Summary

Further arguments are given in support of the viewpoint of Wightman that the cause of latent fog formation from the action of certain oxidizing agents and acids is probably formation of bromine from the soluble bromide in the plate, with which hypothesis Lüppo-Cramer is in disagreement. The hypothesis was originally based on the fact, discovered by Lüppo-Cramer himself, that very dilute bromine solution causes fog and on a previously proposed mechanism of latent image intensification and fog formation by hydrogen peroxide, further evidence for which is now presented.

ROCHESTER, NEW YORK

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

OBSERVATIONS ON THE RARE EARTHS. XXX. STUDIES IN THE ABSORPTION SPECTRA[1]

BY LAURENCE L. QUILL AND PIERCE W. SELWOOD WITH B. S. HOPKINS

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The purpose of this investigation was to make a careful examination of the effects of a common ion on the absorption spectra of solutions of certain rare earth salts. The spectra of the colored rare earths are an invaluable aid for the rapid estimation of these elements, and although there are several references in the literature to the fact that the absorption bands are displaced by the presence of other substances, yet there appears to be little definite information available as to the precise nature of the changes to be observed. These studies were therefore undertaken with the intention of determining the conditions under which the absorption spectra may be relied upon for the analysis of rare earth mixtures.

An extensive bibliography of the literature prior to 1920 is given by Yntema.[2] Since then methods of quantitative spectral analysis for the rare earths have been suggested by Inoue[3] and by Delauney.[4] Irregularities in the absorption spectrum of neodymium have been observed by Prandtl[5] as mentioned in his criticism of the discovery of illinium.

Delauney, on the assumption that Beer's Law is observed by rare earth salt solutions, has suggested a method of quantitative analysis based on the variation in the width of certain of the absorption bands with change in concentration. He made analyses of solutions of praseodymium and neodymium nitrates and his results were accurate to 5%, which is better

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[1] In memory of Ira Remsen.

[2] Yntema, THIS JOURNAL, **45**, 907 (1923).

[3] Inoue, *Bull. Chem. Soc., Japan*, **1**, 9 (1926).

[4] Delauney, *Compt. rend.*, **185**, 354 (1927).

[5] Prandtl, *Z. angew. Chem.*, **39**, 897 (1926).

than can be done without a very careful equivalent weight determination. He also states that any changes in the neodymium nitrate bands on the addition of nitric acid are within the limits of experimental error.

Experimental

Procedure.—The absorption spectra were photographed on a Hilger quartz prism spectrograph with a dispersion of approximately 20 cm. Trichromatic "Spectrum Process" plates were used and the source of illumination was a tungsten ribbon incandescent lamp which gave a steady light and a continuous spectrum. The iron arc was used as standard of reference. The absorption spectra were exposed for five minutes in all cases. A Baly absorption cell with quartz windows was used throughout the investigation. The neodymium was atomic weight purity material which had been prepared in this Laboratory. The praseodymium contained about 1% of lanthanum. The samarium (except that purposely mixed with neodymium) was a few fractions removed from atomic weight material. The erbium was relatively impure, being several fractions removed from atomic weight material and containing thulium and yttrium. The various solutions were made up by weighing the freshly ignited oxides and dissolving them in nitric or hydrochloric acid as the case might be and evaporating just to dryness several times. The dry salts were then dissolved in water or in acid of the desired strength and made up to the required concentration in a volumetric flask. With the less basic samarium and erbium it was impossible to remove the last trace of acid without hydrolysis taking place. The trace left was insufficient to affect the absorption bands appreciably.

Neodymium Nitrate.—In the first part of the work 0.1 *N* neodymium nitrate solutions were prepared in various concentrations of nitric acid. The effect with the lower acid concentrations is very slight. Nevertheless, there is an unmistakable shift of 3 or 4 Å. toward the red in the 5700–5800 Å. region and the three bands visible tend to merge into one another. No change is observed in the 5200 Å. region, while the sharp band at 4272 Å. becomes very faint and is shifted about 1 Å. toward the red. As the acid concentration increases, the shifts become more and more pronounced until in 15.8 *N* acid the appearance of the spectrum is greatly altered. Spectrum No. 2 shows 0.1 *N* neutral $Nd(NO_3)_3$ through 5 cm. of solution and No. 1 shows 0.1 *N* $Nd(NO_3)_3$ in 15.8 *N* nitric acid through the same depth of solution. The three bands at 5710–5726 Å., 5731–5763 Å. and 5775–5780 Å. have merged together to 5758–5800 Å., while the region 5701–5758 Å. is only slightly absorbed.[6]

