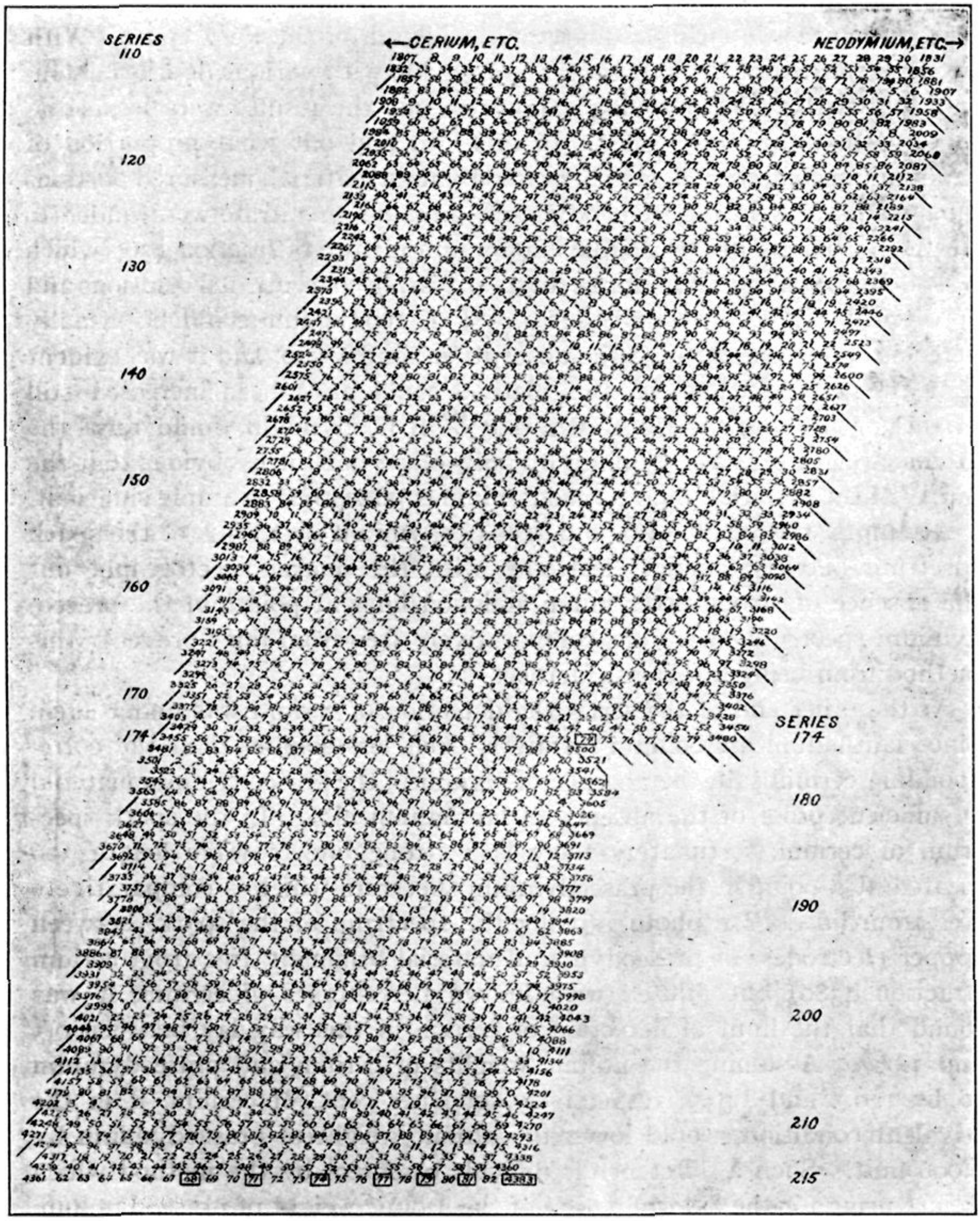
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The Purity of the Fractions of Praseodymium Material.

The purity of the fractions in the final series was determined as follows: In neither fraction 3474 nor the more soluble fractions of the last series, 4383 and 4381, could any of the neodymium absorption lines be detected, either visually with a Hilger wave-length spectroscope or by photography with a Hilger quartz spectrograph of the Féry type. With the latter instrument photographs were made with various depths of solution and with widely varying exposures, but the results were less satisfactory than the visual ones. In order to find out what proportion of neodymium could be detected in praseodymium material, measured portions of a standard solution of neodymium ammonium nitrate were added to weighed portions of the double ammonium nitrate of fraction 4367 which was as free from neodymium as any. By using concentrated solutions and a 10 cm. layer it was found that 0.05% of neodymium could be visually detected with ease through the absorption band λ 520, and it was evident that the sensitiveness of the method could have been increased still further if necessary. Since even 0.05% of neodymium would raise the atomic weight of praseodymium by only 0.002 unit, it is obvious that the purity of the material so far as neodymium is concerned is amply sufficient.

Attempts were made also to detect neodymium by means of the spark spectrum between copper electrodes with the quartz spectograph, but the absence of strong neodymium emission lines at points in the praseodymium spectrum which are comparatively free from lines prevents this method from being at all satisfactory.

