THE ABSORPTION SPECTRA OF SOLUTIONS AS AFFECTED BY TEMPERATURE AND BY DILUTION: A QUANTITATIVE STUDY OF ABSORPTION SPECTRA BY MEANS OF THE RADIOMICROMETER

By

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PREFACE.

The effect of high temperatures on the absorption spectra of nonaqueous solutions was worked out in the Johns Hopkins University and published in monograph No. 160. By means of a form of apparatus devised by Dr. Strong, this work has now been extended to aqueous solutions and the results are herein recorded.

Our previous work on the absorption spectra of solutions, which has now been in progress continuously for eight years, had shown that the effect of dilution on absorption spectra is much less than had hitherto been supposed. A form of apparatus and method of procedure were worked out by Professor Anderson, one of my former coworkers in this field, and this method has been applied, with unusual skill, by Dr. Guy, to the effect of dilution on absorption spectra. The results that he has obtained are also recorded in this monograph.

The grating spectrograph as a means of studying absorption spectra has now supplanted the prism spectroscope. The grating spectrograph, however, has its limitations. The results are photographed. This means that the method is limited to the range of the photographic plate. This is, for the best plates, from about 0.2μ to 0.8μ. It is, however, very desirable to study absorption spectra in the region of wave-lengths which are much greater than 0.8μ. For this purpose, some method had to be devised which did not make use of the photographic plate. The radiomicrometer was the obvious instrument to use, if it could be built sufficiently sensitive and at the same time with sufficiently short period. This has been accomplished by Dr. Guy.

With this instrument the absorption spectra of a number of salts have already been mapped, and some surprising results have been obtained in reference to the relative absorption of free water as compared with water of hydration.

It gives me pleasure to express our thanks to Dr. E. J. Shaeffer, who has assisted in making the radiomicrometer readings during the second half of the past year, and who has also aided in the chemical work. Dr. Shaeffer will continue the work on the absorption spectra of solutions, using the radiomicrometer. We are especially indebted to Professor A. H. Pfund for a large number of valuable suggestions, and for frequent advice during the progress of this week. Professor J. S. Ames has kindly placed ample space at our disposal for carrying out this investigation.

I am deeply grateful to the Carnegie Institution of Washington for financial aid in carrying out this entire work, and in publishing the results obtained. Without this aid, the work recorded in monographs Nos. 60, 110, 130, 160, and herein could not have been done.

Harry C. Jones.

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CHAPTER I.

INTRODUCTION.

An investigation of the effect of temperature on the absorption spectra of certain solutions has already been carried out by Jones and Strong.[1] The apparatus used was devised by Professor John A. Anderson,[2] who worked somewhat earlier with Jones on the absorption spectra of solutions. The solutions were heated in an open vessel, and the temperature could, of course, not be raised much above 100° F. It was found that, even over this range of temperature, the effect of rising temperature was to cause the general absorption of any salt in water to increase, and also to cause the bands to broaden and become more diffuse. The results were entirely unambiguous so far as they went, but were limited by the boiling-points of the solutions in question. Indeed, it was not possible to work quite up to the boiling-point of the solution, since the change in the concentration of the solution resulting from boiling would have been too great, and there would have been too much gas formed on the quartz windows through which the light was to pass.

We wanted to study the effect of rise in temperature on the absorption spectra of solutions to as high temperatures as it was possible to go. For this purpose closed forms of apparatus devised by Anderson[3] and by Strong[4] were employed by Jones and Strong[5] for nonaqueous solutions. The apparatus consisted of a gold-plated steel tube, whose ends were closed with glass windows. This worked very well with nonaqueous solvents up to temperatures of approximately 200° C. Usually before this temperature was reached a precipitate formed in the tube, which prevented work at higher temperatures.

Some interesting results were obtained at the higher temperatures with this apparatus. The general effect of rise in temperature is to deepen the color of the solution of an inorganic salt. This is usually due to a widening of the absorption bands. For details in reference to the effect of temperature on the absorption of light by nonaqueous solutions, reference must be had to the Carnegie Institution of Washington monograph,[6] where the results in question are published in full.

The apparatus used by Jones and Strong for nonaqueous solutions did not work satisfactorily for solutions in water as the solvent. The water vapor, under the high pressure produced within the apparatus, worked its

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[1] Carn. Inst. Wash. Pub. **130**. Amer. Chem. Journ., **43**, 37, 97 (1910); **45**, 1, 113 (1911).
[2] Carn. Inst. Wash. Pub. **110**, p. 20. Amer. Chem. Journ., **41**, 276 (1909).
[3] Carn. Inst. Wash. Pub. **160**, p. 28. Amer. Chem. Journ., **47**, 30 (1912).
[4] Carn. Inst. Wash. Pub. **160**, p. 29. Amer. Chem. Journ., **47**, 30 (1912).
[5] Carn. Inst. Wash. Pub. **160**. Amer. Chem. Journ., **47**, 27, 126 (1912).
[6] Carn. Inst. Wash. Pub. **160**.

way through the layer of gold laid down on a layer of copper electrolytically, rusted the steel, and caused the separation of the gold from the steel walls. To avoid this, the apparatus, which was designed by Dr. Strong,[1] was made of brass and will be described in some detail in this monograph. It was plated electrolytically with gold and this adhered firmly to the brass, even when the aqueous solution contained in the apparatus was heated to 200° C. We could work as satisfactorily with this apparatus with aqueous solutions as with the former apparatus with nonaqueous solutions.

The work described in this monograph on absorption spectra of aqueous solutions at high temperatures was all carried out in the gold-plated brass apparatus. The results obtained and the bearing of these results on the nature of solution will be discussed later in this monograph. Suffice it to say here that up to 200° the effect of temperature on the absorption spectra of aqueous and nonaqueous solutions has now been studied pretty extensively on a large number of salts and a fairly large number of solvents.

The effect of dilution on the absorption spectra of solutions was taken up with the following idea in mind: It was long a question as to what is the nature of the absorber of light, say in aqueous solutions. It was at one time supposed that chemical molecules were the absorbers, since these were regarded as the ultimate units in solution. It was supposed that the molecules were thrown into resonance by certain wave-lengths of light, and that these were, consequently, stopped; while the remaining wave-lengths passed through the solution and gave to it its characteristic color.

When the theory of electrolytic dissociation was proposed in 1886, the view as to the nature of solution of electrolytes underwent a serious change. When electrolytes were dissolved in water, or in any other dissociating solvent, they dissociated into charged parts or ions, and these were the ultimate units in solution. If the solution was fairly concentrated we had both ions and undissociated molecules in the solution, and the question in such cases was, which is the absorber?

It was further recognized that a dilute solution of salt often has very different color from a concentrated solution; and, moreover, solutions of nonelectrolytes are often colored, *i. e.*, have the power to absorb certain wave-lengths of light and to allow others to pass on through. It was supposed, then, that molecules have the power to absorb light, and ions also have absorbing power. When a concentrated and a dilute solution of an electrolyte had the same absorption spectrum—the same color—it was supposed that the chemical molecule and the ions resulting from it had the same absorption. When the dilute solution had a different color from the concentrated solution, it was thought that the ions were the chief absorbers of light. And since it frequently happens that a dilute solution of an electrolyte has a very different color from a more concentrated solution, it was supposed that in dilute solutions of electrolytes the ions are the chief absorbers of light; since in very dilute solutions of electrolytes there are

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[1] Carn. Inst. Wash. Pub. **160**. Amer. Chem. Journ., **47**, 30 (1912).

mainly ions and practically no molecules present, it is obvious that in such solutions it is not the molecules which are absorbing light. It must be the ions, since these are the only units present, or something contained within the ions. This was the view of absorption of light introduced by the theory of electrolytic dissociation.

We have now gone much farther than this. We now know that the ions are not the ultimate units in a solution of an electrolyte. The simplest ion is very complex. It is made up of a large number of electrons, which are unit negative charges of electricity. There is every reason to-day to believe that the electrons are the real absorbers of light, are the units which are thrown into resonance by the various wave-lengths of light. Granting this, there is still a difference between an ion and the atom or atoms from which it was formed. An ion contains one or more free electrons within it or on it, *i. e.*, one or more negative charges than would correspond to the positive electricity within the atom. It would be interesting to know whether the free electron or electrons upon the ion have anything to do with its power to absorb light. This can be tested by studying the absorbing power of molecules and then the absorption of light by the ions which are formed when these molecules dissociate. It was with this idea in mind that the second chapter of the work described in this monograph was undertaken.

A concentrated solution of a salt contains many molecules, and if the solution is sufficiently concentrated there are chiefly molecules and only a few ions present. As the dilution is increased the dissociation increases; the number of molecules becomes less and less and the number of ions greater and greater. The problem, then, is to photograph the absorption spectrum of a very concentrated solution of a salt, the layer being, say, 0.5 cm. deep. Then take the spectrum of a more dilute solution of the same salt; if the dilution is increased 100 times the depth of layer used would be 50 cm. Under these conditions there would be the same number of parts of dissolved substance in the path of the beam of light; in the second case there would be more ions and less molecules than in the first. By comparing the two spectra we could see whether there is any difference between the absorbing power of ions and molecules, *i. e.*, whether the free electrons upon the ions have anything to do with their power to absorb light. We then took another step, increasing the dilution of the second solution five times and also increasing the depth of the layer of the solution through which the light passed five times, *i. e.*, making the depth 250 cm. This second diluting still further reduced the number of molecules present and increased the number of ions. By comparing the three spectrograms we ought to be able to say whether molecules and ions have the same or different resonance with respect to light-waves; and, if it is different, to point out in what the difference consists. This would then enable us to determine whether the free electrons upon the ions played any part in the absorption of light.

We shall see that ions have somewhat different absorbing powers from molecules, and in what this difference consists will appear later from the text and from the plates.

The work done on the absorption spectra of solutions by Jones and Uhler,[1] Jones and Anderson,[2] and Jones and Strong,[3] which extended over five years, and in which some 6,000 solutions were studied, all involved the photographing of the various spectra. In this way the positions of the various absorption lines and bands were determined.

A question even more fundamental than the positions of the lines and bands is their intensities, and the relative intensities of different parts of the same band. The photographic method gave only a means of dealing qualitatively with this problem. Some general idea could be gained of the relative intensities of the various lines and bands on the photographic plate, but these changed with the time of exposure, the intensity of the light used, and with other conditions, so that we were able to learn very little about the intensities of the various lines and bands by means of the photographic method.

Further, the photographic plate is sensitive only between the wave-length 2,000 Ångstrom units and 7,600 A.U.,[4] which is a comparatively small part of the spectrum. It is especially important to work also into the region of the infra-red.

A method was used which dealt quantitatively with the intensities of the various lines and bands. This same method, instead of being limited by the above-named wave-lengths, could be used down into the infra-red to wave-lengths as great as 20,000 A.U. to 30,000 A.U. Indeed, the method can be used for even greater wave-lengths, if solvents can be found that are transparent to the longer waves. This method involves the use of the radiomicrometer.

The description of the instrument which we built, the method of work, and the results thus far obtained, will be found on pp. 29 to 93.

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[1] Carn. Inst. Wash. Pub. **60**. Amer. Chem. Journ., **37**, 126, 207 (1907).

[2] Carn. Inst. Wash. Pub. **110**. Amer. Chem. Journ., *loc. cit.*

[3] Carn. Inst. Wash. Pub. **130** and **160**. Amer. Chem. Journ., *loc. cit.*

[4] Throughout this paper we have employed this expression to designate Ångstrom units.

CHAPTER II.

ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS AS AFFECTED BY TEMPERATURE.

Jones and Strong[1] studied the effect of temperature on the absorption spectra of various nonaqueous solutions up to nearly 200°. The solutions were usually heated until a precipitate formed, which cut off the light and prevented work at still higher temperatures. Some work was also done by Jones and Strong on the effect of temperature on the absorption spectra of aqueous solutions. This was, however, not large in amount and did not extend to very high temperatures.

The reason that the work with aqueous solutions was not pushed to higher temperatures was that the form of apparatus then in use did not admit of it. This consisted of a steel tube,[2] lined on the inside with copper and plated with gold on all of the inner surfaces. This worked very satisfactorily with nonaqueous solutions, the gold plate adhering firmly to the copper, which, in turn, remained adherent to the steel. When an aqueous solution was heated in the apparatus from 100° to 200° the result was unsatisfactory. The water, under the high pressure, forced its way through the copper and the gold and rusted the iron, as has already been stated. The result was that the copper, with the gold, separated from the steel, and the solutions, after heating for a time, gave the iron reaction. This apparatus had the further disadvantage, that when a precipitate formed with rising temperature it was necessary to open the entire apparatus and remove the glass ends in order to clean them.

To overcome these difficulties the apparatus shown in fig. A was constructed by Jones and Strong and used to study the effect of rising temperature on the absorption spectra of aqueous solutions. The quartz ends are fastened into the ends *E'*. The plunger *P* has guide grooves instead of guide pins. A part of the plunger is provided with screw-threads for removing it. The entire cap is removed from tube *T* by unscrewing *E'*, during which the quartz end is untouched. When the ends are removed the quartz window can be easily cleaned. Gold washers were inserted between *T* and *E'* and between *E'* and *U*.

The general arrangement of the apparatus is also shown in fig. A. The cell is kept in a horizontal position, so that any bubbles that may form will rise in the side tube. The spectroscope, containing the grating *G*, photographic-plate holder *C*, and slit *S*, being kept vertically, a 45° quartz prism was used to change the horizontal beam of light into a vertical beam, the beam being totally reflected by the hypothenuse surface of *O*. The source of light *NG* (Nernst glower) or *SG* (spark gap) was focused by the concave

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[1] Amer. Chem. Journ., **47**, 27, 126 (1912).

[2] *Ibid.*, **47**, 30 (1912).

speculum mirror *M* on the slit *S*. A similar arrangement was used for the fused silica cell. *DTS* is a double-throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. *B* is a ballast. *R* is a variable resistance, by means of which the current in the Nernst glower, as shown by the ammeter *A*, may be kept constant. *OC* is an oil-condenser. *IC* is an X-ray induction coil and R_2 is a resistance in the primary circuit of this coil.

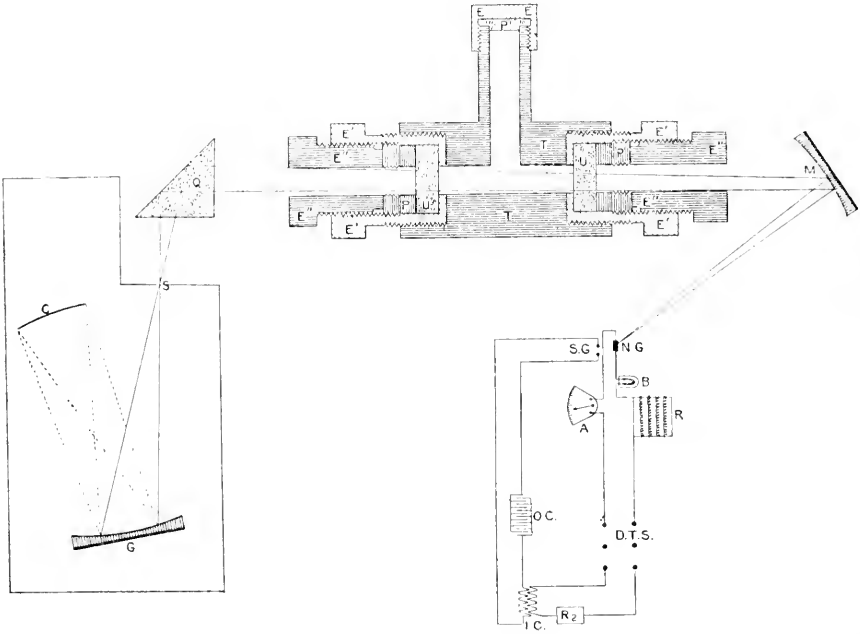

Fig. A.