With increasing concentrations of neodymium the effect of adding nitric acid is similar, with, however, the addition of several new bands. Spectra 5, 6, 7, 8 and 9 show 0.5 *N* $Nd(NO_3)_3$ in acid concentrations of 15.8, 10, 5, 2.5 *N* and neutral, respectively, through 5 cm. of solution. A new band is to be seen in No. 5 at 5970 Å. In still more concentrated neodymium the addition of acid brings out a line between 5360 and 5370 Å. This is very plain in No. 3, while No. 4 shows the appearance of the neutral salt at the same concentration. These bands at 5970 Å. and 5360–5370 Å. are entirely distinct from any hitherto mentioned in the literature and might be mistaken by an inexperienced worker for bands characteristic of praseodymium and holmium, respectively. In addition to these changes the following were observed: the band at 6875–6908 Å. is spread out and shifted toward the red, while the band at 6774–6806 Å. is broadened and shifted toward the violet. The 5800 Å. region is broadened and shifted

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[6] The figures given for the positions of the bands refer to the outer edges, rather than to the centers, and owing to the diffuse nature of the absorption edges the measurements are only approximate.

nearly 50 Å. toward the red. The bands in the region 5100–5200 Å. are in general broadened and shifted more to the violet than to the red. The band at 4744–4762 Å. is shifted to the violet to 4726–4763 Å. and becomes very faint; the band at 4683–4693 Å. is shifted to 4698–4709 Å. and the 4272 Å. band is broadened and shifted toward the red.

The next examination was made on the influence of magnesium nitrate on the absorption bands of neodymium nitrate. This suggested itself not only because magnesium nitrate is very soluble but also because it is commonly associated with the cerium group rare earths in the form of the double magnesium nitrates used in fractional crystallization. The solutions, all of which were neutral, were made up as before with the addition of the calculated amount of magnesium carbonate, which was dissolved in as little nitric acid as possible. The 10 N $Mg(NO_3)_2$ solution was, of course, considerably supersaturated and after introduction of the hot solution to the absorption cell it was carefully cooled to room temperature and the photograph was taken without delay. The absorption bands of the neodymium were shifted by the magnesium nitrate in the same manner as by nitric acid. In a 0.25 N $Nd(NO_3)_3$ solution containing 0.25 N $Mg(NO_3)_2$, which corresponds to the composition of the neodymium double magnesium nitrate, the changes are slight but readily apparent. The most noticeable effect is the broadening of the bands in the 5800 Å. region.

While the changes produced by magnesium nitrate are similar to those produced by nitric acid, they are slightly more pronounced for a given normality. Spectrum No. 10 is of 0.5 N $Nd(NO_3)_3$ in 10 N HNO_3 while No. 11 is of 0.5 N $Nd(NO_3)_3$ in 10 N $Mg(NO_3)_2$. Both pictures were taken on the same plate and through the same depth of solution. The magnesium nitrate produces a slightly greater broadening of the 5800 Å. band, while the bands at 5089–5113 Å. and at 5190–5254 Å. are smaller, particularly the former. The differences become more apparent with solutions more dilute with respect to neodymium.