At the other end of the series the detection of cerium was undertaken. Since lanthanum ammonium nitrate is even less soluble than the corresponding cerium salt, the absence of cerium in the praseodymium material is sufficient proof of the absence of lanthanum also. In the spark spectrum of cerium, fortunately there is a strong line of wave length 306 located at a point in the praseodymium spectrum which is comparatively free from lines. By photographing the spectrum of the spark, between copper electrodes, of praseodymium material originally free from cerium (fraction 4380) but diluted with known percentages of cerium, it was found that the limit of detection of cerium in this way lay between 0.5 and 1.0%. Assuming the atomic weights of cerium and praseodymium to be 140.3 and 140.9, respectively, one per cent. of cerium, if in the trivalent condition, would lower the atomic weight of praseodymium by 0.006 unit. Such a difference is difficult to detect by the method which we are using for the determination of the atomic weight of praseodymium. Upon photographing the spark spectra of the extreme fractions 4361, 4364 and 4368 (the most impure analyzed), it was found by comparison that the first fraction of the three was rich in cerium, the second contained much less, and fraction 4368 contained no more at any rate than 1%

Because of the uncertainty in estimating proportions of impurity from the intensity of the spectrum lines, fractions 4365, 4368, and 4371 were further tested for cerium as follows: The solution was precipitated with an excess of sodium hydroxide and the precipitated hydroxides were washed several times. Carefully scrubbed chlorine gas was next passed into the solution in order to dissolve the praseodymium hydroxide. The residual ceric hydroxide was dissolved and the process was repeated. The second residue was collected upon a filter paper, washed and ignited. Then the dissolved praseodymium was precipitated as oxalate and ignited to oxide which was weighed. In this way fraction 4365 was found to contain 2.5%, fraction 4368, 0.4% and fraction 4371, 0.1% of cerium. Besides the small and unimportant percentage of cerium in fractions 4368 and 4371, which were analyzed, the rapid falling off of the cerium percentage is worth noting.

The Absorption Spectrum of Praseodymium Chloride.

The absorption spectrum of praseodymium chloride prepared from fraction 4181 was measured in the region of the visible spectrum by means of a Hilger wave-length spectroscope, provided with an extra dense prism and achromatic lenses. The accuracy of measurement with this spectroscope was not far from 0.1 $\mu\mu$ even for the longer wave lengths. Of the four broad absorption bands shown by concentrated solutions, only the one in the yellow visibly resolves into two narrower ones as the dilution increases. The wave lengths of the middle of each band at the lowest concentration at which it could be plainly seen are given below, together with observations by some other observers.[1] Praseodymium nitrate was found to give an exactly similar absorption spectrum.

Baxter and Stewart. (1914).	Aufrecht. (1904).	Auer. (1903).	Böhm. (1902).
597	595.5	596	...
587	590.1	592–587	589.6
481.5	482.0	482–481	481.2
469	468.9	470.6–466.2	469.0
443.5	444.0	447.8–440.3	444.0

Photographs of the absorption spectrum also were taken with a Féry quartz spectrograph. When the source of illumination was a Nernst filament, no absorption bands beyond the visible region could be found with any exposure or any concentration of solution. When the spark from "Nichrome" wire was employed, however, it was found that the light is completely cut off at from λ 280 to λ 270 according to the concentration of the solution, and that the solution is opaque up to the extreme limit of the spectrograms, about λ 210. In these spectrograms there were noticeable at certain concentrations very faint minima of absorption in the middle of all three bands in the blue. These minima

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[1] Kayser. *Handb. d. Spectr.*, 3, 440.

could be seen over a considerable range of concentration in all three cases but the particular concentration at which they were most marked was different for the three bands. Measurements were made of the position of these minima with a comparator and the cadmium spark spectrum as a standard, and the minima were found to coincide with the centers of the absorption bands observed with the most dilute solutions both visually and in the spectrograms.

The ultraviolet absorption bands at 354 and 353 reported by Forsling[1] and the one at 346 given by Exner[2] correspond to strong absorption bands of neodymium. As we could not find the least trace of these bands in the spectrograms, it seems probable that they were produced by neodymium impurity.

The Preparation of Praseodymium Chloride.

Each fraction of double nitrate investigated was converted to chloride as follows: The salt was dissolved, and the solution, after dilution to about two liters, was filtered. A considerable quantity of nitric acid was added, the solution was heated to boiling and praseodymium oxalate was precipitated by an excess of oxalic acid. After the precipitate had been thoroughly washed by decantation, it was collected upon a disk of filter paper in a large porcelain Gooch crucible, and dried in an electric oven at 105°. In order to change the oxalate to oxide it was heated to dull redness in a platinum boat in an electrically heated porcelain muffle. Care was taken that the temperature should not be high enough to vaporize platinum from the boat into the oxide.[3] The black oxide was next dissolved in a quartz dish in a large excess of nitric acid which had been distilled through a quartz condenser, and the oxalate was reprecipitated from dilute solution by adding a solution of twice recrystallized ammonium oxalate. After thorough washing, the oxalate was collected, dried and ignited as before. The chloride was now prepared by dissolving the oxide in a quartz dish in hydrochloric acid which had been distilled through quartz. Free chlorine was expelled by heating on an electric stove, and the salt was crystallized three or four times from concentrated solution by "salting out" at 0° with hydrochloric acid gas made by boiling the fuming solution and conducting the gas to the solution through a quartz tube. The crystals were each time centrifugally drained and rinsed in platinum Gooch crucibles.[4] The product was preserved in quartz in a vacuum desiccator over fused potassium hydroxide.