In a recent paper Merton[1] states that he has studied the effect of pressure on the absorption spectra of solutions. This was studied here by Jones and Strong and the results published in the American Chemical Journal.[2] The quotation of a paragraph from our earlier paper will show what was found:

> Some preliminary tests were made with the cells at high pressures. The Cailletet pump belonging to the Johns Hopkins University was used for this purpose, the cell being made so as to fit into this pump. It was not at all difficult to obtain pressures of 200 atmospheres with water and alcohol solutions. Spectrograms were made of the absorption spectra of neodymium solutions under pressures as high as 275 atmospheres. *No effect of pressure was detected.* The work at high pressures is easier than at high temperatures, on account of the fact that there is an expansion of the cell due to heating.

It should be stated that in all of the work on absorption spectra which has been carried out in this laboratory for the past seven years, a grating spectroscope has been used. The arrangement of the heated cell, the grating, photographic plate, etc., will now be discussed.

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[1] Proc. Roy. Soc., (A) **87**, 146.

[2] Amer. Chem. Journ., **47**, 32, January 1912.

THE MAKING OF A SPECTROGRAM.

The apparatus used throughout the entire study of the effect of high temperature has already been discussed. Two cells were used, one 10 cm. and the other 1 cm. in length, both having the same general design and differing only in length.

The cell, placed in a bath suitable for keeping the temperature constant, was arranged as indicated in the diagram, and the source of light so located that the rays, reflected from a concave mirror, passed longitudinally through the cell and formed an image of the Nernst glower on the slit of the camera. The position of the prism is so adjusted as to fill the grating uniformly with light. Holding the eye directly above the grating, in a position later to be occupied by the photographic plate, we could easily tell when the light was falling properly upon the grating. When the cell was correctly adjusted the lights were extinguished and the photographic plate inserted. With the plate in position, the light was turned on and an exposure made at room temperature. The position of the plate was then moved a given distance, and the temperature of the cell raised very slowly, this process being repeated at intervals of about 20° or 25°.

It is clear that, with such pressures as are developed by heating water to 200°, it is very difficult to obtain a tight joint between glass and metal. This difficulty, however, has been partly overcome by the special form of apparatus designed by Dr. Strong and described on page 6 of this monograph. We were not able to secure a closing that would hold above 200°, but once a good closing was secured it was not necessary to remove the ends for several operations.

Great care had to be taken in heating the cell, on account of the difference in expansion of the glass ends, and the metal in contact with them. When the temperature was raised more than 40° an hour the glass ends usually broke. At such high temperatures as we were employing the glass was rapidly attacked by the water; later, when we were using the clear uviole glass, a single heating rendered the glass ends almost opaque, especially if they were allowed to stand for any length of time.

It was found that in many cases precipitates would appear in the cell at a temperature slightly above 100°. This precipitate, however, formed rapidly, once it began, and almost as quickly disappeared. By properly regulating the intervals at which exposures were made, the effect of the precipitate could be avoided; hence this effect does not appear on any of the strips photographed.

It is probable that slight hydrolysis took place at first, as

$$2NdCl_3 + 3H_2O = 2Nd(OH)_3 + 3HCl$$

The presence, then, of a slight excess of hydrochloric acid would hinder the reaction in the direction indicated above by the arrow. Since most hydroxides lose water at temperatures above 100°, it is possible that the following reaction would take place:

$$2Nd(OH)_3 = Nd_2O_3 + 3H_2O$$

The neodymium oxide, being heavy and very slightly soluble in water, settles to the bottom of the cell, and the solution clears up. In this way it is evident that the solution becomes slightly more dilute as the temperature is raised; but this would lessen the number of absorbers in the path of the beam of light, and thereby produce a narrowing of the bands and could only decrease the effect indicated on the plates. This antagonistic influence could certainly not cause a widening of the absorption bands, with rise in temperature.

NEODYMIUM CHLORIDE IN WATER. (SEE PLATE 1.)

The solution whose spectrum is given in section *A* was saturated, the depth of absorbing layer being 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140°, and 165°, respectively. Absorption bands which are unchanged by the range of temperature from 20° to 200° appear at λ3800, λ4025, λ4200, λ4325, λ4440, λ4600, λ4690, λ4750 and λ4820. The double band from λ5050 to λ5270 is only slightly affected, if at all.

The two most interesting absorption bands are those whose centers are near λ4275 and λ5800. The former of these in strip 1 is very sharp and intense, though only a few A.U. wide. Both edges were well defined. As the temperature is raised the violet edge remains very sharp, while a rapid shading off of the red edge takes place. At a glance the band appears to be less intense in the higher temperature strips, but on close examination it is seen to be more diffuse, the red edge diffusing over a range of about 20 A.U. at the highest temperature. This is exactly in accord with what Jones and Anderson[1] had found. They showed that when the number of molecules in the path of light was kept constant, this band remained practically constant; while it has been shown by Jones and Anderson and by ourselves that this band changes with dilution, being more intense in the most concentrated solution.

The λ5800 band is affected most by temperature as well as by dilution. In strip 1 this band is about 200 A.U. wide, the width increasing regularly as the temperature is raised, until at the highest temperature it is over 250 A.U., or there is a total widening of 50 A.U. The violet edge remains perfectly sharp, while the shading is toward the red end of the spectrum.

It occurred to us that whatever effect might be produced by a rise in temperature, if it was a true temperature effect, the reverse should happen when the solution was allowed to cool.

With this in view *B* was made. The concentration of the solution and the depth of layer photographed in section *B* were exactly the same as in *A*. In fact, the same solution was used. As soon as the film *A* had been exposed with rising temperature, it was removed from the camera and developed. Without even allowing the cell to cool, another film was placed in the camera

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[2] Carn. Inst. Wash. Pub. 110.

and section *B* made with falling temperature. In *B* the temperatures were 165°, 140°, 115°, 95°, and 70°, the highest temperature being nearest the numbered scale, which is not accurately adjusted.

A study of the original film shows changes only in bands λ4275 and λ5800; and this change is exactly the reverse of that shown by these same bands in *A*. The λ4275 band appears in strip 1, with a sharp violet edge and shading off toward the red over a range of 15 or 20 A.U. As we pass to the succeeding strips in the direction of falling temperature the red edge becomes sharper and sharper, until in strip 5, which represents the lowest temperature, the band assumes its normal sharp edge on the red side and covers less than 10 A.U. The λ5800 band narrows uniformly from the red end as the temperature falls, the total narrowing being about 40 A.U.

NEODYMIUM BROMIDE IN WATER. (SEE PLATE 2.)

The concentration of the solution used in making the negative for *A* was 1.66 normal; the depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 120°, 140°, 175°, and 190°, respectively. This plate seems to have had just the proper length of exposure for the given concentration, and every known neodymium absorption band appears on the negative in excellent condition. With the bromide, as with the chloride discussed in plate 1, only λ4275 and λ5800 show appreciable changes with rise in temperature. The λ4275 band, which has both violet and red edges sharp in strip 1, feathers out toward the red end of the spectrum as the temperature is raised.

The λ5800 band widens toward the red as much as 60 A.U. The concentration of solution used in making *B* was 0.166 normal, one-tenth that of *A*; the depth of absorbing layer was 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 135°, 155° and 190°, respectively. This is probably the best negative produced in this part of the work, and the bands λ4275 and λ5800 show well the characteristic changes spoken of above. The widening of band λ5800, though well marked, is not so great as in *A*, the total change being about 40 A.U., as compared with 60 A.U. in the former. If such a band be due to molecules this is what we should expect, since, *B* being a more dilute solution, the total number of molecules is less than in *A*. Hence, any change associated with molecules would be more clearly apparent in *A*. This is in accord with changes produced in this same band by dilution.

NEODYMIUM NITRATE IN WATER. (SEE PLATES 3 AND 4.)

The solution used in spectrogram *A*, plate 3, was saturated, the depth of cell being 1 cm. The temperatures, beginning with the strip nearest to the numbered scale, were 15°, 40°, 65°, 115°, 140°, and 165°, respectively.

The exposures were not as long here as in the previous plates, in order to bring out more clearly the group of bands between λ4200 and λ4800. The change in the λ4275 band is here especially marked. At 15° this band is very sharp and intense, while at 165° it has become broad and hazy, being about 30 A.U. wide. The λ4425 band shows a widening of about 15 A.U. over the range shown in this plate.

The broad bands with the centers near λ5125 and λ5800 show most marked changes. In each case the most marked change is almost entirely toward the red end of the spectrum, the violet edge of the band remaining almost unchanged. This is the case especially with the λ5800 band.

The concentration of the solution used in *B*, plate 3, was one-tenth saturated, the depth of the cell being 10 cm. The temperatures, beginning next to the numbered scale, were 20°, 45°, 70°, 95°, 120°, and 145°.

Although the total number of absorbers in *B* are the same as in *A*, yet it is seen that the change in the bands is far greater in *A*, *i. e.*, where the concentration is greatest. Only the λ5800 band shows appreciable change in *B*, and even this does not widen more than 40 A.U.

The concentration of the solution used in making the negatives of *A*, plate 4, was one-tenth of saturation, the depth of absorbing layer 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140°, 165°, and 190°.

Aside from the slight tendency of all the absorption bands to become a little more diffuse at the higher temperatures, though not more intense, there is no marked change in any band except λ4275 and λ5800. The former of these, as we go toward the higher temperatures, remains perfectly sharp and constant on its violet edge, while there is a regular shading toward the red end of the spectrum. Again, the greatest change takes place in band λ5800, the violet end remaining fixed and the red edge widening between the first and last strips to the extent of about 50 A.U. All the exposures of this plate were made as the temperature of the cell was raised.

The identical solution used in *A* was photographed in *B*, plate 4, the cell, intensity of light-source, and all of the apparatus remaining unchanged, the only difference being that the exposures of *B* were made at regular intervals as the temperature of the cell was *lowered*. The temperatures of the successive strips in *B* were, beginning with the strip nearest the numbered scale, 190°, 165°, 140°, 115°, 95°, 70°, 45°, 20°.

The original films show *A* and *B* to be exactly the reverse of each other. Just those changes produced in *A* by a rise in temperature are reversed by the corresponding fall of temperature in *B*. Of course this is only qualitative, since we can establish no definite quantitative relations from the photographic plates. In order to do this, energy measurements must be made, not only on each band, but on different parts of the same band. Such work is now in progress. This would be very difficult to do with a narrow band like λ4275, but should be comparatively simple with band λ5800.

Band λ4275, which in strip 1 appears broad and hazy on its red edge, gradually acquires the characteristic sharp intense edges as the temperature falls, until in strip 8 it is only about 8 A.U. wide. The total change in band λ5800 is a narrowing of about 60 A.U. There is no sudden or decided change between any two successive strips, but, on the contrary, so far as the photographic plate is able to show, the change is a gradual one.

NEODYMIUM ACETATE IN WATER. (SEE PLATES 5 AND 6.)

In plate 5 we have photographed the change in the absorption bands of neodymium acetate, produced by rise in temperature, section *A*, and by the corresponding lowering of temperature, section *B*. The concentration of the solution used for both negatives was one-tenth of saturation; the depth of absorbing layer was 10 cm.

The temperatures of the strips in *A*, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 120°, 140°, 160°, 190°. This negative shows changes in bands λ4275 and λ5800; the former, as in the other plates on the study of the effect of temperature, shows a marked shading towards the red, while the remainder of this band virtually remains fixed. The λ5800 band widens rapidly toward the red, as the temperature is raised, the total amount being about 80 A.U. All the absorption bands with the acetate are more intense and broader than for the same concentration of any of the other salts of neodymium studied. The acetate is not nearly so soluble as the other salts, nor is the dissociation so great, yet we find in *A*, which is the spectrogram of a one-tenth saturated solution of neodymium acetate, greater changes than for the saturated solution of the chloride. This is in accord with the results obtained from the effect of dilution; this, it will be seen, was greatest with the acetate. This tends to strengthen the view that the bands λ4275 and λ5800 are in some way associated with the molecules.

In *B* of this plate there is given the spectrogram of the same solution as the temperature was lowered. The temperatures, beginning with the strip nearest the spark spectrum, were 190°, 165°, 145°, 125°, 100°, 75°, 50°, 25°; the cell and arrangement of apparatus were the same as in *A*. The negative shows changes the reverse of those discussed in section *A*. The λ4275 band gradually assumes the sharply defined edges as the temperature falls, and strip 8 of *B* corresponds exactly to strip 1 of *A*. In a word, there has been no permanent change produced by heating the solution. This change in the width of the absorption bands could not have been produced by any substance dissolved from any parts of the apparatus, as there is no reason to suppose that this should disappear as the solution was cooled. It seems, then, that the broadening is solely a temperature phenomenon.

Plate 6 was made to show the relative effect of rise in temperature on a solution of neodymium acetate, as compared with the same concentration of neodymium chloride. The concentration in each case was one-tenth saturation, the cell depth being 10 cm. The temperatures in *A* (neodymium acetate), beginning with the strip nearest the numbered scale, were 20°, 40°, 60°, 80°, 100°, and 125°, respectively. The temperatures in *B* (neodymium chloride), reading in the same order from the strip nearest the spark lines, were 15°, 40°, 65°, 90°, 115°, 140°, 165°, and 190°, respectively. A comparison of the two sections of this plate shows, first, that for the same concentrations of the two salts the absorption bands are wider and more pronounced with the acetate than with the chloride.

In each of these plates only the λ4275 and λ5800 bands show appreciable change with rise in temperature. While the percentage change in the former of these two bands is perhaps greater, this shows very poorly on the prints from the original films. The λ4275 band is very sharp at the lower temperatures, but shades rapidly towards the red as the temperature is raised, the λ5800 band, which is most affected by temperature changes, showing decidedly more widening with the acetate than with the chloride. This is exactly what we should expect if this band were associated with the undissociated molecules of the salt in question. The acetate, being a salt of a very weak acid, is dissociated considerably less than the chloride, and consequently the change is greater in the case of the acetate where there are present a larger number of molecules.

The facts, then, are: The number of molecules in a given concentration of neodymium acetate is greater than in the corresponding concentration of neodymium chloride. Hydration decreases with rise in temperature. The band λ5800 is more marked in the acetate than in the chloride, and widening with rise in temperature indicates that it is in some way associated with the hydrated molecules.

NEODYMIUM SULPHATE IN WATER AND COBALT CHLORIDE IN WATER.

(See Plate 7.)

On account of the slight solubility of neodymium sulphate in water, only the saturated solution was studied. The depth of cell was 10 cm. and the temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 75°, 90°, 115°, and 140°, respectively.

It is seen that the first four strips of *A* (neodymium sulphate) show the regular widening of λ4275 and λ5800. In strips 5 and 6 all of the bands decrease in width. This is especially noticeable in bands λ5800, λ5100, and λ5225. This is no doubt due to the fact that some of the salt crystallized out at this temperature, and the solution consequently became more dilute. When the cell was opened it was found that nearly all of the salt had crystallized out.

It is, however, obvious that the sulphate presents no exception to the general rule that the bands widen with rise in temperature. This is certainly true up to 115°, at which temperature the crystals form rapidly, and the effect of increase in dilution more than overcomes the counter effect of rise in temperature.