It was next desired to examine the influence of the nitrate of a tervalent metal and especially that of other rare earths on the absorption bands of neodymium nitrate. The extraordinary difficulty attendant upon the preparation of the pure rare earths made it undesirable to mix such pure salts as were at hand. However, by mixing lanthanum, of which a considerable amount was available, with neodymium, no very great damage was done because although these elements lie close together in the solubility series it is possible to introduce cerous salts between them in a fractionation series and so quantitatively separate the lanthanum from the neodymium. The cerium may then be removed by oxidation, leaving pure lanthanum on the one hand and pure neodymium on the other. It was also desirable to examine the effect of a colored rare earth and especially that of samarium because it occurs close to neodymium in the natural sequence of the elements and because of the bearing it has upon the control of concentration of illinium in neodymium and samarium rich fractions. On no account was it desired to mix pure neodymium with pure samarium, but fortunately a large quantity of material was available which was free from neodymium and was composed chiefly of samarium and gadolinium with traces of europium, terbium and holmium. The chief interest lay in the 5800 Å. region and this material was free from absorption bands in that vicinity. Both lanthanum and samarium solutions were made up 0.5 N in $Nd(NO_3)_3$ and 5 N in $La(NO_3)_3$ and $Sm(NO_3)_3$, respectively. In order to show which bands are characteristic of samarium itself, a photograph (No. 12) was taken of its spectrum before the addition of the neodymium. Spectrum No. 13 shows the neodymium and samarium, while No. 14 shows the neodymium and lanthanum. As lanthanum has no bands in the visible region it was not necessary to photograph its spectrum alone. Spectrum No. 15 shows 0.5 N $Nd(NO_3)_3$ in the pure state. The differences between the changes caused by lanthanum nitrate and by samarium nitrate are slight and unimportant but they both produce changes similar to those brought about by the addition of magnesium nitrate. Compared with the pure neodymium it is found that the bands in the extreme red have disappeared, the 5800 Å. region is extended about 50 Å. toward the red, the 5200 and 5100 Å. bands are narrower, the 4690 Å. band has disappeared, while the 4272 Å. band is shifted slightly toward the red.

Several investigators have assumed that Beer's Law is observed by the rare earth salt solutions. In order to show conclusively that this is not the case, a comparison was made on the same plate of two neutral neodymium nitrate solutions, one 0.025 N the absorption spectrum of which was taken through a depth of 500 mm. of solution, and the other 10 N which was taken through a depth of 1.25 mm. The two solutions should be of equivalent thickness, that is, the incident illumination strikes an equal number of neodymium atoms or ions as the case may be in the two solutions. The changes in the absorption bands are very pronounced. Spectrum No. 16 shows the concentrated solution and No. 17 the dilute solution. In the former the 5800 Å. region has been extended about 30 Å. toward the red. The 5209–5231 Å. band is narrower and shifted toward the red. The 5198–5208 Å. band has disappeared, while the faint bands at 5082–5092 Å. and 5108–5131 Å. are more diffuse and much fainter. The 4744–4757 Å. and 4683–4692 Å. bands have disappeared. The 4272 Å. band is much fainter and shifted toward the red. In addition to these changes it is possible in the case of the concentrated solution to see a faint band at 5970 Å. (compare p. 2930) provided a spectroscope of low dispersion is used. This band does not appear to have been reported hitherto for neutral neodymium nitrate.

During the course of the work several absorption bands were photographed in the ultraviolet. These bands have received little attention from investigators in this field and are probably identical with the bands recently reported by Gardiner.[7] Inoue reports no bands for neodymium chloride in the ultraviolet.

Praseodymium Nitrate.—Since nitric acid had such a marked effect on the absorption spectrum of neodymium nitrate, it was decided to investigate its effect on other rare earth nitrates. The changes observed in the case of praseodymium were not as pronounced, in general, as in the case of neodymium. Spectrum No. 18 records the absorption of a 5 cm. layer of 1.0 N $Pr(NO_3)_3$ in the presence of 15.8 N HNO_3, while No. 19 is a neutral solution of the same concentration and depth. The band at 5985–5840 Å. suffers a marked decrease in intensity and is narrowed approximately 48 Å. to 5969–5872 Å. The band at 4839–4799 Å. is shifted slightly toward the red, the more refrangible edge being more so than the other. The band at 4725–4629 Å. is narrowed 35 Å., and the band at 4497–4380 Å. is narrowed 30 Å. The absorption edges were in all cases more diffuse. In the case of 0.1 N $Pr(NO_3)_3$, the shifts and variations in intensity were similar to those in the more concentrated solutions.

Samarium Nitrate.—The effect of free nitric acid upon the absorption spectra of samarium nitrate was also studied. Samarium does not exhibit as strong absorption in the visible region as do neodymium and praseodymium, except in highly concentrated solutions. It shows very strong absorption, however, in the violet and ultraviolet, especially from 3000 Å. to 4400 Å. The spectra of samarium reproduced here do not show below 4100 Å. but marked changes were observed as low as 3000 Å. upon the addition of nitric acid. Spectrum No. 20 is the absorption of 1.0 N $Sm(NO_3)_3$ in 15.8 N HNO_3, while No. 21 is that of the neutral solution through the same depth, 5 cm. The acid decreases the intensity of absorption in the 4823–4736 Å. region, as is also the case with the 4661–4613 Å. band. The two bands in the blue ordinarily listed as 4177 Å. and 4154 Å. are blended together in the acid solution, the resulting absorption area being about 20 Å. less in width than the total width of the two original bands.