The Purification of Silver and Reagents.

The greater part of the silver used in this work was prepared by Mr. W. H. Whitcomb for an investigation upon the atomic weight of neo-

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[1] Kayser, *Loc. cit.*

[2] *Ibid.*

[3] See Baxter and Chapin, THIS JOURNAL, **33**, 16 (1911).

[4] Baxter, THIS JOURNAL, **30**, 286 (1908).

dymium, which will be published shortly. No innovations were made in the processes of purification which have been frequently described in papers from the Harvard Laboratory. These processes were in brief as follows: Crude silver was dissolved in nitric acid, and the chloride was precipitated with a large excess of hydrochloric acid. The precipitate, after being washed, was dissolved in ammonia and reprecipitated with nitric acid. Then the silver chloride was reduced with sodium hydroxide and sugar, and the metal was fused on charcoal before a blast lamp. The metallic buttons were cleansed by scouring and etching, dissolved in distilled nitric acid, and the metal reprecipitated with ammonium formate made from distilled ammonia and formic acid. After thorough washing the product was again fused on the purest lime before a blast lamp. Electrolytic deposition, with silver nitrate as the electrolyte and with a dissolving anode of the pure silver buttons, followed and the electrolytic crystals were fused in a current of electrolytic hydrogen on a pure lime boat. Adhering lime was removed by etching with nitric acid, and the buttons were washed with water and ammonia, dried, and heated to about 500° in a vacuum. The silver was preserved over potassium hydroxide in a desiccator. In some of the later analyses the silver used had been purified exactly as described above by Mr. F. L. Grover for work upon the atomic weight of lead, or by Dr. H. C. Chapin for the investigation upon neodymium.

In Analyses 1 and 2 silver nitrate was employed which had been freed from chloride by repeated crystallization. This material was prepared by Dr. Grinnell Jones for work on the atomic weight of phosphorus.[1]

In the preparation of reagents the precautions usual in exact work were taken. The ordinary distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone, through block-tin condensers. Hydrochloric and nitric acids were distilled through quartz condensers, in the case of the hydrochloric acid the first and last running being rejected, in the case of the nitric acid two distillations being carried out, the first third being rejected in each distillation. Nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is nearly free from the latter element.

Quartz or platinum utensils were employed wherever glass would have introduced objectionable impurities, and electrical heaters were used whenever the products of combustion of illuminating gas were to be avoided. In the crystallization of solids centrifugal drainage was always used to assist in the mechanical removal of mother liquor from crystals, except in the fractional crystallization of the praseodymium material where it would have been of little assistance.

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[1] *Proc. Amer. Acad.*, **45**, 137 (1909); THIS JOURNAL, **31**, 298.

The Drying of Praseodymium Chloride.

The drying of the chloride for analysis was effected according to the recommendations of Matignon[1] and in very much the same way that neodymium chloride was dried by Baxter and Chapin, except that while the neodymium salt was not fused, and hence retained a trace of water, which was subsequently determined, the praseodymium chloride was rendered anhydrous by fusion. Bearing in mind the earlier experience with neodymium chloride, that the dehydration of the salt must be made as complete as possible before the actual fusion occurs, in order to prevent the formation of basic salt, the salt was caused to lose its crystal water by a process of efflorescence in a current of dry nitrogen and hydrochloric acid gases at gradually increasing temperatures. Richards[2] has pointed out that a hydrated salt may be freed from moisture much more effectively in this way than when melting is allowed to take place. We found the transition temperature of the heptahydrate[3] to be 111° but when the salt is heated in a current of hydrochloric acid gas, the melting point is somewhat lowered. Therefore, until a very considerable proportion of the water had been expelled, the temperature was kept below 100°. The temperature was then raised to bout 165° where the last molecule of crystal water begins to evaporate, according to Matignon,[4] and when the salt was essentially anhydrous it was gradually heated to about 350°. During the latter part of the heating only hydrochloric acid was passed through the tube. The aluminum block oven[5] which had been used for heating the salt up to this point was now replaced by a sleeve which could be heated electrically and the salt was first heated to dull redness for a few minutes and then quickly to its fusing point, which Matignon[6] states to be 818°.

The platinum boat with the salt was placed in a quartz tube which formed part of the "bottling apparatus"[7] containing the weighing bottle with its stopper in which the boat originally had been weighed, and the bottling apparatus was connected with systems for the production of pure dry hydrochloric acid, nitrogen, and air. The hydrochloric acid gas was generated by adding C. P. concentrated sulfuric acid to C. P. fuming hydrochloric acid, and the gas was dried by passing through five towers filled with beads moistened with concentrated sulfuric acid which had previously been heated nearly to its boiling point. Nitrogen was prepared by Wanklyn's method of saturating air with ammonia and passing the mixture over

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[1] *Compt. rend.*, **134**, 427 (1902).

[2] *Z. physik. Chem.*, **46**, 194 (1903).