B is the spectrogram of a solution of cobalt chloride, 1 cm. deep and 0.25 normal. The temperatures, beginning with the strip nearest the numbered scale, were 12°, 32°, 52°, 76°, 92°, 112°, 132°, and 152°. This plate shows an intense absorption in the violet up to λ3600; also a broad, hazy band with its center near λ5100. On account of the haziness of the cobalt bands, it is difficult to discuss them in detail. The change produced by rise in temperature, however, is very slight. The cobalt salt was hydrolyzed very greatly at the higher temperatures, and this also interfered with the study of its absorption.

PRASEODYMIUM CHLORIDE IN WATER. (See Plate 8.)

A represents the effect of rise in temperature on the absorption spectra of a 2.56 normal solution of praseodymium chloride, the depth of cell being 1 cm. The temperatures, beginning with the strip nearest to the numbered scale, were 20°, 50°, 80°, 100°, 120°, 140°, and 160°, respectively. The original film shows general transmission from λ3400 to λ4350, with the sharply defined absorption band extending from λ4300 to λ4750. There is faint transmission near λ4550. There is practically no change in either edge of this band as the temperature of the solution is raised. There is a slight widening of that band whose center is near λ4825. The λ5900 band changes less than 25 A.U. over the entire range of temperature studied.

B is the absorption of a solution of the same salt, having a concentration of 0.256 normal and a depth of layer of 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 40°, 65°, 90°, 115°, 140°, 165°, and 190°, respectively. There are well-defined bands having their centers near λ4425, λ4650, λ4820, and λ5900. None of these bands shows any appreciable change with rise in temperature.

PRASEODYMIUM NITRATE IN WATER. (See Plate 9.)

The concentration of the solution used in making *A* was 2.6 normal; the depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 12°, 32°, 52°, 72°, 92°, 112°, 125°, and 145°, respectively.

In the ultra-violet the absorption extends to about λ3500 in strip 1, but rapidly increases as the temperature is raised, until in strip 8 there is complete absorption as far as λ3800.

There is a very intense double absorption band from λ4350 to λ4725 with faint transmission near λ4540. This transmission rapidly decreases as the temperature is raised, and entirely disappears at a temperature slightly above 100°. The λ4650 band widens towards the red end about 25 A.U. Band λ4825 shows a total widening of about 30 A.U. over the range of temperature studied. The orange band near λ5900 shows a uniform total widening of about 25 A.U. From this plate it is seen that none of the praseodymium bands shows very marked change with rise in temperature; at this concentration all of them become slightly wider at the higher temperatures.

In section *B* of this plate is given the spectrogram of a 0.26 normal solution of the same salt, the depth of the absorbing layer being 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 135°, and 165°, respectively. On this plate, bands appear which have their centers near λ4425, λ4650, λ4825, and λ5900; the ultra-violet absorption bands near λ3500. None of these bands shows any appreciable change over the range from 20° to 165°.

The plate which was used to study the effect of dilution upon this same salt reveals the fact that only in the most concentrated solutions were the bands affected at all, while in the dilute solutions all the bands remained unchanged. Plate 9 shows that temperature also has a slight effect only in the concentrated solutions, while in the dilute solutions the bands remain unchanged. In a word, rise in temperature and decrease in dilution produce the same effect upon solutions of praseodymium nitrate.

URANYL NITRATE IN WATER. (See Plate 10.)

The concentration of the solution used in making *A* was 0.2 normal, the depth of layer being 1 cm. The temperatures, beginning with the strip nearest the spark spectrum, were 20°, 40°, 60°, 80°, 100°, and 120°, respectively. In every strip the exposure to the entire spectrum was made for 30 seconds, a screen cutting off all wave-lengths beyond λ4500 was inserted, and the ultra-violet end exposed an additional 8 minutes.

Since all the uranyl bands occur in the violet and ultra-violet end of the spectrum, where general absorption is greatest, due to precipitates formed by heating the solutions, etc., it was found very difficult to obtain satisfactory results. So far as this plate shows, there is no decided change in any particular band. The entire series seems to widen as the temperature is raised, and at the same time the center of the band is slightly shifted toward the red end of the spectrum. The general absorption, ending near λ3500 in strip 1, advances rapidly towards the red as the temperature is raised. The broad diffuse edges of all the bands shade uniformly into each other, until at the highest temperature they appear as one broad, hazy absorption band, extending from λ3800 to λ4300. At least a part of this is due to general absorption.

In section *B* is given the absorption of a 0.02 normal solution of uranyl nitrate, the depth of absorbing layer being 10 cm. The red end of the spectrum, beyond λ4500, was exposed 8 seconds, while the ultra-violet below λ4500 had an exposure of 3½ minutes to the same source of light. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140°, and 165°, respectively. Eleven bands occur between λ3500 and λ4600. As the temperature is raised, all the bands become more diffuse and broader; the band whose center is near λ4180 seems to be most affected. The red edge of the band shades towards the red end of the spectrum as much as 25 A.U. The effect produced on this band by elevated temperatures is more marked than in any of the other bands. There is very broad and hazy absorption around λ5100, λ5600, and λ6200. This increases with rise in temperature.

It has been found very difficult to give an exact description of what takes place in any uranyl band as the temperature is raised, since the edges of the bands are so hazy and the general absorption so marked in the region of the spectrum at which these bands occur. Only the general statement can be made that all uranyl bands become more diffuse with rise in temperature, and in the band λ4165 there is a decided shading on the red edge.

URANYL SULPHATE IN WATER. (See Plate 11.)

The concentration of the solution used in making *A* was 0.166 normal and the depth of cell 1 cm. The respective temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 90°, 115°, 135°, 155°, and 185°. The part of the spectrogram above λ4550 was exposed 40 seconds, while below that wave-length the exposure was 10 minutes. The apparent band extending entirely across the spectrogram near λ4550 is the edge of the screen used in making the long exposure on the violet end of the spectrogram and must not be confused with an absorption band.

Absorption bands λ4175 and λ4325 have their centers shifted towards the red end of the spectrum about 25 A.U. The red edges of bands λ4325 and λ4550 shade rapidly towards the red. The well-marked band λ4750 remains unchanged throughout the spectrogram.

The encroachment of the general absorption in the ultra-violet towards the red causes band λ3625 to disappear above the fourth strip, while band λ3750 is scarcely visible above strip 5. All bands below λ4500 become very diffuse as the temperature is raised, and at the highest temperature are hardly more than a single broad, hazy absorption band extending from λ4000 to λ4400.

Section *B* is the spectrum of a 0.02 normal solution of uranyl sulphate, the depth of absorbing layer being 10 cm. The respective temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140°, and 165°. The exposures were 8 seconds in the visible part of the spectrum and an additional exposure of 4 minutes to the ultra-violet. The same changes described in *A* take place here, *i. e.*, a strong general absorption in the ultra-violet beyond λ3500, and increasing towards the red as the temperature is raised. The most marked widening is in bands λ4100, λ4200 and λ4350; in each the center shifted slightly towards the red. Such is also the case with the red edge of band λ4600. The λ4750 band remains fixed throughout the spectrogram. The very broad, hazy bands around λ5100, λ5600, and λ6200 appear, and are not appreciably affected by changes in temperature.

URANYL ACETATE IN WATER. (SEE PLATE 12.)

In plate 12, *A* shows the effect of dilution, *B* of temperature. The concentrations of the solutions used in *A*, beginning with the strip farthest removed from the numbered scale, were 0.25, 0.125, 0.062, 0.042, 0.0025, and 0.0005 normal. So far as we can judge from this plate, none of the absorption bands changes. Beer's law seems to hold to the dilution 0.0005 normal.

B shows the effect of rise in temperature on a 0.02 normal solution of uranyl acetate. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, and 140°. The exposures at that part of the spectrum having a wave-length greater than λ4500 was 8 seconds, while an additional exposure of 3 minutes was given to the ultra-violet end. Every one of the nine bands shows a slight widening with rise in temperature. While in strip 1 the bands are well marked, they appear much more diffuse as the temperature is raised. The apparent change in the band near λ4475 is probably due to the screen used to cut off the visible spectrum, while additional exposure was made to the ultra-violet region.

CHAPTER III.

EFFECT OF DILUTION ON THE ABSORPTION OF LIGHT BY SOLUTIONS.

The question as to the effect of dilution on the power of solutions to absorb light is an old one. This question became especially prominent at the time the theory of electrolytic dissociation was proposed. In dilute solutions of electrolytes there are practically only ions present, very few molecules existing as such. All of the properties of such solutions are the properties of the ions contained in them. Therefore, the power of these solutions to absorb light must be due to the ions present in them. This was the reasoning in vogue and the conclusion drawn. It was at the same time freely recognized that molecules in solution have the power to absorb light. This was shown by the fact that solutions of non-electrolytes, or completely unionized substances, are often colored; and color in solution means selective absorption of light.

The result of the conclusion drawn from the theory of electrolytic dissociation was that an enormous amount of work was done on the absorption spectra of dilute solutions of both electrolytes and non-electrolytes. Ostwald carried out an elaborate investigation on the relation between color and dissociation, and published the work under the title "Über die Farbe der Ionen."[1] A large number of salts were brought within the scope of this investigation—salts of an acid having a colored anion, with colorless cations, This is illustrated by the various permanganates, hydrogen, sodium, ammonium, magnesium, zinc, cadmium, etc. Ostwald showed that these salts of any given acid had essentially the same spectra. In a similar manner, he studied salts of fluorescein, eosin, iodoeosin, rosolic acid, diazoresorcinol, etc. Ostwald then reversed the process and compared the salts of a given colored base with colorless acids, thus studying the salts of *p*-rosaniline with acetic, chloric, benzoic, hydrochloric, nitric, butyric, salicylic, lactic, etc., acids and finding practically the same absorption spectra for all of these salts.

From the standpoint from which he undertook his investigation, Ostwald may be said to have solved the problem of the rôle of ions in the absorption of light, as far as that could be done with the prism spectroscope.

The problem that we studied was of a different nature. It had to do with the absorption spectra of ions relative to that of the molecules from which they were formed. Some earlier work of Jones and Anderson[2] had shown that if molecules have different action on light from ions, the difference is so slight that there would be no hope of detecting it by ordinary means, even with a grating spectroscope. This problem was attacked in the following manner:

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[1] Zeit. phys. Chem., **9**, 579 (1892).

[2] Carn. Inst. Wash. Pub. No. **110**.

MAKING A DILUTION SPECTROGRAM.

Before entering upon a detailed discussion of the spectrograms, it is wise to state briefly the method used in making any given spectrogram. Throughout all the work done on the effect of high dilution on absorption spectra, under the conditions of Beer's law, only three exposures were made for any given spectrogram, *i. e.*, only three dilutions were compared. The depths of cell in all cases were 0.5 cm., 50 cm., and 250 cm., the dilution being increased 100 times between the first two solutions and 5 times between the last two; or a total dilution of 500 times between the first and last solution. Smaller depths of cell than 5 mm. were not used, on account of the large percentage error in measuring such depths.

Much difficulty was experienced in getting sufficient light through the longer cells to fill the grating completely; nor was this possible unless the tube containing the solution was constantly moved backwards and forwards so that the image of the source of light was moved along the slit of the camera. By such a procedure the surface of the grating could be illuminated fairly uniformily, and the exposures gave good results on the photographic plate, as is shown by the spectrograms.

In order to insure complete illumination of the grating a uniform procedure was adopted. The longest cell, containing the most dilute solution, was first placed in position, the light passed through, and the image of the Nernst glower sharply focused on the slit of the camera in such a manner as to throw as much light as possible on the grating. By holding the eye in the position later to be occupied by the photographic plate, we could easily tell when the grating was properly illuminated.

After everything was properly adjusted the lights were extinguished and the plate inserted in the camera. Great care was taken not to move any parts of the apparatus, the camera was closed, the source of light again turned on, and the exposure made. It is clearly seen that in making any spectrogram, using three cells differing in length so markedly, we virtually had three different sources of light, and, consequently, the length of exposure sufficient to give comparable results on the photographic plate had to be determined by a long series of trials. In the case of the longest cell, exposures as long as several minutes were made, while with the shortest cell only a few seconds were necessary to give good clear spectrograms on the photographic plate.

The remaining procedure was essentially the same as that described by Jones and Anderson[1] and by other workers in this laboratory.

NEODYMIUM CHLORIDE IN WATER. (SEE PLATE 13.)

The concentrations of the solutions used in making the negative for *A*, beginning with the one whose spectrum is farthest from the spark spectrum, were 2.05, 0.0205, and 0.00401 normal, respectively, the corresponding depths of absorbing layer being 0.5 cm., 50 cm., and 250 cm.

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[1] Carn. Inst. Wash. Pub. 110.

For *B* the concentrations used were 1.025, 0.01025, and 0.00205 normal. The depths of layer were the same as used in *A*. It is seen that the dilutions are just one-half those of the corresponding layers in *A*.

The concentrations of solutions used in making *C* were just half of those in *B*, *i. e.*, 0.512, 0.00512, and 0.00102 normal. In the entire plate, as in all the dilution work, the most dilute solution is always nearest the spark spectrum.

Since very much of the finer detail and several of the narrowest bands are lost in reproducing and printing the films, our discussion is always based upon the original photographic film. Lines will frequently be discussed which do not appear on the printed plates, but which are very clear and distinct on the photographic film.

A study of *A* shows complete absorption in the violet up to λ3350, then slight transmission for about 50 A.U. The faint hazy band λ3400 and the well-defined band λ3450–λ3600 are not affected by the change in dilution. Hazy bands appear at λ3820, λ4040, and λ4200. Their intensities do not seem to be affected by dilution. The beautiful sharp band λ4275 is slightly more intense in the most concentrated solution. The effect of dilution, if any, on the bands λ4325, λ4440, λ4600, λ4690, λ4750, λ4820 is not measurable. On the original film they appear slightly broader, but not more intense, on the third strip.

Bands which have their centers near λ5100, λ5200, and λ5800 are decidedly affected by dilution, the former two appearing distinctly as independent bands in the most dilute solution, diffuse with a single broad band with the center near λ5150. There is the greatest change between the second and third strips (in discussing any plate, strip 1 is always nearest the spark lines). The broadening of these bands with increase in concentration, both of which have rather hazy edges, is fairly uniform, *i. e.*, they widen both towards the red and violet ends of the spectrum.

The intense band which extends from λ5690 to λ5850 is affected very markedly by concentration, the widening being almost entirely towards the red end of the spectrum. The violet edge is hardly affected, while the widening towards the red is about 50 A.U. Here also the change in the width of the band is greatest where the change in concentration of the solution is greatest. There is a very faint band, λ6225, which appears slightly more diffuse in the most concentrated solution.

The concentrations of the solutions used in *B* are just one-half those of *A*, and it is seen that some of the smaller bands are lost, while the broader ones have split into two or more smaller bands. In this film, bands near λ3425, λ3475, λ3520, λ3575, λ4275, λ4340, λ4450, λ4700, λ4750, λ4820, λ5100, λ5120, show no change with dilution. The broad band λ5700–λ5825 shows a widening of about 25 A.U., being the only band which is changed by concentration.

C of this plate is the spectrogram of solutions twice as dilute as those of *B*. No band on this plate shows any appreciable change produced by dilution, except probably a slight widening of λ5750.

We then see, from a study of this plate, that in *A* bands λ4270, λ5100, λ5200, and λ5750 narrow with dilution, the amount of change being in the order given; that is, least in λ5100 and greatest in λ5700. In *B* there is an appreciable change in only λ5750, while in *C* none of the bands are affected by dilution.

NEODYMIUM BROMIDE IN WATER. (SEE PLATE 14.)

The concentrations of the solutions used in making negative *A*, beginning with the solution whose spectrum is farthest from the scale, were 1.66, 0.0166, and 0.0033 normal; the corresponding depths of absorption layer being 0.5 cm., 50 cm., and 250 cm., respectively.