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[7] Gardiner, *J. Chem. Soc.*, **1926**, 1518.

The 4154 Å. band may be said to have shifted toward the red in forming the new band. The 4071 Å. and 4013 Å. bands are also blended into one by the acid. The decrease in width is marked by a shift toward the blue of the less refrangible edge. In general the absorption is less in the acid than in the neutral solution. Observations on other depths of solutions agree with the above, with other bands of less persistence appearing in the neutral solutions and also being changed by the acid.

Erbium Nitrate.—Erbium exhibits, with neodymium, the largest number of absorption bands of any of the rare earth elements. It seemed advisable, therefore, to study the effect of excess nitric acid on erbium nitrate, since the acid caused such decided shifts in the case of neodymium. Although the erbium material was impure, and the presence of foreign salts does affect the absorption spectrum of an element, the presence of nitric acid caused a marked change. As seen in spectrum No. 22, there is a slight decrease in intensity of the band occurring at 6536–6486 Å. with a shift toward the blue of about 5 Å. in the 15.8 N acid as compared with the slightly acid solution shown in No. 23. The bands in the 5350–5400 Å. region are broader and more diffuse in the acid solution and are shifted toward the blue. The same is true of the 5170–5240 Å. region, the absorption area being increased about 40 Å. and shaded off on both sides. The 4860–4878 Å. band is increased in width to 4830–4920 Å. with the heaviest absorption being shown from 4830–4855 Å. This is a decided shift toward the blue of the maximum of absorption and a broadening of the band at the same time. The 4495–4500 Å. is shifted toward the violet about 10 Å. Whenever two bands are in close proximity in the neutral solution, they are blended together by the acid.

Neodymium Chloride.—In order to determine whether or not the changes in the absorption bands were peculiar to the nitrates, the effect of concentrated hydrochloric acid was studied on neodymium chloride. The changes in this case were different from what they were for neodymium nitrate, showing that the effect of different acids upon the absorption of a rare earth element is not the same. The concentration of the solution with respect to neodymium was that of a saturated solution of neodymium chloride in 12 N hydrochloric acid. As is the case with most chlorides, the solubility of the rare earth chlorides is repressed to a very considerable extent by the presence of free hydrochloric acid. The concentration of the neodymium chloride was approximately 0.4 N. Spectrum No. 24 represents the absorption of a neutral solution of 0.4 N $NdCl_3$ 5 cm. thick, and No. 25 is that of the same concentration of $NdCl_3$ in 12 N HCl. In the extreme red the acid brings out a new band at 6821–6848 Å. The change in the 5800 Å. region is very pronounced. The band shades off toward the red with an increase in width of between 90 and 100 Å. The 5200–5220 Å. band is shaded off toward the red by the acid. The 5123 Å. band is narrowed about 5 Å. The 5091 Å. band is very much fainter and seems to be shifted to the blue slightly. The 4754 Å. band is fainter in the acid solution and is broadened toward the red. The 4691 Å. band is repressed and shifted toward the red. In the neutral solution there is only one distinct band at 4271 Å., while in the acid solution there are three faint, fuzzy bands at 4330 Å., 4297 Å. and 4271 Å.