[3] Matignon found 105°. *Loc. cit.*

[4] *Loc. cit.*

[5] *Proc. Amer. Acad.*, **44**, 184 (1909); THIS JOURNAL, **31**, 206.

[6] *Compt. rend.*, **140**, 1340 (1905).

[7] Richards and Parker, *Proc. Amer. Acad.*, **32**, 59 (1896).

hot copper gauze. The excess of ammonia was removed by dilute sulfuric acid, and the nitrogen was further purified and dried in towers containing glass beads moistened with silver nitrate solution, fused potassium hydroxide, concentrated sulfuric acid, and phosphorus pentoxide. Nitrogen made in this way invariably contains a small proportion of hydrogen,[1] owing to catalytic decomposition of the excess of ammonia on the copper tube, but this gas would do no harm in the present instance. Air was purified and dried by reagents similar to those used for purifying the nitrogen. The apparatus was constructed wholly of glass with either ground or fused joints, except at the beginning of the air and nitrogen apparatus. By means of stopcocks any one of the three gases could be delivered to the bottling apparatus at will. This apparatus is identical with that used by Baxter and Hartmann[2] for the drying of cadmium chloride, and by Baxter and Grover[3] for the drying of lead chloride. After the fusion of the neodymium chloride, the hydrochloric acid was displaced by nitrogen and the nitrogen in turn by air. Then the boat and contents were transferred to the weighing bottle, which was allowed to stand in a desiccator near the balance for some hours before being weighed.

A solution of praseodymium chloride, which has been fused in this way, sometimes contains a small amount of insoluble glistening particles, practically invisible unless examined in a strong light in a vessel whose curvature magnifies their apparent size. A similar difficulty was met by Baxter and Chapin in the preparation of pure anhydrous neodymium chloride. Under unfavorable conditions, which will be described shortly, the amount of this insoluble material may be considerably augmented, but when prepared under the most favorable conditions the salt dissolves rapidly without leaving even a trace of insoluble matter. Even when a small amount of insoluble material is formed, a clear solution is usually obtained after a day or two. The conditions under which the extent of the difficulty is too small to have an appreciable effect upon the results, have been found to be very careful preliminary dehydration of the salt, and a very short period of fusion. These conditions were maintained in the preparation of all of the specimens of material which were analyzed, but only in Analyses 5, 6, 9, 10, 16, 24, 25, 30, 31, 38 and 39 was the solution of the salt absolutely clear at the start.

Many experiments were carried out, however, first, to find out the nature of the insoluble matter, and second, to discover the extent of the difficulty. At the outset there seemed to be three possibilities as to the nature of the substance. The most probable one was that the substance is a basic

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[1] Dr. R. C. Wells first pointed out this fact to us.

[2] THIS JOURNAL, 37, 113 (1915).

[3] Investigation not yet published.

chloride, but it was possible that it might be either an insoluble allotropic form of the trichloride or a lower chloride, *i. e.*, praseodymium dichloride. The fact that prolonged fusion of the salt invariably resulted in the formation of relatively large amounts of insoluble material seemed to point toward one of the last two explanations, although there seems to be no certain evidence of the existence of such compounds in the case either of praseodymium or of other rare earths.

In order to find out the composition of the insoluble substance, amounts large enough to be analyzed were prepared by dehydrating the crystals with the usual care, and then fusing the salt for periods from one-half hour to one hour in a current of dry hydrochloric acid gas. The product was then treated with water, and as soon as the soluble portion of the salt had dissolved, the insoluble residue was collected upon a small weighed platinum-sponge Gooch crucible, dried and weighed. The residue, which was distinctly crystalline, did not change in appearance during the drying, so that it is improbable that its composition was appreciably altered during this treatment. The praseodymium content of the residue was then determined by dissolving the residue from the crucible in dilute hydrochloric acid, precipitating the base with ammonium oxalate, collecting the precipitate upon a filter, and igniting in a weighed platinum boat. The weight of the black oxide Pr_4O_7 was checked by igniting the residue in a stream of hydrogen and reweighing. The weights of oxide obtained in two experiments correspond very closely to the weight which should be obtained, assuming the residue to be praseodymium oxychloride, PrOCl. About 6 g. of anhydrous salt were used in each experiment.

Period of fusion. Min.	Gram insoluble residue.	Gram Pr_4O_7 observed.	Gram Pr_4O_7 calc. from PrOCl.	Gram Pr_4O_7 calc. from $PrCl_3$.	Gram of Pr_4O_7 calc. from $PrCl_2$.	Gram of Pr_2O_3 observed.	Gram of Pr_2O_3 calc. from PrOCl.
35	0.2002	0.1760	0.1757	0.1366	0.1597	0.1700	0.1715
60	0.0131	0.0117	0.0115	0.0090	0.0104	0.0114	0.0112

The composition of the residue was further checked by determining the chlorine content. Residues were collected and weighed as above, and then after solution in dilute nitric acid, the chlorine was precipitated as silver chloride, collected and weighed. During the solution of the residue the crucible and contents were placed in a closed tube through which a current of air was passed into a solution of ammonia, so that in case chlorine was liberated during the solution, it would be caught in the ammonia. The results of the chlorine determinations check closely those of the praseodymium determinations.