The concentrations used in making *B* were half of those of *A*, and those of *C* half those of *B*. The same range of cell depth was used in all three sections of this plate, viz, 0.5 cm., 50 cm., and 250 cm., respectively, beginning with the strip farthest from the spark lines. In *A*, characteristic absorption bands appear at λ3400, λ3525, λ3800, λ4275, λ4450, λ4700, λ4750, λ4800, which are hardly affected by change in dilution, except for a slight increase in the intensity of band λ4275 in the most concentrated solution.

The three bands, λ5090, λ5120, and λ5210, narrow uniformly with dilution, the greatest change being between strips 2 and 3, where the change in dilution is the greatest. With the bromide, as is seen in plate 14, the effect of dilution is most pronounced in band λ5750. The shading is almost exclusively towards the red, the violet edge remaining practically unchanged. This edge shows no change between strips 1 and 2, yet the red edge is widened as much as 30 A.U.

In *B*, where the concentrations were 0.83, 0.0083, and 0.00166 normal, respectively, the depths of absorbing layer were the same as used in *A*. There is no measurable change in any of the absorption bands except the band whose center is near λ4800. This band shows the characteristic narrowing with dilution, as the dilution is increased. The total change is not greater than 20 A.U. Band λ5200 is slightly more intense in the third strip.

When we reach the dilution used in *C*, which is four times that of *A*, any change due to dilution has disappeared except a narrowing of probably 10 A.U. between the third and second strips.

Taking plate 14 as a whole we see, first, the narrowing due to increased dilution is most marked in *A*, less in *B*, and least in *C*. This is seen to be the same order as their respective concentrations. Considering an individual section, we find the most pronounced narrowing where the change in dilution is greatest—that is, between strips 2 and 3.

NEODYMIUM NITRATE IN WATER. (SEE PLATE 15.)

The concentrations of neodymium nitrate used in making negative *A* of this plate, beginning with the strip farthest from the numbered scale, were 2.15, 0.0215, and 0.00430 normal, the corresponding depths of absorbing layer being 0.5 cm., 50 cm., and 250 cm., respectively.

In discussing the absorption bands of this, as well as other plates throughout this paper, we do not attempt to give the exact position of the band in question, as has previously been done by many workers; but we simply indicate the position of the band by selecting a wave-length near its center. For instance, in speaking of band λ5800, we mean that broad band extending from λ5700 to λ5850. This is not confusing and saves space and time in the description of any plate.

This is probably the best plate we have illustrating the effect caused by dilution. Bands which are hardly affected over the range of dilution given in *A* are located at λ3525, λ3820, λ4440, λ4620, λ4750, λ4830. In strip 3 the well-defined band λ4275 is more diffuse, though probably not so intense. This is in keeping with the behavior of this same band as shown by other salts of neodymium, though probably a little more marked. There is faint transmission at λ5100 for about 10 A.U. In strip 3, representing the most concentrated solution, the bands λ5090 and λ5125 have so broadened that they coalesce. The λ5220 band widens uniformly towards the red and violet as the solution becomes more concentrated.

Band λ5800, which is most affected by dilution, shows a total change of probably as much as 70 A.U.. the shading being largely towards the red. In strips 1 and 2 the violet edge is hardly changed, while in strip 3 it is probably shifted 20 A.U. On the original film these three strips show absolutely the same development, hence are directly comparable.

Section *B* represents the absorption of neodymium nitrate. Beginning with the strip farthest from the numbered scale, the concentrations are 1.075, 0.01075, and 0.00215 normal, the corresponding depths of cell being the same as in *A*. In this section only a few bands need be discussed. Bands λ5090 and λ5125, which appear as distinct bands in strips 1 and 2, have slightly broadened so as to form a single hazy band whose center is near λ5120. The λ5750 band narrows as much as 40 A.U., almost the entire change being between strips 2 and 3.

In *C*, the λ5750 band alone is noticeably changed, narrowing about 20 A.U. from strip 3 to strip 2, but is not changed in the last dilution, *i. e.*, from strips 2 to 1.

NEODYMIUM SULPHATE IN WATER. (SEE PLATE 16.)

A gives the absorption spectra of a solution of neodymium acetate. The concentrations of the solutions used, beginning with the strip farthest removed from the numbered scale, were 0.5, 0.01, and 0.002 normal. The corresponding depths of cell were 1, 50, and 250 cm.

This additional plate of neodymium acetate was made to study the effect of exposure on the apparent widening of the bands with concentration. Strip 2 was more exposed than strip 1, and strip 3 had a longer exposure than strip 2. Nevertheless the λ5800 band has widened as much as 50 A.U. between the first and third exposures. In view of the unequal exposures of these strips, it is not thought advisable to discuss the other bands. These results show that difference in exposure can not account for the changes in the widths of the bands in question.

Spectrograms *B* and *C* of this plate give the absorption of solutions of neodymium sulphate. On account of the slight solubility of this salt, we observe only slight changes in any of its absorption bands.

The concentrations in *B* were 0.1, 0.004, and 0.0008 normal; the corresponding depths of cell being 2, 50, and 250 cm. The concentrations in *C* were 0.1, 0.001, and 0.0002 normal, and the corresponding depths of cell were 0.5, 50, and 250 cm.

In both *B* and *C*, those bands having their center near λ3500 appear well defined and remain unchanged both in position and intensity as the dilution is changed. The band λ5750 widens with concentration in *A* as much as 25 A.U.; it remains practically unchanged in *B*, where the solutions are more dilute.

The plate brings out the fact already mentioned, that only the more concentrated solutions show marked change, either with change in temperature or with change in dilution.

NEODYMIUM ACETATE IN WATER. (SEE PLATE 17.)

The concentrations of solutions used in making *A* of this plate were saturated, one-hundredth saturated, and five-hundredth saturated, the corresponding depths of cell being 0.5 cm., 50 cm., and 250 cm., respectively. The most dilute solution is nearest the numbered scale.

This plate was made with very long exposures, to see if the apparent widening of the bands could be due to the difference in the amounts of light falling upon the photographic plate. In such a procedure the most concentrated solution was given the longest exposure and yet had the broader bands. It is possible to narrow any given absorption band by lengthening the time of exposure, but this can not account for so large a difference as is shown by strip 3 of section *A*. Even in this section it is seen that the third strip has wider bands than either of the other two strips of this section, notwithstanding the fact that the actual exposure of the strip is greater. Thus we see that the difference of exposure can not account for the changes in the width of bands such as we have noted.

In section *A* the violet group of bands in the region λ3500 came out beautifully. Such is only the case when quite a long exposure is made. Indeed, in order to show these lines clearly, the exposure must be long enough to destroy those fine, sharp lines in the region of λ3800 to λ4600. Hence, in this plate the latter group of lines do not appear distinctly, though traces of them can be seen on the original film.

The hazy bands λ3300 and λ3400 appear on this plate and remain unchanged by dilution.

The three bands, λ3460, λ3500 and λ3540, remain perfectly constant throughout the section. Band λ5120, which appears broad and diffuse, shows no change. Band λ5210 narrows about 10 A.U. from the third to the second strip, and remains unchanged with the next dilution. The broad band λ5750 narrows about 40 A.U. from the third to the second strips, and about 15 A.U. with the next dilution.

The concentrations used in *B* were again just half those in *A*, the most concentrated solution being one-half saturated, with succeeding dilutions of 100 and 5 times, respectively; the depths of cell, beginning with the strip farthest removed from the scale, were 0.5 cm., 50 cm. and 250 cm.

Again, only bands λ5220 and λ5750 are changed, but with the acetate the change extends farther with the more dilute solutions. In a word, the narrowing of the bands with dilution is more marked in *B* and *C* than in the case of the chloride, bromide, and nitrate. The group of bands near λ3500 is not altered with dilution.

The concentrations used in *C* are again half of those in *B*, and the corresponding depths of cell the same as used throughout this plate. Their respective sequence is the same. In this spectrogram only band λ5750 changes, and, indeed, this is the only salt of neodymium with which a change with dilution has been noted in so dilute a solution. This band narrows about 20 A.U.

Neodymium acetate, being the salt of a weak acid, is of course less dissociated at any given concentration than a salt of a strong acid. This salt approaches complete dissociation much more slowly than the others studied. Spectrograms *A*, *B*, and *C* show also that the changes caused by dilution are more marked and extend into more dilute solutions than with the chloride, bromide, or nitrate. In a word, the changes in the absorption bands due to dilution seem to follow the change in dissociation; that is, they are a direct function of the number of molecules present.

PRASEODYMIUM CHLORIDE IN WATER. (See Plate 18.)

The concentrations of solutions used in making *A*, beginning with the strip farthest removed from the numbered scale, were 2.56, 0.0256, and 0.00512 normal, the corresponding depths of absorbing layer being 0.5 cm., 50 cm., and 250 cm., respectively.

The absorption is complete in the ultra-violet up to about λ3100. The bands of praseodymium are for the most part broad and have well-defined, sharp edges. The violet edge of band λ4450 is very sharp and unchanged by dilution, while the hazy red edge is hardly affected. Band λ4675 narrows towards the violet about 20 A.U., while band λ4830 is entirely unchanged. The broad band λ5900, with slightly hazy edges, shows a total narrowing of about 25 A.U.

The concentrations of *B* and *C*, beginning with the strips farthest from the numbered scale, are 1.28, 0.0128, and 0.00256 normal and 0.64, 0.0064, and 0.00128 normal, respectively. The corresponding depths of absorbing layer were the same as in *A*. None of the bands is affected by dilution, and we may say that Beer's law holds very well for praseodymium chloride, except for bands λ4675 and λ5900 in the most concentrated solutions. Even here the change is very slight and not to be compared with corresponding changes with dilution in salts of neodymium.

PRASEODYMIUM NITRATE IN WATER. (See Plate 19.)

The concentrations of the solutions used in *A*, beginning with the strip farthest removed from the numbered scale, were 2.6, 0.026, and 0.0052 normal; the corresponding depths of cell being 0.5, 50, and 250 cm.

The concentrations in *B* were just half of those in *A*, and those in *C* were half of those in *B*. None of the absorption bands shows any change with dilution in either *B* or *C*. In *A* there is a slight change in the λ4450 and λ4650 bands. Each of these bands widens about 20 A.U. with concentration over the range of concentration studied.

With praseodymium nitrate, as with the chloride previously discussed, there is only very slight change in the absorption with change in dilution.

URANYL CHLORIDE IN WATER. (See Plate 20.)

The concentrations of solutions used, beginning with the strip farthest removed from the numbered scale, were 1.363, 0.682, 0.341, 0.227, 0.01363, and 0.00272 normal; the corresponding depths of cell being 0.5, 1, 2, 3, 50, and 250 cm. In making this spectrogram, no additional exposure was made in the ultra-violet. The last four strips, one being nearest the numbered scale, were each exposed 30 seconds to the Nernst glower. The first two strips, on account of the length of cell used, had to be exposed a much longer time. In this, as in all other cases, the length of exposure was governed solely by the time required to give a clear print on the plate.

There is complete absorption of all the light having wave-lengths shorter than λ4500, well-defined bands with rather hazy edges appearing near λ4700 and λ4900. There is also rather diffuse absorption near λ5500 and λ6100. The two last-named bands are too ill-defined for detailed discussion.

The λ4700 band shows marked widening with increase in concentration, the change being greater towards the red end of the spectrum. The entire band is about 50 A.U. The λ4900 band shades off rapidly towards the red end of the spectrum, but not so much as the band λ4700. The greatest change is between strips 5 and 6, *i. e.*, where the change in dilution is greatest.

The concentrations in *B* were just half of those in *A*. Starting with the strip away from the scale, they were 0.685, 0.340, 0.170, 0.1135, 0.00685, and 0.00136 normal. The depths of the cell were the same as in *A*, 0.5, 1, 2, 3, 50, and 250 cm.

The changes produced by dilution, as shown in *B*, are much less marked than in *A*. Indeed, this would be expected, since the concentrations of the solutions were less. There is, however, a gradual widening of both λ4600 and λ4700 bands as the solution becomes more concentrated. The greatest change is in strips 5 and 6.

URANYL BROMIDE IN WATER. (See Plate 21.)

The concentrations of the solutions used in making *A*, beginning with the strip farthest removed from the numbered scale, were 1.365, 0.682, 0.341, 0.227, 0.01365, and 0.0027 normal; the corresponding depths of layer being 0.5, 1, 2, 3, 50, and 250 cm.

This spectrogram shows complete absorption in the violet to about λ4500, with a well-defined band near λ4700. The latter widens uniformly with increase in concentration. It is scarcely visible in strip 1, but becomes about 75 A.U. wide in the top strip. The most concentrated solution (strip 6) shows decidedly more absorption towards the red. The change in both of these bands is decidedly the most pronounced between strips 5 and 6, *i. e.*, where the percentage change in dilution is greatest.

B contains the absorption spectra of a series of solutions whose respective concentrations are just half of those in *A*, the corresponding depths of absorbing layer being the same as in *A*.

There is faint transmission near λ3800, with complete absorption of all of the wave-lengths from this region to λ4400. None of the bands shows any change with dilution. In a word, Beer's law seems to hold perfectly for these dilutions.

URANYL NITRATE IN WATER. (SEE PLATE 22.)

The concentrations of *A*, beginning with the strip farthest removed from the numbered scale, were 1.55, 0.775, 0.387, 0.269, 0.0155, and 0.0031 normal, the corresponding depths of cell being 0.5, 1, 2, 3, 50, and 250 cm.

In *B*, the concentrations were just half of those in *A*, the same depths of cell being employed. The negative of *A* shows the bands with special clearness.

In strip 1 there is complete absorption of the violet to λ4500. This gradually recedes towards the red, with increase in concentration amounting to as much as 100 A.U. The λ4700 band widens about 20 A.U. There is a sharp band, λ4878, which widens slightly with increase in concentration.

B shows faint transmission around λ3750, with broad, intense absorption to λ4350. Absorption bands, which are unchanged by change in dilution, appear at λ4550, λ4700, and λ4850. The only change in the bands on this plate is a slight encroachment on the red of the broad violet absorption in strip 6.

The results recorded on this plate are in complete accord with those of plates 20 and 21, which are the corresponding absorptions of uranyl chloride and uranyl bromide. *A*, in all three of these plates, represents the most concentrated solutions, while *B* represents half the concentrations in *A*. Most of the bands in *A* show well-marked widening with increase in the concentration, while in *B* the change is scarcely detectable.

DESCRIPTION OF PLATES.

Plate

1\. *A*. Neodymium Chloride in Aqueous Solution. Concentration, saturated. Depth of layer, 1 cm. Respective temperatures, 20°, 45°, 70°, 95°, 115°, 140°, and 165°, with lowest temperatures nearest spark lines. Exposures made on rising temperature.

B. The same solution used in *A*, with exposures made as cell cooled. Depth of layer and concentration the same as in *A*. Temperatures, 165°, 140°, 115°, 95°, 70°, respectively. Highest temperatures nearest spark lines.

2\. *A*. Neodymium Bromide in Aqueous Solution. Concentration, 1.66 normal. Depth of cell, 1 cm. Respective temperatures, 20°, 45°, 70°, 95°, 120°, 140°, 175°, 190°. Lowest temperature nearest spark spectra.

B. Neodymium Bromide in Aqueous Solution. Concentration, 0.166 normal. Depth of cell, 10 cm. Respective temperatures, 20°, 45°, 70°, 95°, 115°, 135°, 155°, and 190°. Highest temperature nearest spark spectra.

3\. *A*. Neodymium Nitrate in Water. Concentration saturated; depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 15°, 40°, 65°, 115°, 140°, and 165°, respectively.