Discussion of Results

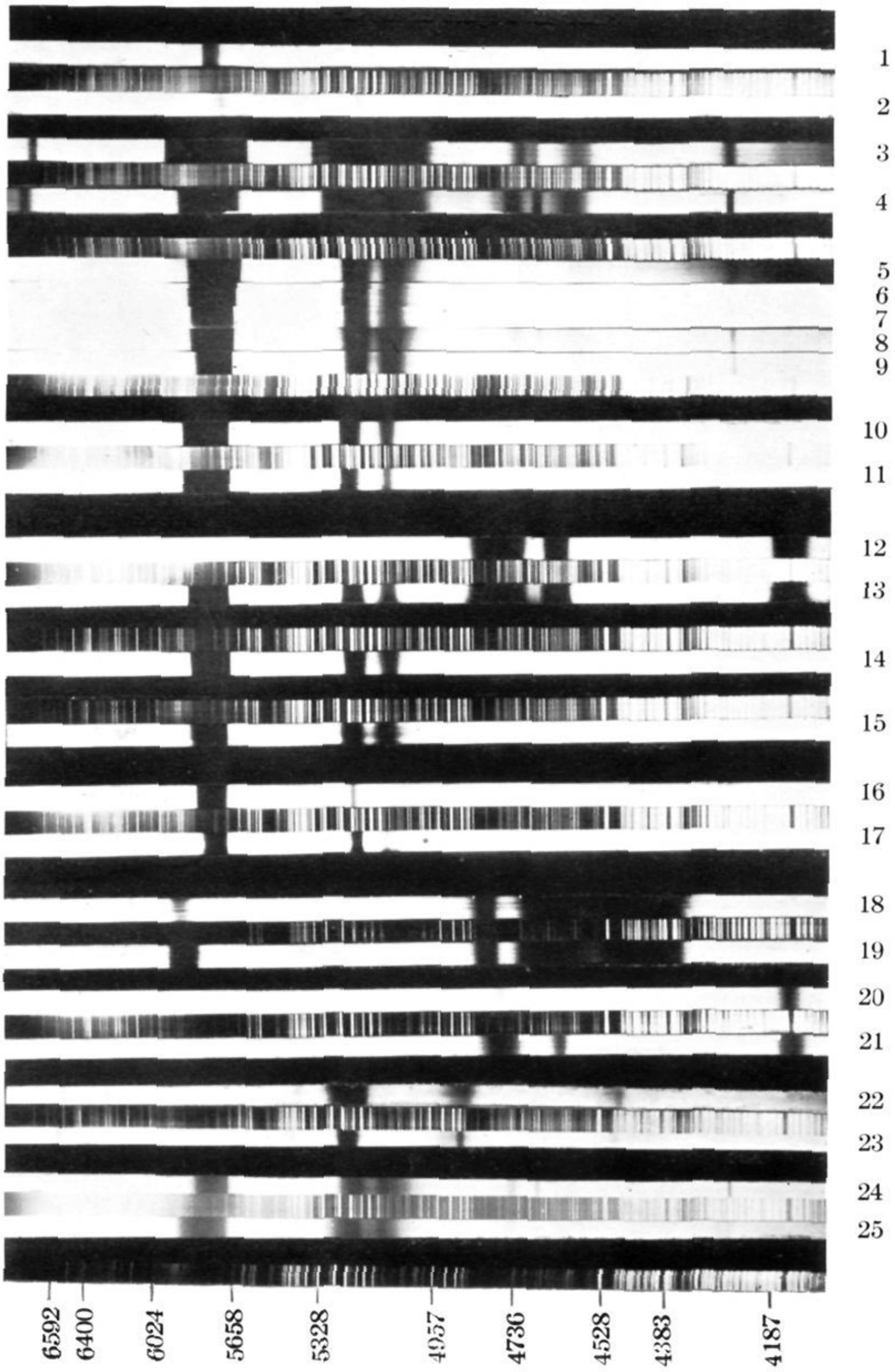
In view of the present unsatisfactory state of our knowledge of atomic structure, it seems unwise to attempt any interpretation of the results presented here in terms of one of the current theories. It is known that even in the case of strong electrolytes the oppositely charged ions in a solution may approach close enough to one another to cause distortion of the outer electron shells. It is probable that this distortion may be

DESCRIPTION OF PLATE

All solutions taken through a 5cm.
layer unless otherwise designated.