Period of fusion. Min.	Gram insoluble residue.	Gram AgCl observed.	Gram AgCl calc. from PrOCl.	Gram AgCl calc. from $PrCl_3$.	Gram AgCl calc. from $PrCl_2$.
60	0.0146	0.0110	0.0109	0.0252	0.0198
60	0.0111	0.0079	0.0083	0.0193	0.0150

Since it is obvious that, if the oxychloride is formed from the trichloride, a loss in weight must occur, further experiments were carried out to discover whether during the formation of the larger amounts of insoluble residue, when the fusion is prolonged, the loss in weight of the salt corresponds to the weight of residue produced. In these experiments the hydrated salt was first very carefully dried, then quickly fused and weighed. During this treatment little, if any, insoluble material is formed. Then the boat with the salt was returned to the quartz tube, and after the apparatus had been thoroughly swept out with dry hydrochloric acid, the salt was brought to the fusing temperature, which was maintained for one hour in every case. After the salt had been reweighed, the insoluble residue was determined as previously described and a few tenths of a milligram of salt which sublimed from the boat to the quartz tube were dissolved in water, the solution was evaporated and the residue was heated and weighed. The weight of sublimed material was of course added to the weight of the fused salt before determining the loss in weight during fusion.

Period of fusion. Min.	Loss on fusion.	Gram of insoluble residue observed.	Gram of insol. residue calc. as PrOCl.	Gram of insol. residue calc. as $PrCl_2$.
60	0.0063	0.0234	0.0220	0.0376
60	0.0034	0.0111	0.0119	0.0203

These experiments agree very satisfactorily with those in which the praseodymium and chlorine were actually determined, in indicating beyond question that the insoluble residue is the oxychloride.

The surprising feature of these results is that the amount of insoluble matter increases with the period of fusion instead of decreasing or even remaining constant. The obvious conclusion is that some source of oxygen exists in the fusion atmosphere. To be sure, in the first of the experiments for the determination of the insoluble residue a tiny hole was discovered in one of the fused joints of the hydrochloric acid apparatus, and in this experiment the weight of insoluble residue was found to be about ten times as large as in the subsequent experiments. Fortunately the defective joint was a comparatively new one, and could have affected only four of the fusions of the salt for analyses. The analyses involved are Nos. 12, 13, 14, 15, 34, 35, 36 and 37. The hole was excessively small, however, and it is not at all certain that any real difficulty was produced. It seemed possible that the hydrochloric acid gas might contain air, originating in the reagents used for generating the gas, or possibly from incomplete sweeping out of the purifying train. By passing the hydrochloric acid gas into water under an inverted tube after the apparatus had been thoroughly swept out, we found that it actually did contain a trace of air. We tried in some experiments to avoid the first difficulty by passing the hydrochloric acid gas through a hydrochloric acid solution of cuprous chloride before it entered the drying towers, and in order to avoid the second difficulty the apparatus was swept out even longer than before previous to the fusion of the salt, but neither of these remedies seemed to have any effect upon the formation of the basic salt. Another source of oxygen might be moisture. However, concentrated sulfuric acid has been found by Morley[1] to be a very effective drying agent. One liter of gas passed over concentrated sulfuric acid retains only 0.003 mg. of moisture. In order to make sure that the hydrochloric acid was really as dry as this, the gas was passed for several hours through a U-tube cooled with alcohol and solid carbon dioxide. A very small amount of white solid was condensed in the tube, presumably a hydrate of hydrochloric acid. But even on the assumption that all of the moisture is removed from the gas by the salt during the fusion, it seems impossible that the residue should have formed wholly from moisture contained by the acid gas. Still another possibility was that the quartz tube was attacked by the acid gas to yield moisture and a chloride of silicon. This point was tested by drying and fusing the salt in a platinum tube instead of in a quartz tube, but even under these conditions the insoluble residue was formed. We are still somewhat uncertain as to the cause of the formation of the basic salt during prolonged fusion, although incomplete preliminary drying is invariably the cause when the fusion period is short, but we are inclined to the opinion that the difficulty is due to a trace of air in the hydrochloric acid gas.

Since we were unable to avoid the formation of the insoluble material in every case, in two experiments in which the salt was dried as for analysis and then fused for a short period, the insoluble residue was collected and weighed. The results of these experiments follow. As before, about 6 g. of anhydrous salt were used in each experiment.

Period of fusion	0.5 min.	4 min.
Wt. of insoluble residue	0.0001 g.	0.0010 g.

In order to discover whether the basic salt dissolves to an appreciable extent, in experiments with three separate portions of material which had been collected, dried and weighed upon a platinum-sponge crucible, about a liter of water was allowed to flow slowly through the crucible during the course of an hour. The crucible and contents were then dried and reweighed. The losses in weight per liter of water were 0.9, 0.5 and 0.3 mg. While these figures are undoubtedly somewhat less than the real solubility in water, they are probably far greater than the solubility in dilute praseodymium chloride solution. This explains the extreme slowness with which a mere trace of the basic salt dissolves in the solution of the neutral salt and supports the conclusion that the quantity of basic salt present in the material fused for a short time is very small.

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[1] *Am. J. Sci.*, 30, 141 (1885).