B. Neodymium Nitrate in Water. Concentration, one-tenth saturation, depth of cell, 10 cm.; temperatures, 20°, 45°, 70°, 95°, 120°, and 145°, respectively. Lowest temperature nearest the numbered scale.

4\. *A*. Neodymium Nitrate in Aqueous Solution. Concentration, 0.1 saturated. Depth of layer, 10 cm. Temperatures, 20°, 45°, 70°, 95°, 115°, 140°, 165°, 190°. Exposures made as temperature was raised. Lowest temperature nearest spark lines.

B. The same solution of neodymium nitrate as used in *A*. Concentration and depth of layer identical with *A*. Temperatures, 190°, 165°, 140°, 115°, 95°, 70°, 45°, and 20°. Exposures made on falling temperatures. Highest temperatures nearest spark lines.

5\. *A*. Neodymium Acetate in Water. Concentration, 0.1 saturated. Depth of cell, 10 cm. Trace of acetic acid added to prevent precipitation. Temperatures, 20°, 45°, 70°, 95°, 120°, 140°, 160°, and 190°. Exposures made on rising temperature. Lowest temperature nearest spark line.

B. Solution, depth of cell and concentration the same as *A*. Temperatures, 190°, 165°, 145°, 125°, 100°, 75°, 50°, and 25°. Exposures made on falling temperatures.

6\. *A*. Neodymium Acetate in Water. Concentration, one-tenth saturation; depth of absorbing layer, 10 cm. The temperatures, beginning with strip nearest the numbered scale, were 20°, 40°, 60°, 80°, 100°, and 125°, respectively.

B. Neodymium Chloride in Water. Concentration one-tenth saturation; depth of cell, 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 15°, 40°, 65°, 90°, 115°, 140°, 165°, and 190°, respectively.

7\. *A*. Neodymium Sulphate in Water. Concentration was saturation, cell depth, 10 cm. Temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 75°, 90°, 115°, and 140°.

B. Cobalt Chloride in Water. Concentration, 0.25 normal; depth of cell 1 cm. Temperatures, 12°, 32°, 52°, 76°, 92°, 112°, 132°, and 152°, respectively. The lowest temperature was nearest the numbered scale.

8\. *A*. Praseodymium Chloride in Water. Concentration, 2.56 normal; depth of absorbing layer 1 cm. Temperatures, beginning with strip nearest the numbered scale, were 20°, 50°, 80°, 100°, 120°, 140°, and 160°, respectively.

B. Praseodymium chloride in water. Concentration, 0.256 normal; depth of cell, 10 cm. Beginning with the strip nearest numbered scale, the temperatures were 20°, 40°, 65°, 90°, 115°, 140°, 165°, and 190°, respectively.

9\. *A*. Praseodymium Nitrate in Water. Concentration, 2.6 normal. Cell depth, 1 cm. Temperatures, 12°, 32°, 52°, 72°, 92°, 112°, 125°, and 145°. Lowest temperature nearest spark lines.

B. Praseodymium Nitrate in Water. Concentration, 0.26 normal. Cell depth, 10 cm. Temperatures, 20°, 45°, 70°, 95°, 115°, 135°, and 165°. Lowest temperature nearest spark lines.

10. *A*. Uranyl Nitrate in Water. Concentration, 0.2 normal. Cell depth, 1 cm. Temperatures, starting with strip nearest spark lines, were 20°, 40°, 60°, 80°, 100°, and 120°, respectively.

B. Uranyl Nitrate in Water. Concentration, 0.02 normal. Depth of cell, 10 cm. Temperatures, starting with exposure nearest spark lines, were 20°, 45°, 70°, 95°, 115°, 140°, and 165°, respectively.

11. *A*. Uranyl Sulphate in Water. Concentration, 0.166 normal. Depth of cell, 1 cm. Temperatures, beginning nearest spark lines, 20°, 45°, 70°, 90°, 115°, 135°, 155°, and 185°, respectively.

B. Uranyl Sulphate in Water. Concentration, 0.02 normal. Cell depth, 10 cm. Respective temperatures, beginning nearest spark lines, were 20°, 45°, 70°, 95°, 115°, 140°, and 165°.

12. *A*. Uranyl Acetate in Water. The concentrations, beginning with the strip most removed from the numbered scale, were 0.25, 0.125, 0.062, 0.042, 0.0025, 0.0005 normal, respectively; the corresponding depths of absorbing layer were 0.5, 1, 2, 3, 50, and 250 cm.

B. Uranyl Acetate in Water. Concentration, 0.02 normal. Depth of cell, 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, and 140°, respectively.

13. *A*. Neodymium Chloride in Water. Concentrations, 2.05, 0.0205, and 0.00401 normal. Respective depths of cell, 0.5, 50, and 250 cm. Most dilute solution nearest spark lines.

B. Neodymium Chloride in Water. Concentrations, 1.025, 0.01025, and 0.00205 normal. Depths of cell, starting with strip farthest from spark lines, were 0.5, 50 and 250 cm., respectively.

C. Neodymium Chloride in Water. Concentrations, 0.512, 0.00512, and 0.00102 normal. Depths of cell, beginning with strip farthest removed from spark lines, were 0.5, 50, and 250 cm., respectively.

14. *A*. Neodymium Bromide in Water. Concentrations, 1.66, 0.0166, and 0.0033 normal. Corresponding depths of cell, 0.5, 50, and 250 cm., respectively. Most dilute solution nearest spark lines.

B. Neodymium Bromide in Water. Concentrations, 0.83, 0.0083, and 0.00166 normal. Corresponding depths of cell, 0.5, 50, and 250 cm., respectively. Most dilute solution nearest spark lines.

C. Neodymium Bromide in Water. Concentrations, 0.415, 0.00415, and 0.000803 normal. Corresponding depths of cell, 0.5, 50, and 250 cm., respectively.

15. *A*. Neodymium Nitrate in Water. Concentrations, 2.15, 0.0215, and 0.00430 normal, respectively. Corresponding depths of cell were 0.5, 50, and 250 cm., respectively. Most dilute solutions nearest spark lines.

B. Neodymium Nitrate in Water. Concentrations, 1.075, 0.01075, and 0.00215 normal. Corresponding cell depths were 0.5, 50, and 250 cm., respectively.

C. Neodymium Nitrate in Water. Concentrations, 0.537, 0.00537, and 0.00107. Corresponding depths of cell were 0.5, 50, and 250 cm., respectively. Most dilute solutions nearest spark lines.

16. *A*. Neodymium Acetate in Water. Concentrations, 0.5, 0.01, and 0.002 normal; the corresponding depths of absorbing layers being 0.1, 50, and 250 cm., respectively.

B. Neodymium Sulphate in Water. Concentrations 0.1, 0.004, and 0.0008 normal, the corresponding depths of cell being 2, 50, and 250 cm., respectively.

C. Neodymium Sulphate in Water. Concentrations, 0.1, 0.001, and 0.0002 normal. Depths of cell, 0.5, 50, and 250 cm., respectively. In each case, the most dilute solution is nearest the numbered scale.

17. *A*. Neodymium Acetate in Water. Concentrations, saturated, 0.01*s* and 0.002*s*, where *s* represents a saturated solution of the salt in water at 25°. Corresponding depths of cell were 0.5, 50, and 250 cm., respectively.

B. Neodymium Acetate in Water. Concentrations, 0.50*s*, 0.005*s*, and 0.001*s* (*s* being a saturated solution as above). Corresponding depths of cell were 0.5, 50, and 250 cm.

C. Neodymium Acetate in Water. Concentrations, 0.25*s*, 0.0025*s*, and 0.0005*s*. Corresponding depths of cell were 0.5, 50, and 250 cm., respectively.

18. *A*. Praseodymium Chloride in Water. Concentrations, 2.56, 0.0256, and 0.00512 normal, respectively. Corresponding depths of cell were 0.5, 50, and 250 cm.

B. Praseodymium Chloride in Water. Concentrations, 1.28, 0.0128, and 0.00256 normal. Corresponding depths of cell were 0.5, 50, and 250 cm., respectively.

C. Praseodymium Chloride in Water. Concentrations, 0.64, 0.0064, and 0.00128 normal. Corresponding depths of cell were 0.5, 50, and 250 cm., respectively.

19. *A*. Praseodymium Nitrate in Water. Concentrations, 2.6, 0.026, and 0.0052 normal, respectively. Corresponding depths of cell, 0.5, 50, and 250 cm., respectively; most dilute solution nearest numbered scale.

B. Praseodymium Nitrate in Water. Concentration, 1.3, 0.013, and 0.0026 normal; cell depths, 0.5, 50, and 250 cm., respectively.

C. Praseodymium Nitrate in Water. Concentration, 0.65, 0.0065, and 0.0013 normal; cell depths, 0.5, 50, and 250 cm. In each case the most dilute solution is nearest the numbered scale.

20. *A*. Uranyl Chloride in Water. Concentrations, 1.363, 0.682, 0.341, 0.227, 0.01363, and 0.00272 normal Depths of cell, 0.5, 1, 2, 3, 50, and 250 cm., respectively.

B. Uranyl Chloride in Water. Concentrations, 0.685, 0.340, 0.170, 0.1135, 0.00685 and 0.00136 normal, corresponding depths of absorbing layers being 0.5, 1, 2, 3. 50, and 250 cm. The most dilute solution in each case is nearest the numbered scale.

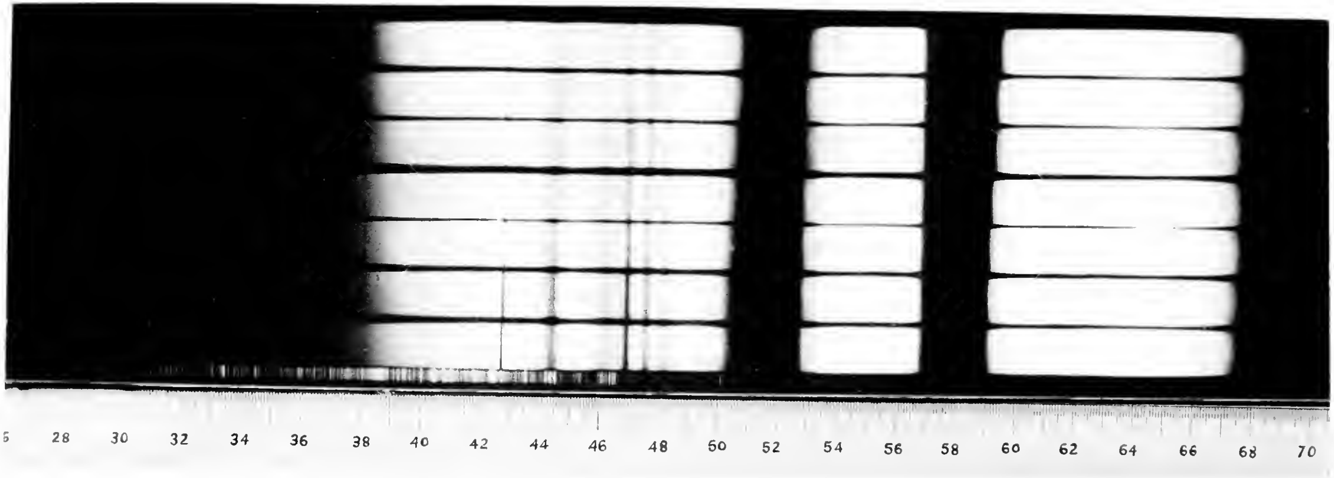
21. *A*. Uranyl Bromide in Water. Concentrations, 1.365, 0.682, 0.341, 0.227, 0.01365, and 0.00273 normal. Corresponding depths of cell, 0.5, 1, 2, 3, 50, and 250 cm. Most dilute solution nearest scale.

B. Uranyl Bromide in Water. Concentrations, 0.682, 0.341, 0.171, 0.113, 0.00682, and 0.00136 normal. Corresponding depths of cell, 0.5, 1, 2, 3, 50, and 250 cm.

22. *A*. Uranyl Nitrate in Water. Concentrations, 1.55, 0.775, 0.387, 0.269, 0.0155, and 0.0031 normal. Corresponding depths of cell, 0.5, 1, 2, 3, 50, and 250 cm., respectively.

B. Uranyl Nitrate in Water. Concentrations, 0.775, 0.387, 0.193, 0.134, 0.00775, and 0.0015 normal, respectively. Corresponding depths of cell, 0.5, 1, 2, 3, 50, and 250 cm., respectively.