1. 0.1 N $Nd(NO_3)_3$ in 15.8 N HNO_3.
2. 0.1 N $Nd(NO_3)_3$ in neutral solution.
3. 1.0 N $Nd(NO_3)_3$ in 15.8 N HNO_3.
4. 1.0 N $Nd(NO_3)_3$ in neutral solution.
5. 0.5 N $Nd(NO_3)_3$ in 15.8 N HNO_3.
6. 0.5 N $Nd(NO_3)_3$ in 10 N HNO_3.
7. 0.5 N $Nd(NO_3)_3$ in 5 N HNO_3.
8. 0.5 N $Nd(NO_3)_3$ in 2.5 N HNO_3.
9. 0.5 N $Nd(NO_3)_3$ in neutral solution.
10. 0.5 N $Nd(NO_3)_3$ in 10 N HNO_3.
11. 0.5 N $Nd(NO_3)_3$ in 10 N $Mg(NO_3)_2$.
12. 5.0 N $Sm(NO_3)_3$ for reference.
13. 0.5 N $Nd(NO_3)_3$ in 5 N $Sm(NO_3)_3$.
14. 0.5 N $Nd(NO_3)_3$ in 5 N $La(NO_3)_3$.
15. 0.5 N $Nd(NO_3)_3$ in neutral solution.
16. 10 N $Nd(NO_3)_3$ through 1.25mm. layer.
17. 0.025 N $Nd(NO_3)_3$ through 500mm. layer.
18. 1.0 N $Pr(NO_3)_3$ in 15.8 N HNO_3.
19. 1.0 N $Pr(NO_3)_3$ in neutral solution.
20. 1.0 N $Sm(NO_3)_3$ in 15.8 N HNO_3.
21. 1.0 N $Sm(NO_3)_3$ in slightly acid solution.
22. 1.5 N $Er(NO_3)_3$ in 15.8 N HNO_3.
23. 1.5 N $Er(NO_3)_3$ in slightly acid solution.
24. 0.4 N $NdCl_3$ in neutral solution.
25. 0.4 N $NdCl_3$ in 12 N HCl.

Variations in the Absorption Spectra.



Wave lengths in Ångström units.

communicated in part, as small energy changes, to the electrons composing the inner sub-group which is thought to be the seat of the spectrum bands in the visible region.[8] Recent observations by Ephraim and Bloch[9] on the ammonia complexes of praseodymium chloride have been successfully explained by them on the basis of their theory of the deformation of the inner electron shell.

The idea is by no means original that the changes in the absorption bands are intimately connected with repression of ionization. This relation is certainly suggested by the similarity between the shifts produced by the addition of a common ion and those produced by increased concentration alone. In view of the fact, however, that the shifts reported here are neither uniform throughout the spectrum of a given salt nor of a similar nature in different salts, it seems that the theory of repression of ionization is inadequate to account for all the facts. Another difficulty is found in connection with the effect of magnesium nitrate. Magnesium nitrate is not commonly supposed to yield a high concentration of nitrate ion, yet there is unmistakably a greater change in the bands of neodymium nitrate upon the addition of 10 N magnesium nitrate than upon the addition of 10 N nitric acid. It was suspected that the metal ion might have something to do with the phenomenon and further investigation on this point is under way. No doubt we have more than one influence to deal with here and the formation of solvates, as suggested by Jones,[10] probably plays a part.

The large deviations observed from Beer's Law suggest that investigations wherein it has been assumed to hold are in error. It has been impossible to confirm Delauney's report on the effect of nitric acid on the absorption bands of neodymium nitrate. In the course of his work he used a spectroscope of only 2 cm. dispersion while the work here was done upon an instrument of 20 cm. dispersion. As the maximum shift observed was of the order of 2 mm., the greatest change which Delauney could have seen would have been about 0.2 mm. Inoue states that the characteristic bands of samarium at 4071 Å. and 4013 Å. remain unchanged upon mixing samarium chloride with the chloride of lanthanum, praseodymium or neodymium. We have found that in the case of the nitrate these bands are blended together and shifted toward the violet on the addition of nitric acid.

The effect of hydrochloric acid on neodymium chloride is interesting because while the changes in the absorption bands are in some degree

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[8] Hevesy, "Die seltenen Erden vom Standpunkte des Atombaues," Julius Springer, Berlin, **1927**, p. 40.

[9] Ephraim and Bloch, *Ber.*, **59B**, 2692 (1926), and **61B**, 72 (1928).

[10] Jones, "Absorption Spectra of Solutions," Carnegie Institute of Washington Publications, No. 130, No. 160.

similar to those produced by nitric acid yet they are by no means identical differing both in intensities and in the positions of the new bands.