In preparing the salt for the actual analyses the period of fusion was less than one minute, so that the weight of residue certainly must have been considerably less than 1 mg. But since even as large a proportion as 1 mg. of oxychloride in 5 g. of salt, if it dissolves eventually, would raise the apparent atomic weight of praseodymium by only 0.028, we feel that little danger is introduced by not attempting to apply any correction for the residue.

In a research upon the atomic weight of neodymium carried out immediately at the conclusion of this research, similar evidence was obtained as to the nature of the insoluble neodymium compound which forms under essentially the same conditions.

The Method of Analysis.

After the salt had been fused and weighed, the boat was transferred to a glass-stoppered Erlenmeyer flask and treated with about 500 cc. of pure water. In eleven of the analyses the salt dissolved immediately, leaving an absolutely clear solution. In the remainder of the analyses, after the bulk of the salt was in solution, by close inspection a small quantity of the insoluble basic chloride could be seen. On allowing the flask to stand for a considerable period, 24 to 48 hours in general, this basic salt disappeared, and in a few instances gentle heating was used to accelerate its solution. When the solution was clear, it was transferred quantitatively to the 3 or 4 liter glass-stoppered Erlenmeyer precipitating flask. The rinsings of the weighing bottle were added and the solution diluted to a volume of from 1200 to 1500 cc. In the meantime a quantity of pure silver as nearly as possible equivalent to the praseodymium chloride was dissolved in nitric acid, in a dissolving flask provided with a column of bulbs to prevent loss by spattering while the metal was dissolving. After diluting the solution of silver nitrate, it was heated to eliminate nitrous acid, and then further diluted to about the same volume as the praseodymium chloride solution. The silver nitrate solution was poured into the chloride solution, both being cold, in small portions with continual gentle agitation. When the silver nitrate had been completely transferred to the precipitating flask, the flask was stoppered and gently shaken to insure thorough mixing, and allowed to stand for several days with occasional shaking. Then it was cooled with ice water in order to lower the solubility of the silver chloride, and after standing for a day in the ice bath, portions of the mother liquor were tested for excess of silver or chloride by adding to separate portions equal amounts of 0.01 N chloride and silver solutions and comparing the opalescences in a nephelometer. If a deficiency of either chloride or silver was found, this deficiency was made up by adding 0.01 *N* silver or chloride solution. The amount of either added, expressed in the silver equivalent, is given in the tables of results under the heading "Silver added or subtracted." When equilibrium had been reached, 0.05 g. of dissolved silver nitrate for each liter of supernatant liquid was added to render the silver chloride less soluble. After the solution had been allowed to stand for at least a day, usually much longer, at room temperature, the precipitate was washed many times by decantation with a solution containing 0.05 g. of silver nitrate per liter, and several times with ice-cold water, and transferred with cold water to a large weighed platinum-sponge Gooch crucible. The crucible with its contents was dried for at least 12 hours in an electric air bath at 160°, cooled in a desiccator and weighed. The crucible had originally been dried in exactly the same way. In order to find out how much moisture had been retained by the dried silver chloride, the greater part of the salt was transferred to a porcelain crucible which was weighed. Then the crucible was heated to the fusing point of the silver chloride and reweighed. The loss in weight is assumed to represent residual moisture. On an average 0.004 % of moisture was found, a proportion which is in accord with earlier experience in the Harvard laboratories.

The solubility of silver chloride in the filtrate and silver nitrate wash waters, which both contained 0.05 g. of silver nitrate per liter, was computed from the solubility products as found by Kohlrausch[1] at 20° and 25°, 1×10^{-10} and 1.7×10^{-10}, respectively. At 20° the solubility in 0.0003 N silver nitrate solution is 0.05 mg., at 25° 0.08 mg. per liter. The former correction was used during the colder months when the laboratory was maintained at about 20°, the latter correction in four analyses which were completed in summer. The total correction in most cases fell between 0.2 and 0.3 mg. The silver chloride dissolved in the aqueous rinsings as well as that obtained by rinsing the precipitating flask with ammonia was determined by comparison with standard solutions of chloride in a nephelometer, the usual precautions being taken to secure uniformity of precipitation. As in earlier researches it was found desirable to dissolve in ammonia the cloud of silver chloride in both the standard solution and that being analyzed, and then to reprecipitate with nitric acid.

Corrections were of course applied for any chloride introduced in order to compensate for excess of silver, and also for the standard chloride solution added to the portions which were tested in the comparison, for these portions were always returned to the precipitating flask. The latter quantity amounts to 1.328 mg. for each test which was made in the comparison. Because of the comparatively large size of this correction, the standard silver and chloride solutions were made up, preserved, and measured with great care.

Weighings were carried out on a No. 10 Troemner balance, sensitive at least to 0.02 mg. In order to avoid difficulties from changes in at-

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[1] *Z. physik. Chem.*, 64, 167 (1908).

mospheric humidity and density, the receptacles containing the salts were always weighed by substitution for counterpoises as nearly as possible like the objects both in material, volume, and external surface. The balance case was provided with a small amount of radioactive material to dissipate electrical charges produced during the transference of the objects to the balance pans. The weights were standardized to hundredths of a milligram by the method described by Richards.[1] Vacuum corrections were applied as follows:

	Specific gravity.	Vacuum correction per gram.
Weights	8.3	....
$PrCl_3$	4.020[2]	+0.000154
AgCl	5.56	+0.000071
Ag	10.49	—0.000031

THE ATOMIC WEIGHT OF PRASEODYMIUM.