PLATE I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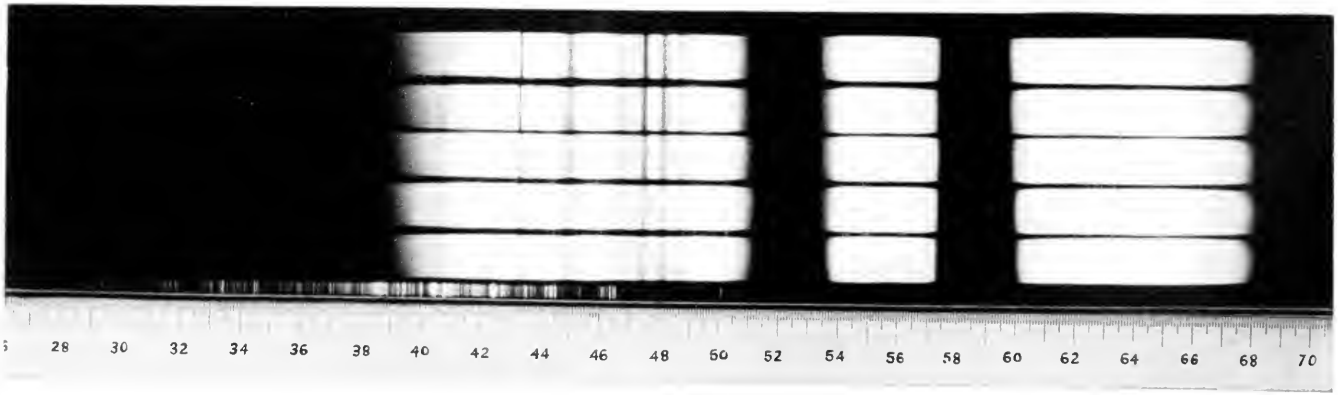
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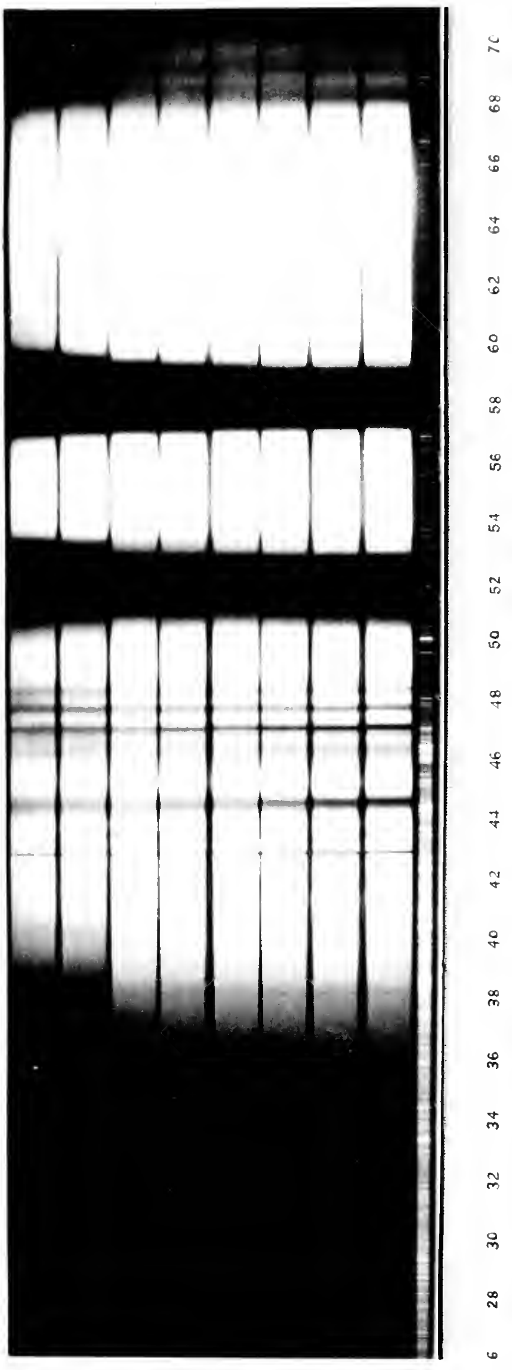
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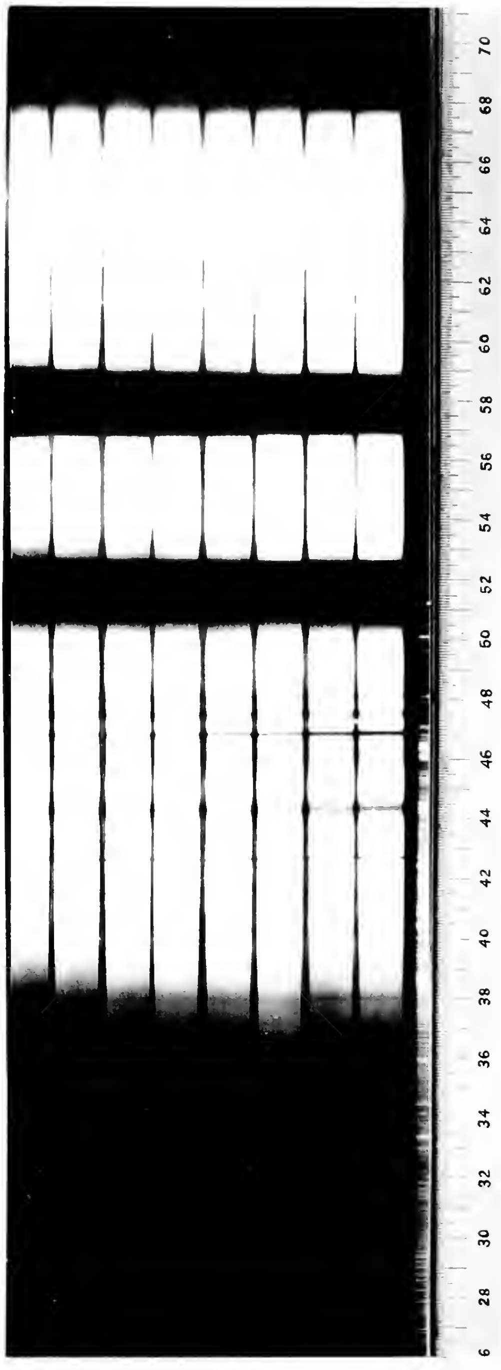
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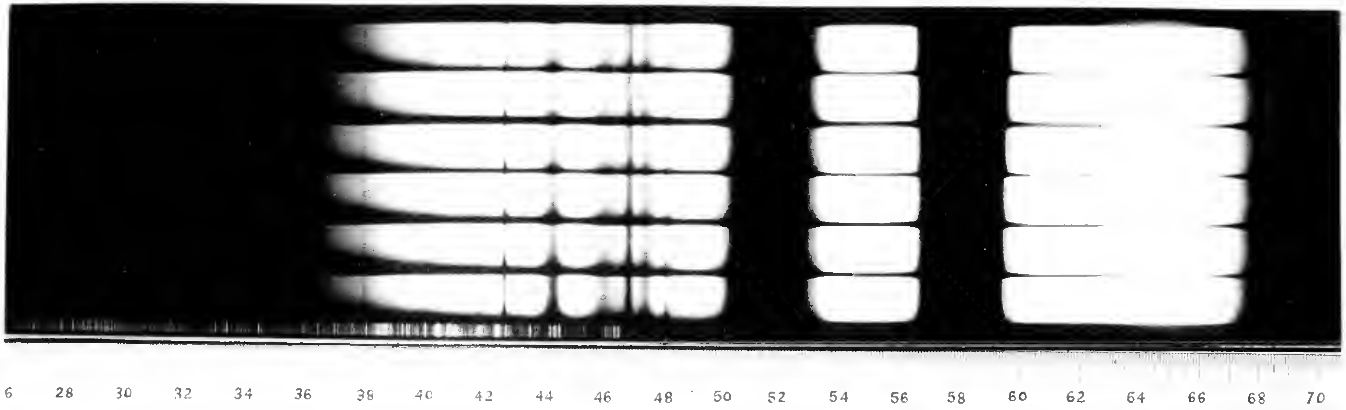
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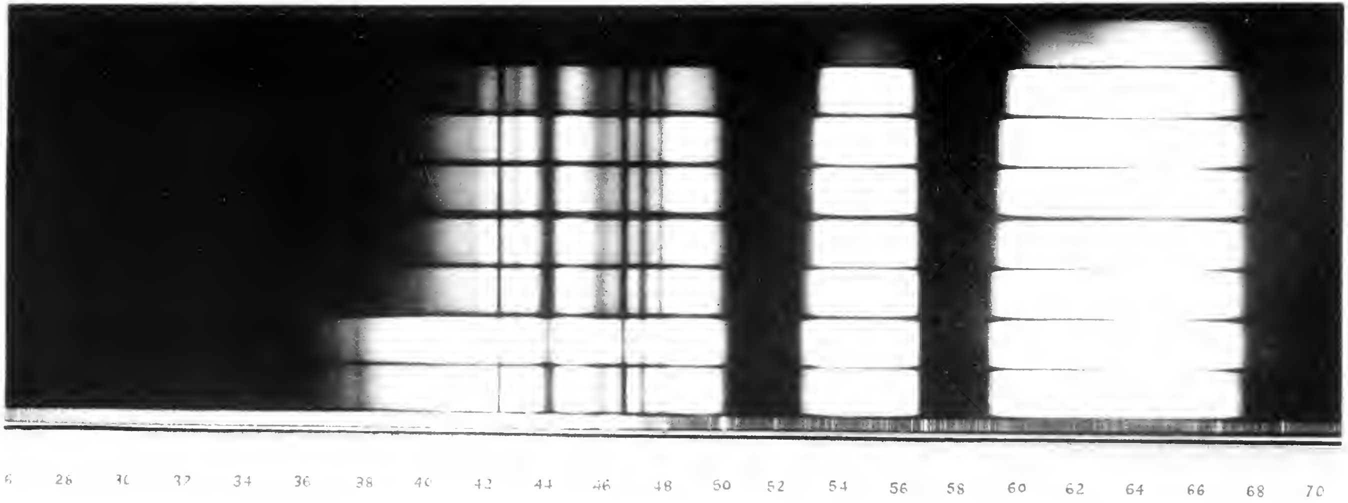
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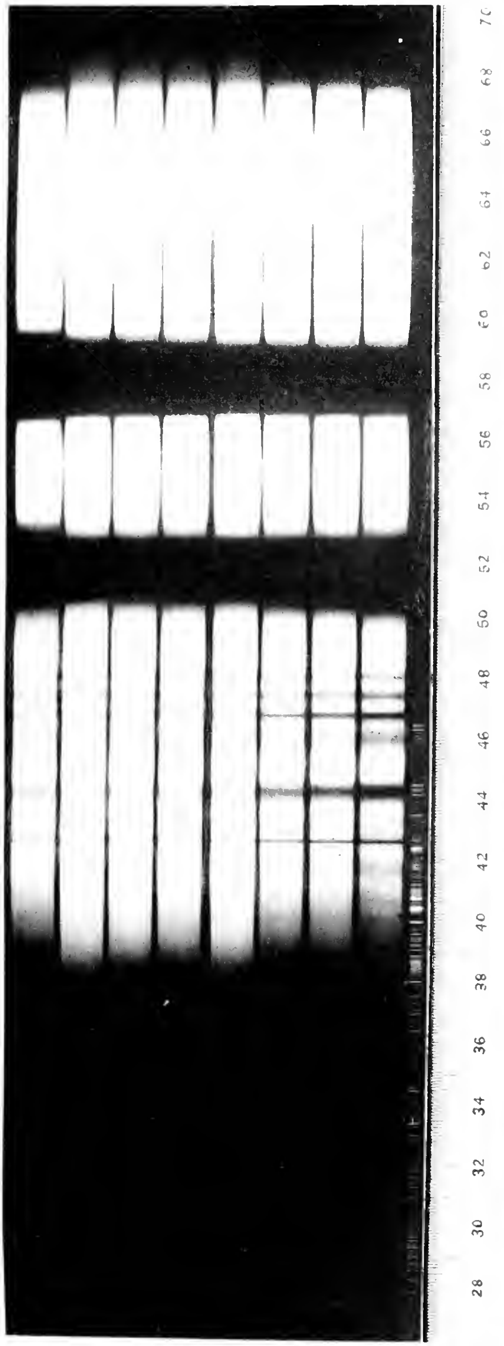
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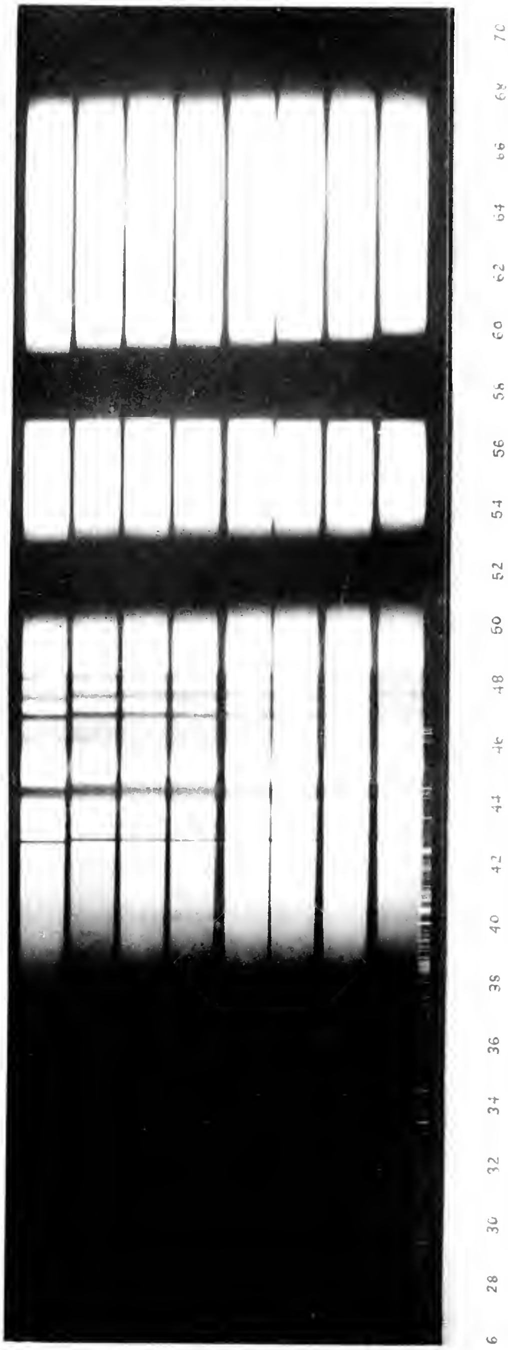
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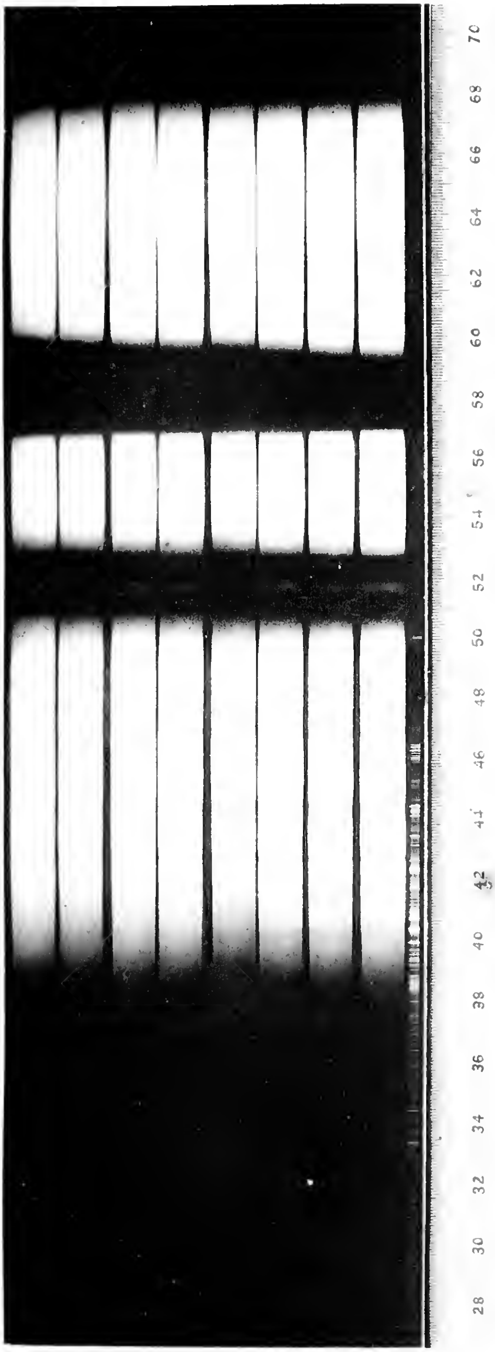

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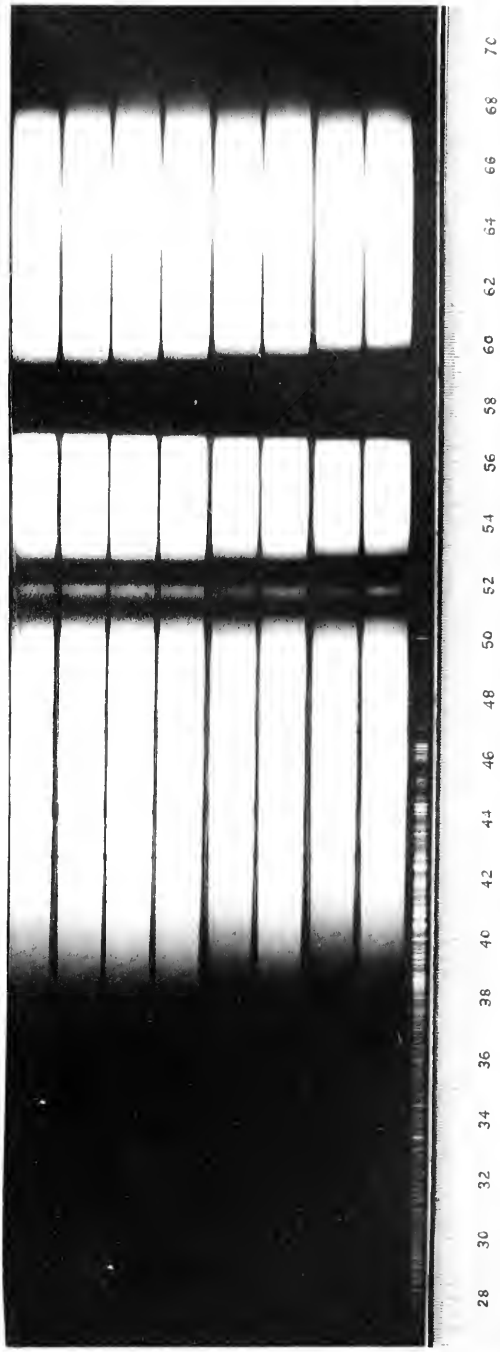