The portion of the work to which the greatest practical interest is attached is that in connection with the influence of one rare earth salt upon the absorption bands of another. It has been shown that in the presence of a colored or colorless rare earth the absorption bands of an element present in small proportions cannot be relied upon for its quantitative analysis and should be used for its identification with the utmost caution. In the cases observed the changes took the form of a distinct shift toward the red, particularly in the 5800 Å. region and of a marked diminution of intensity of the bands in the blue and violet. None of the changes observed was of such a nature as not to be distinct from the bands at 5816 Å. and 5123 Å. reported for illinium by Harris and Hopkins[11] and criticized by Prandtl. In dealing with relatively pure rare earth salts, it should be sufficient to remove all excess of the common ion and particularly to remove all excess acid before attempting spectroscopic analysis; but the quantitative estimation of a small amount of one rare earth in the presence of a large amount of another cannot be relied upon unless use is made of other means than the visible absorption spectra.

Summary

1. The absorption spectra of solutions of praseodymium, neodymium, samarium and erbium nitrates, which were the only ones investigated, are influenced by the addition of nitric acid. Salts of other rare earths showing absorption are undoubtedly affected.
2. No generalization can be made as to the effect of excess nitric acid on the nitrates of the different rare earths.
3. Hydrochloric acid does not produce the same effect as nitric acid on the corresponding neodymium salts.
4. Addition of magnesium nitrate to neodymium nitrate solutions produces a similar but slightly greater change than an equal normality of nitric acid.
5. Colored or colorless rare earth nitrates affect the bands of neodymium nitrate similarly to magnesium nitrate.
6. The deviations from Beer's Law of neodymium nitrate solutions resemble to some extent the effect of the addition of nitric acid.
7. Observations of Jones and others have been confirmed, while it has been impossible to confirm the work of Delauney.
8. Absorption spectra of solutions of rare earth salts should be used for qualitative analysis with the utmost caution and are not suitable for their quantitative estimation in the presence of one another.

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[11] Harris and Hopkins, THIS JOURNAL, **48**, 1585 (1926).

9. In no case do the observed changes coincide with those reported by Harris and Hopkins during the concentration of illinium.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THREE LABORATORY DEVICES: A VACUUM STIRRER, A PRESSURE ALTERNATOR AND A GAGE FOR MEASURING LOW PRESSURES OF PERMANENT GASES IN CONDENSABLE VAPORS[1]

BY ROGER K. TAYLOR

RECEIVED JULY 30, 1928 PUBLISHED NOVEMBER 6, 1928

An apparatus devised by the author for the stirring of liquids *in vacuo* has been of service in several researches at this University, and may be useful elsewhere. The purpose for which it has been used is the freeing of liquids from dissolved gases; periodic removal of the vapor above the liquid is ineffective, unless the liquid is stirred.

One form of the device is shown in Fig. 1. The liquid, resting above mercury, is contained in bulb A; above it is C, a tower of beads. By a method to be described, the level of the mercury is alternated between l_1 and l_2. The cycle of operation is this: when the mercury falls to l_2, it drains from the small bulb B, which fills with the liquid from A. Then, as the mercury rises again to l_1, it refills B, and the liquid contained is forced into C, where it spreads over and trickles through the beads and returns to A. In this way the establishment of equilibrium of dissolved gas between the liquid and vapor phases, which ordinarily is a very slow process, is rapidly effected. This results both from the large surface offered by the beads and the fact that the liquid is constantly being withdrawn from the bottom and returned to the top of A. Periodic removal of the vapor in A and C soon leaves the liquid practically free of dissolved gases.

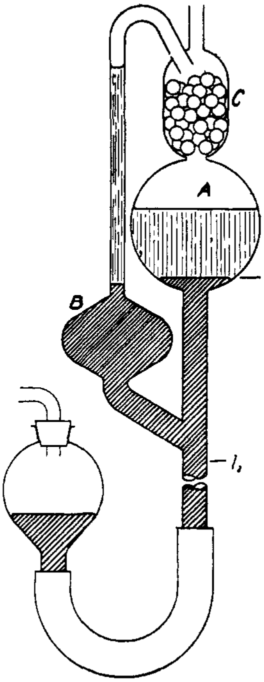

Fig. 1.

In one case, where air was to be removed from an alcoholic soap solution, it was feared that the beads would occasion troublesome foaming. The difficulty was avoided by replacing C with a helix of tubing wide enough to permit the solution to flow along its bottom instead of filling it completely.

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[1] In memory of Ira Remsen.