Series I. $PrCl_3 : 3AgCl$.

Ag = 107.880. Cl = 35.457.

No. of analysis.	Fraction.	Grams of $PrCl_3$ in vacuum.	Grams of AgCl in vacuum.	Loss on fusion.	Dissolved AgCl.	Corrected weight of AgCl in vacuum.	Ratio $PrCl_3$: 3AgCl.	Atomic weight of praseodymium.
1	3474	4.12848	7.17753	0.00004	0.00166	7.17915	0.575065	140.913
2	3474	6.91605	12.02366	0.00016	0.00183	12.02533	0.575123	140.939
3	3474	7.66554	13.32562	0.00023	0.00392	13.32931	0.575089	140.923
4	3474	5.01155	8.71232	0.00026	0.00173	8.71379	0.575128	140.941
						Av.,	0.575101	140.929
5	4383	6.04235	10.50645	0.00027	0.00126	10.50744	0.575054	140.909
6	4383	6.14745	10.68933	0.00029	0.00146	10.69050	0.575039	140.902
						Av.,	0.575047	140.906
7	4381	6.32550	10.99679	0.00030	0.00206	10.99855	0.575121	140.937
8	4381	4.59463	7.98763	0.00022	0.00199	7.98940	0.575090	140.925
						Av.,	0.575106	140.931
9	4379	5.96661	10.37370	0.00040	0.00224	10.37554	0.575065	140.913
10	4379	6.87536	11.95356	0.00030	0.00182	11.95508	0.575100	140.928
						Av.,	0.575083	140.921
11	4377	4.64585	8.07649	0.00052	0.00161	8.07758	0.575154	140.951
12	4374	6.85492	11.91575	0.00000	0.00199	11.91774	0.575186	140.965
13	4374	8.01711	13.93737	0.00008	0.00224	13.93953	0.575135	140.943
14	4374	6.17045	10.72789	0.00005	0.00049	10.72833	0.575155	140.952
15	4374	6.90040	11.99805	0.00022	0.00163	11.99946	0.575059	140.911
16	4374	7.08498	12.31948	0.00043	0.00114	12.32019	0.575071	140.916
						Av.,	0.575121	140.937
17	4371	6.20845	10.79439	0.00003	0.00116	10.79552	0.575095	140.926
18	4371	7.07590	12.30310	0.00025	0.00116	12.30401	0.575089	140.924
						Av.,	0.575092	140.925
19	4368	5.77646	10.04305	0.00021	0.00119	10.04403	0.575113	140.935
20	4368	5.72002	9.94547	0.00021	0.00125	9.94651	0.575078	140.919
						Av.,	0.575096	140.927

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[1] THIS JOURNAL, **22,** 144 (1900).

[2] Determined at 25° by Mr. C. F. Hawkins, not yet published. Matignon found 4.017 at 18°. *Compt. rend.*, **140,** 1340 (1905).

The Atomic Weight of Praseodymium.

Series II. $PrCl_3 : 3Ag$.

Ag = 107.880. Cl = 35.457.

No. of analysis.	Fraction.	Grams of $PrCl_3$ in vacuum.	Grams of Ag in vacuum.	Grams of Ag added.	Corrected weight of Ag in vacuum.	Ratio $PrCl_3$: 3Ag.	Atomic weight of praseodymium.
21	3474	7.66554	10.02872	0.00257	10.03129	0.764163	140.943
22	3474	8.78959	11.49955	0.00356	11.50311	0.764106	140.924
23	3474	5.01155	6.55888	0.00010	6.55898	0.764075	140.914
					Av.,	0.764115	140.927
24	4383	6.04235	7.90826	—0.00006	7.90820	0.764061	140.910
25	4383	6.14745	8.04493	0.00070	8.04563	0.764073	140.914
					Av.,	0.764067	140.912
26	4381	6.32550	8.27440	0.00446	8.27886	0.764054	140.908
27	4381	5.12982	6.71246	0.00113	6.71359	0.764095	140.920
28	4381	4.59463	6.01206	0.00125	6.01331	0.764077	140.915
29	4381	4.77556	6.24933	0.00061	6.24994	0.764097	140.921
					Av.,	0.764081	140.916
30	4379	5.96661	7.80878	0.00030	7.80908	0.764060	140.910
31	4379	6.87536	8.99794	0.00030	8.99824	0.764079	140.915
					Av.,	0.764070	140.913
32	4377	5.73602	7.50710	—0.00003	7.50707	0.764082	140.917
33	4377	4.64585	6.08004	0.00025	6.08029	0.764084	140.917
					Av.,	0.764083	140.917
34	4374	6.85492	8.97128	0.00020	8.97148	0.764079	140.916
35	4374	8.01711	10.49205	0.00045	10.49250	0.764080	140.916
36	4374	6.17045	8.07517	—0.00092	8.07425	0.764214	140.959
37	4374	6.90040	9.03078	—0.00014	9.03064	0.764110	140.926
38	4374	7.08498	9.27297	—0.00023	9.27274	0.764065	140.911
39	4374	5.81310	7.60811	0.00000	7.60811	0.764066	140.911
					Av.,	0.764102	140.923
40	4371	6.20845	8.12468	0.00073	8.12541	0.764079	140.915
41	4371	7.07590	9.26026	0.00019	9.26045	0.764099	140.922
					Av.,	0.764089	140.919
42	4368	5.77646	7.56013	—0.00013	7.56000	0.764082	140.916
43	4368	5.72002	7.48696	—0.00100	7.48596	0.764100	140.922
					Av.,	0.764091	140.919

Results and Discussion.