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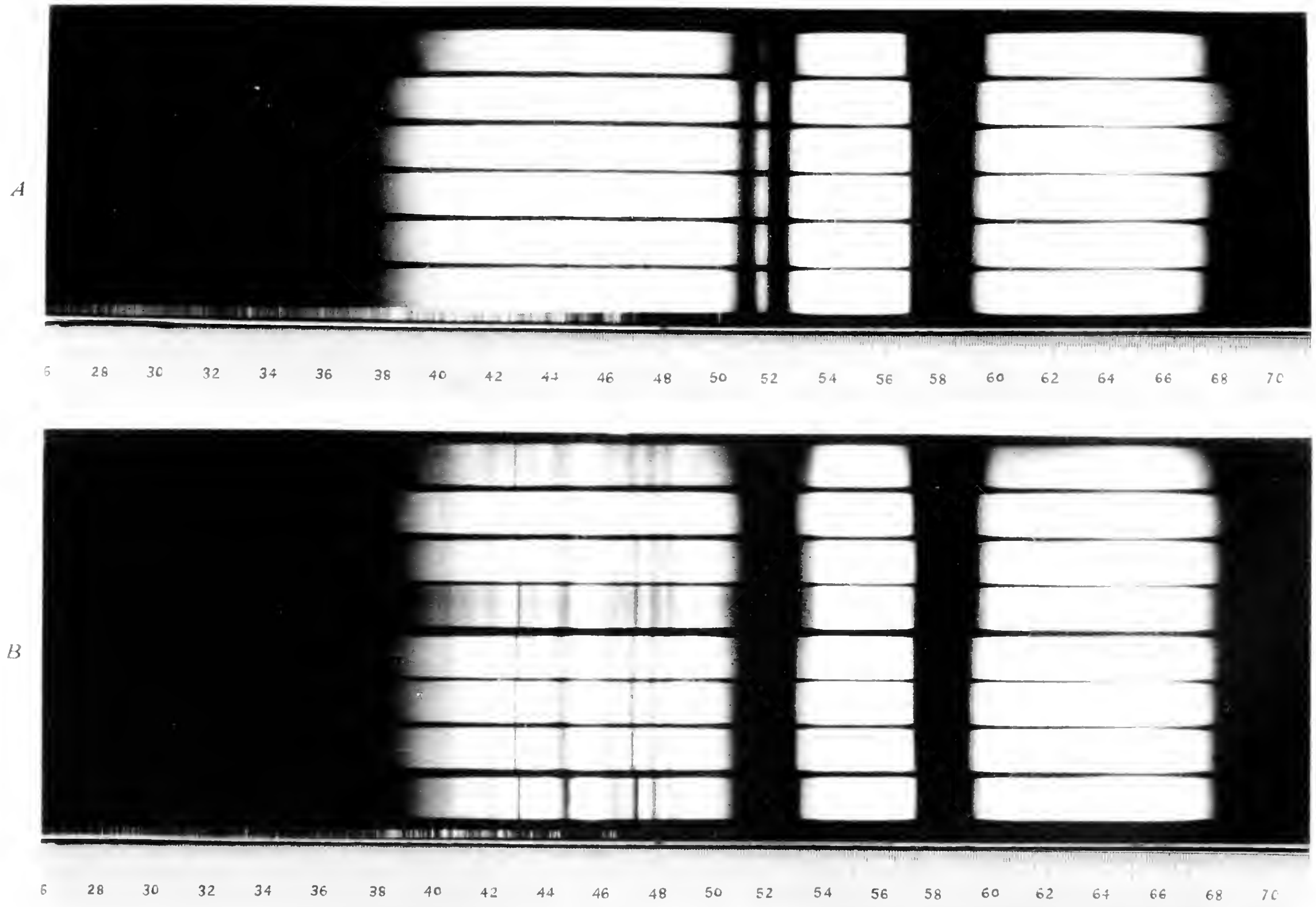
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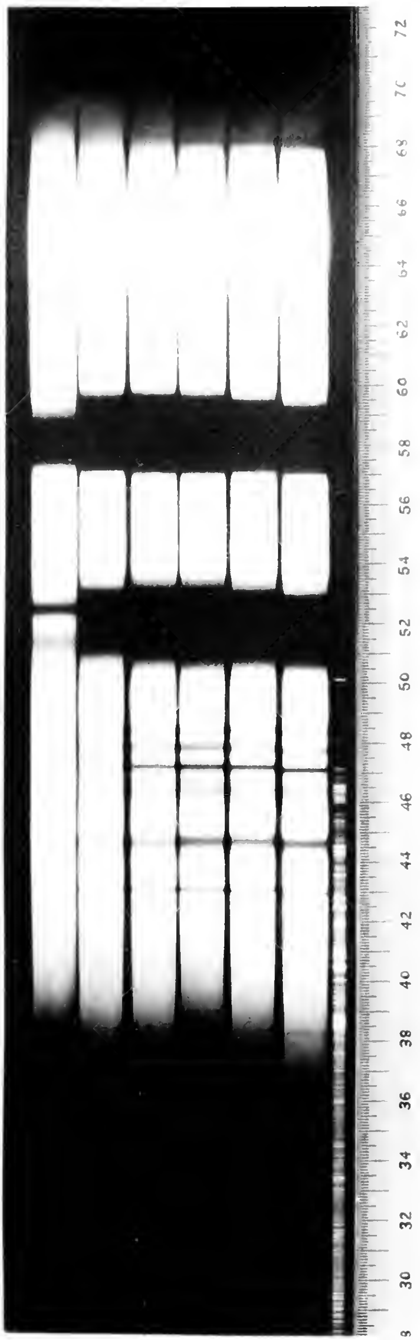
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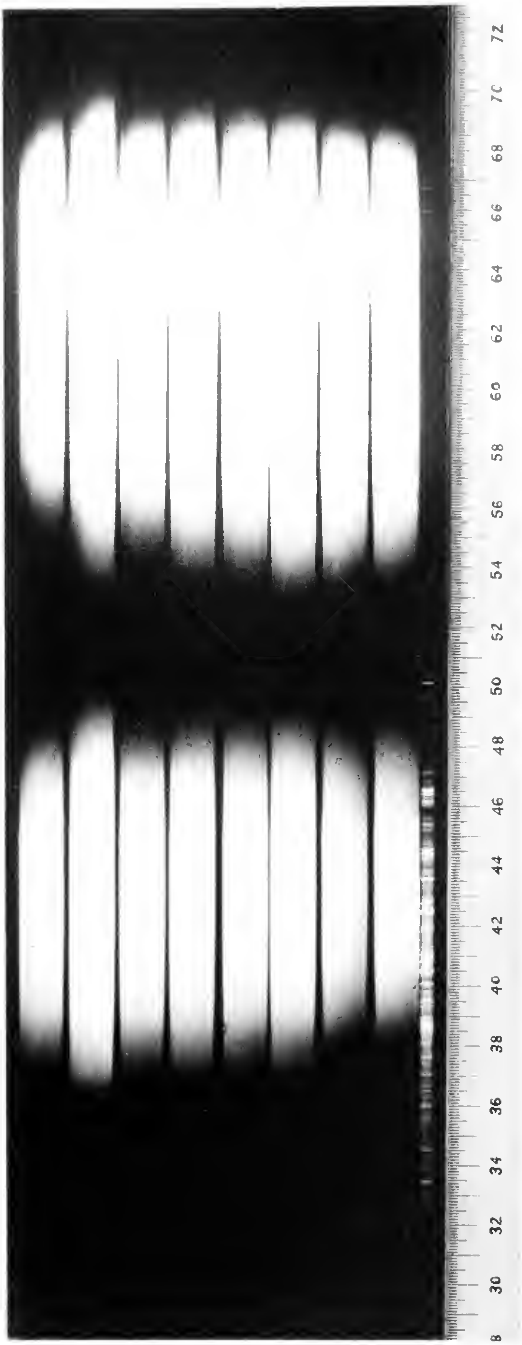
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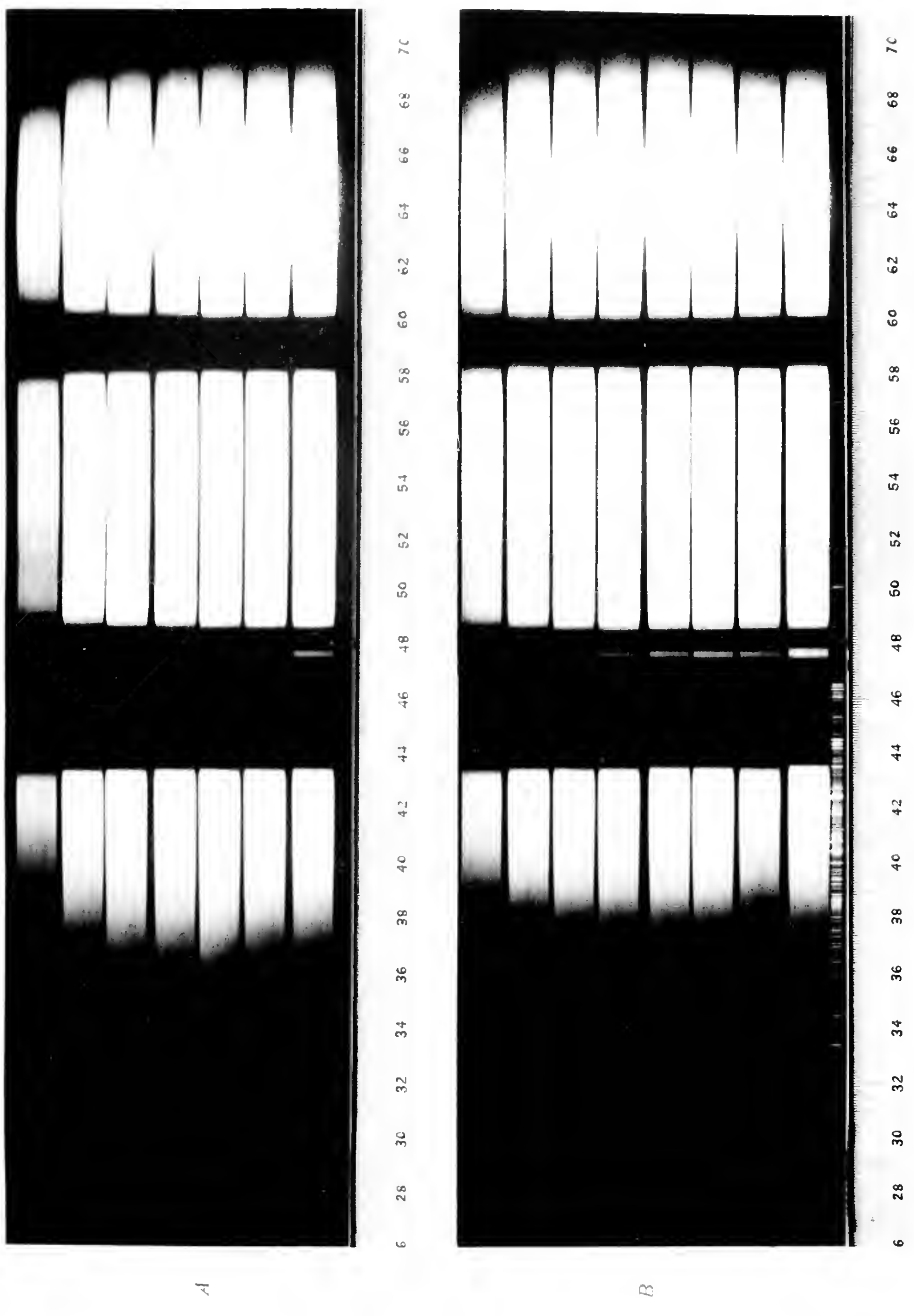
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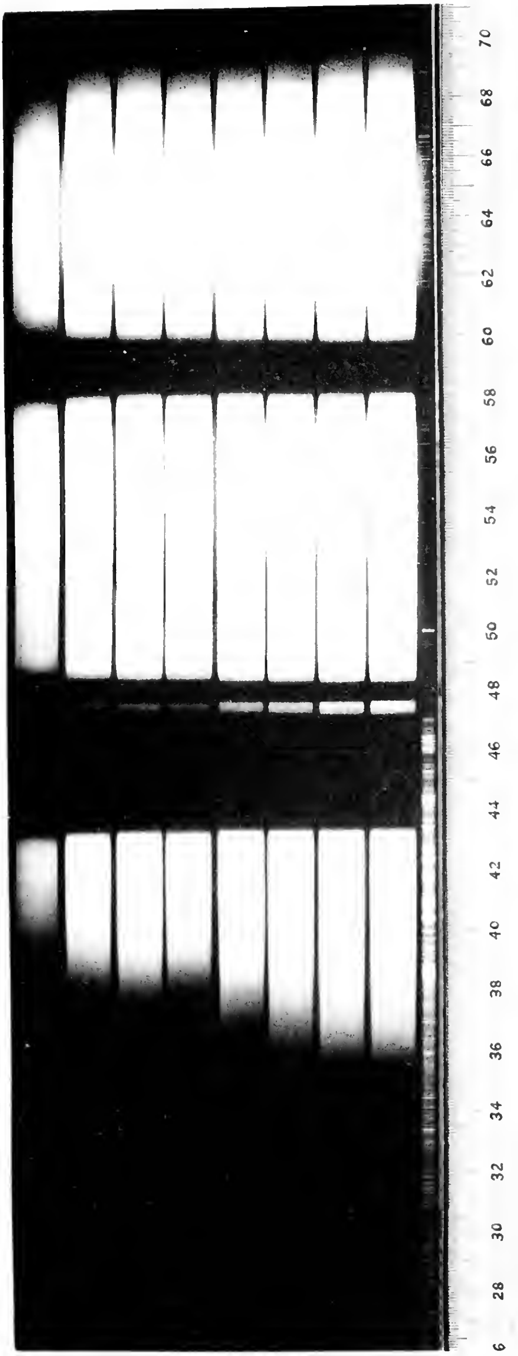
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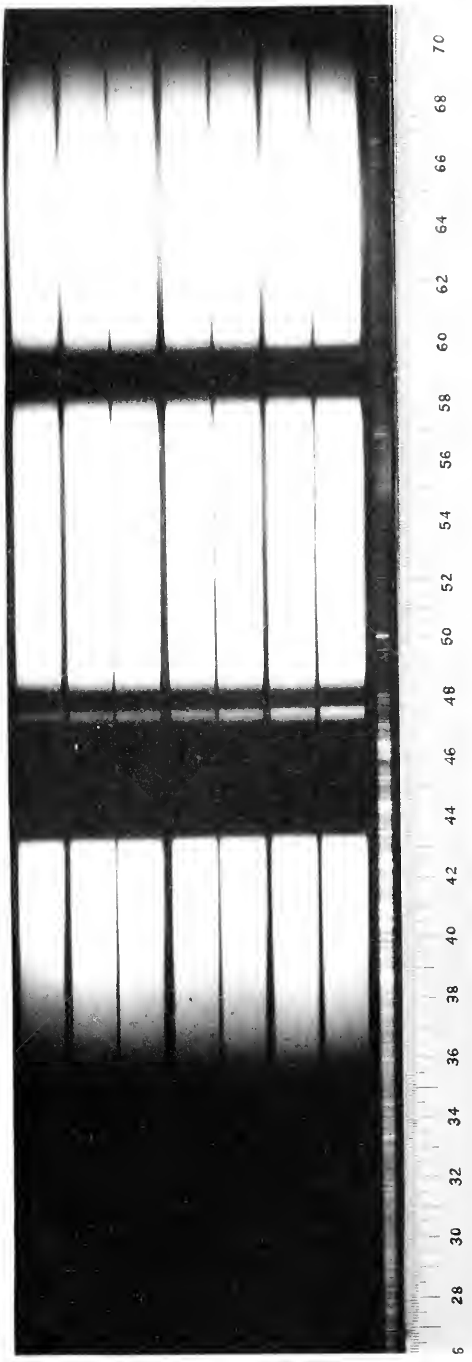
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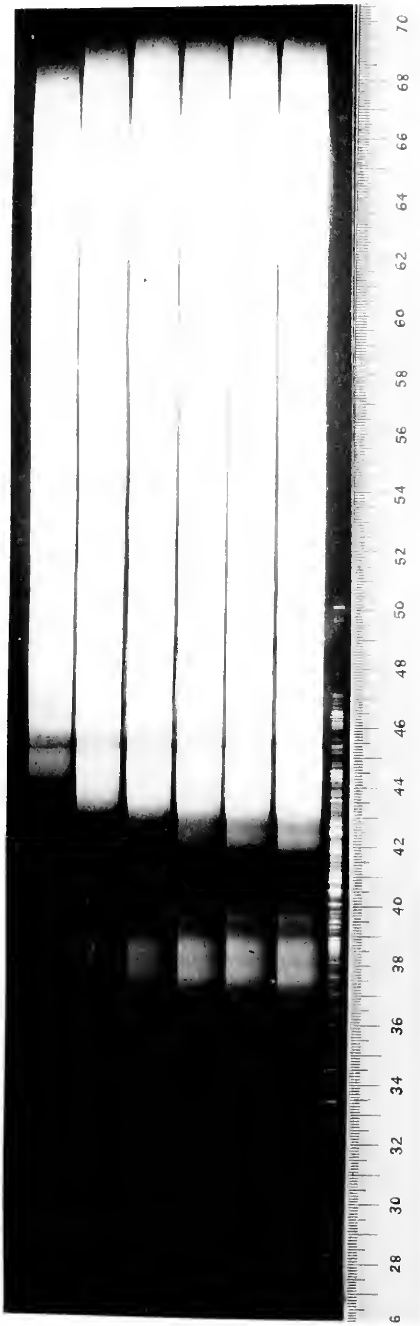
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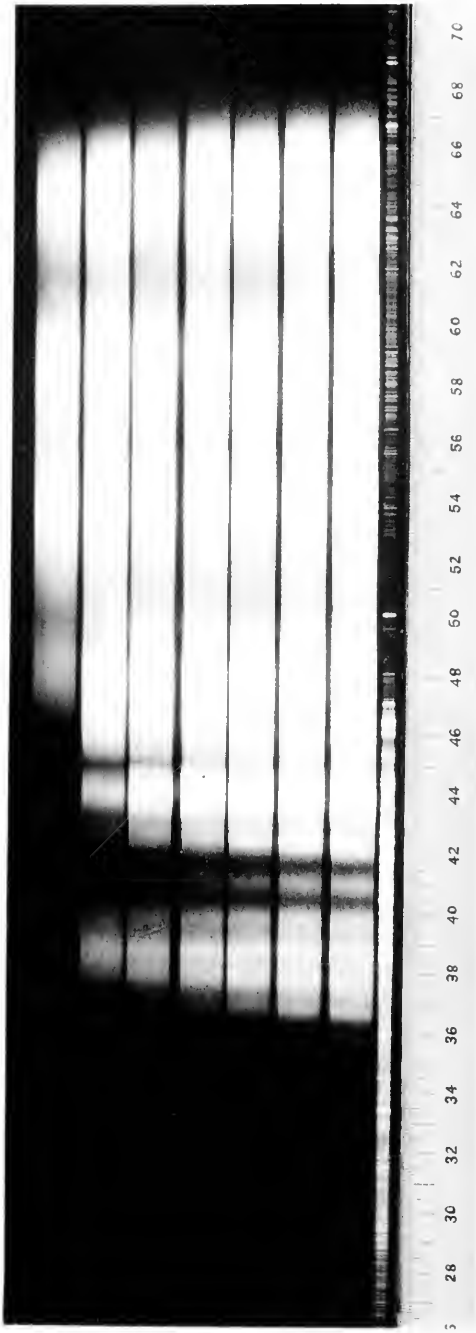
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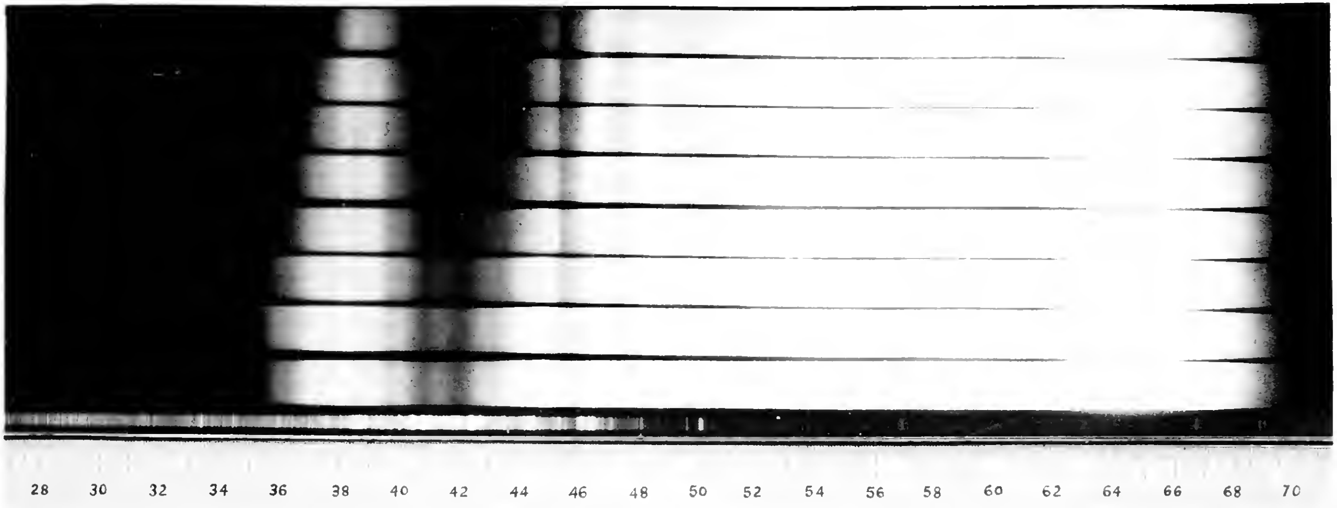
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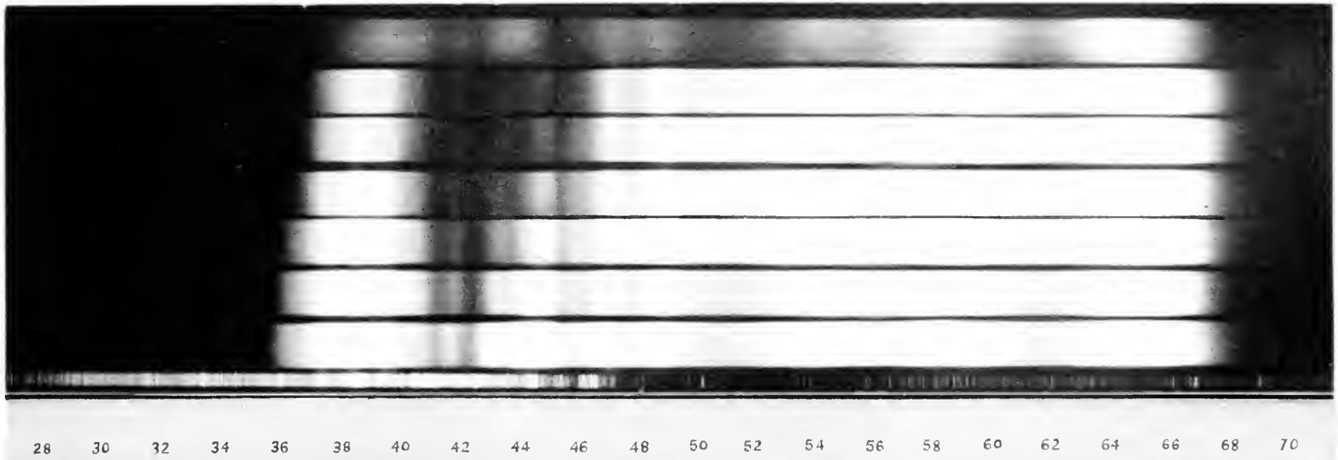
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PLATE 12