In order to show that no considerable error occurred, owing either to occlusion by silver chloride or from loss of silver chloride in solution, the ratio between the silver used and the silver chloride obtained has been calculated in the eighteen pairs of analyses for which the data are available.

The average ratio of silver to silver chloride is within less than four thousandths of a per cent. of that obtained by Richards and Wells,[1] 0.752634 : 1.000000. Part of the discrepancy is due to the fact that in a few analyses, notably Nos. 12, 13 and 14, the platinum-sponge crucible allowed traces of solid silver chloride to pass through. The difficulty

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[1] *Pub. Car. Inst.*, No. **28** (1905); This Journal, **28**, 456.

Analyses.	Ag: AgCl.
3 and 21	0.752573
4 and 23	0.752711
5 and 24	0.752628
6 and 25	0.752597
7 and 26	0.752723
8 and 28	0.752660
9 and 30	0.752644
10 and 31	0.752671
11 and 33	0.752735
12 and 34	0.752784
13 and 35	0.752716
14 and 36	0.752610
15 and 37	0.752587
16 and 38	0.752647
17 and 40	0.752664
18 and 41	0.752637
19 and 42	0.752685
20 and 43	0.752630
Average,	0.752661

was not detected in time to determine the extent of the error, but in one of these analyses silver chloride was found to have settled out of the mother liquor on long standing. This is undoubtedly the reason why the atomic weight of praseodymium determined in these analyses is slightly higher than in most other experiments. Needless to say, the crucible was repaired and in Analyses 15 and 16, made subsequently with the same fraction of material as Analyses 12, 13 and 14, the results are in accord with the general mean of all the determinations. These defective analyses as well as a very few other discrepant determinations, have not been omitted in computing averages, since, because of the large number of experiments, their influence is not large.

RESULTS AVERAGED BY FRACTIONS.

Fraction.	$PrCl_3 : 3Ag$.	$PrCl_3 : 3AgCl$.	Average of individual determinations.	Average corrected for cerium content.
3474	140.927	140.929	140.928	140.928
4383	140.912	140.906	140.909	140.909
4381	140.916	140.931	140.921	140.921
4379	140.913	140.921	140.917	140.917
4377	140.917	140.951	140.928	140.928
4374	140.923	140.937	140.930	140.930
4371	140.919	140.925	140.922	140.923
4368	140.919	140.927	140.923	140.925
			Average,	140.923
			Average of all Individual Determinations,	140.924

When the results are averaged by fractions, further evidence is added to that obtained by the spectroscope, that all the fractions analyzed were of a high degree of purity.

Fraction 4383, which contained all the neodymium which may have accumulated in forty-one series of crystallizations, gives a slightly lower instead of higher figure than the average, while fraction 4368 which contained more cerium than any other fraction gives a result identical with the average. This close similarity is very striking when one considers that a range of sixteen fractions is included in those examined. Fraction 3474, selected at an earlier stage of the fractionation as being very pure, also shows no sign of being different from the other fractions.

The foregoing results leave little opportunity for choice. There seems to be no reason for preferring the value obtained with any one or more fractions to those resulting with the others. Possibly the average of Analyses 5, 6, 9, 10, 16, 24, 25, 30, 31, 38 and 39, 140.913, is more reliable than the average of all, for in these analyses the praseodymium chloride dissolved rapidly and completely at the start, and was probably entirely free from basic salt, but we believe that the final corrected average of all the experiments, 140.92, represents fairly the best material we succeeded in preparing. This result is not far from the value obtained by Brauner in both his researches, but is over three-tenths of a unit higher than the choice of the International Committee upon Atomic Weights.

We are indebted particularly to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels, as well as to Dr. H. S. Miner of the Welsbach Light Company for the praseodymium material.

CAMBRIDGE, MASS.

RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

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It might seem too soon for publication of chemical research to feel the effects of the war, especially as nearly half of the period that has elapsed since the outbreak of hostilities covered the summer vacation in the continental universities, yet that there has already been a decided influence is apparent in the fact that the *Zentralblatt* from August 9 to December 9 contains only 964 pages as against 1548 pages for the similar dates in 1913. A far more serious diminution of research is to be expected, when we realize that such a large proportion of the students of European and Colonial universities are "with the colors."

There is little that is particularly striking to chronicle in the progress of inorganic chemistry in 1914. The only radical departure from well-established ideas is found in variations in the atomic weight of lead from different sources. The theoretical considerations are discussed by Fajans[1]

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[1] *Physikal. Ztsch.*, **14**, 951, and *Sitzber. Heidelb. Akad. Wiss., Math-naturw. Kl.*, **1914**, 11, *Abh.* 22.