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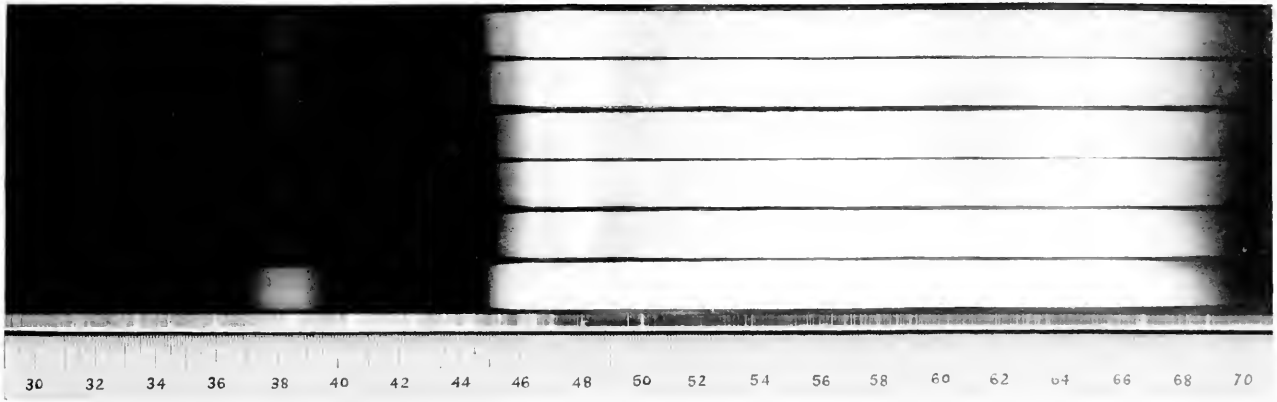
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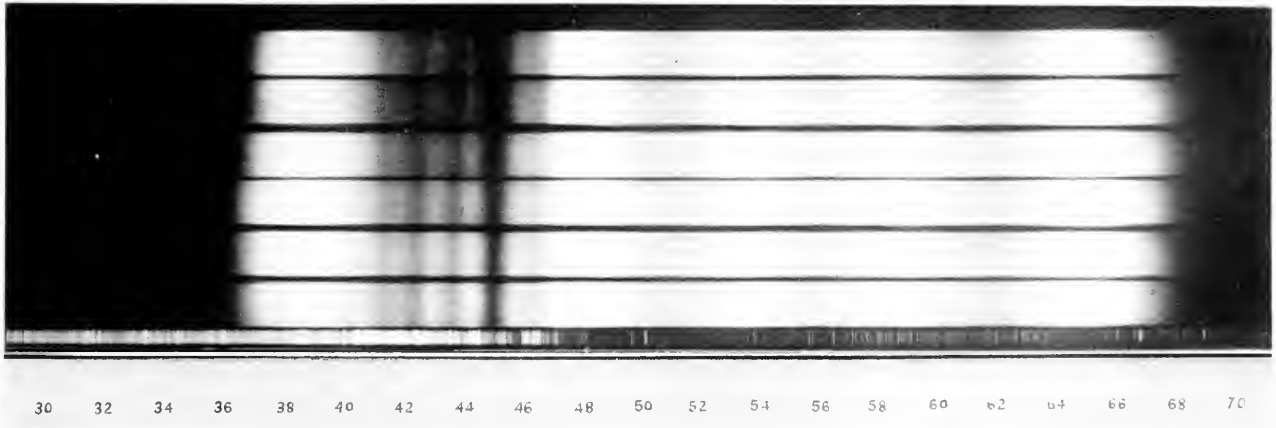
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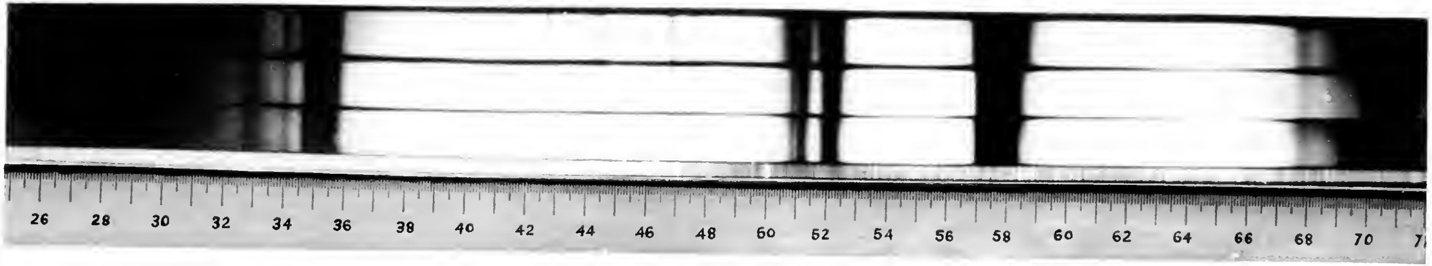
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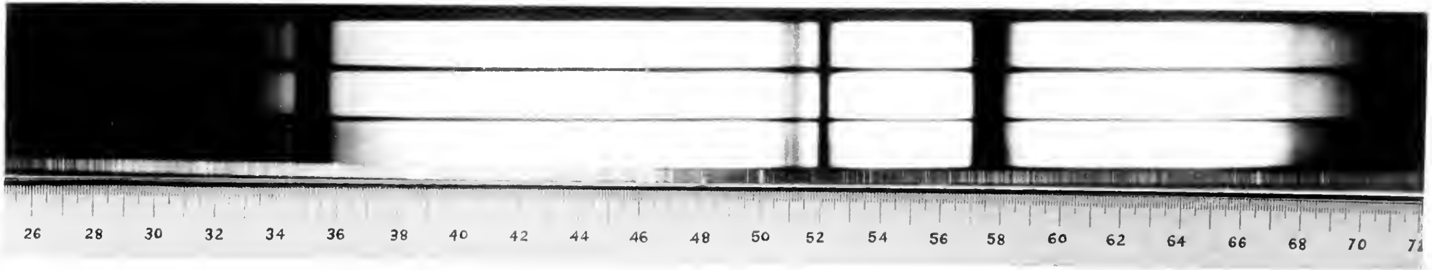
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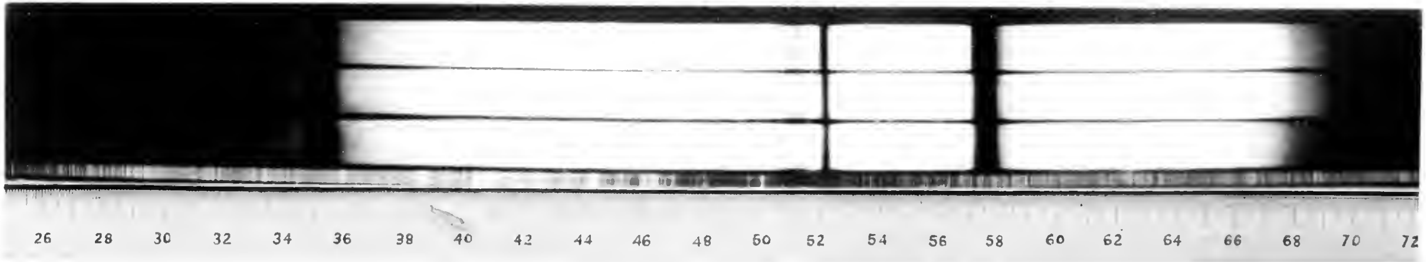
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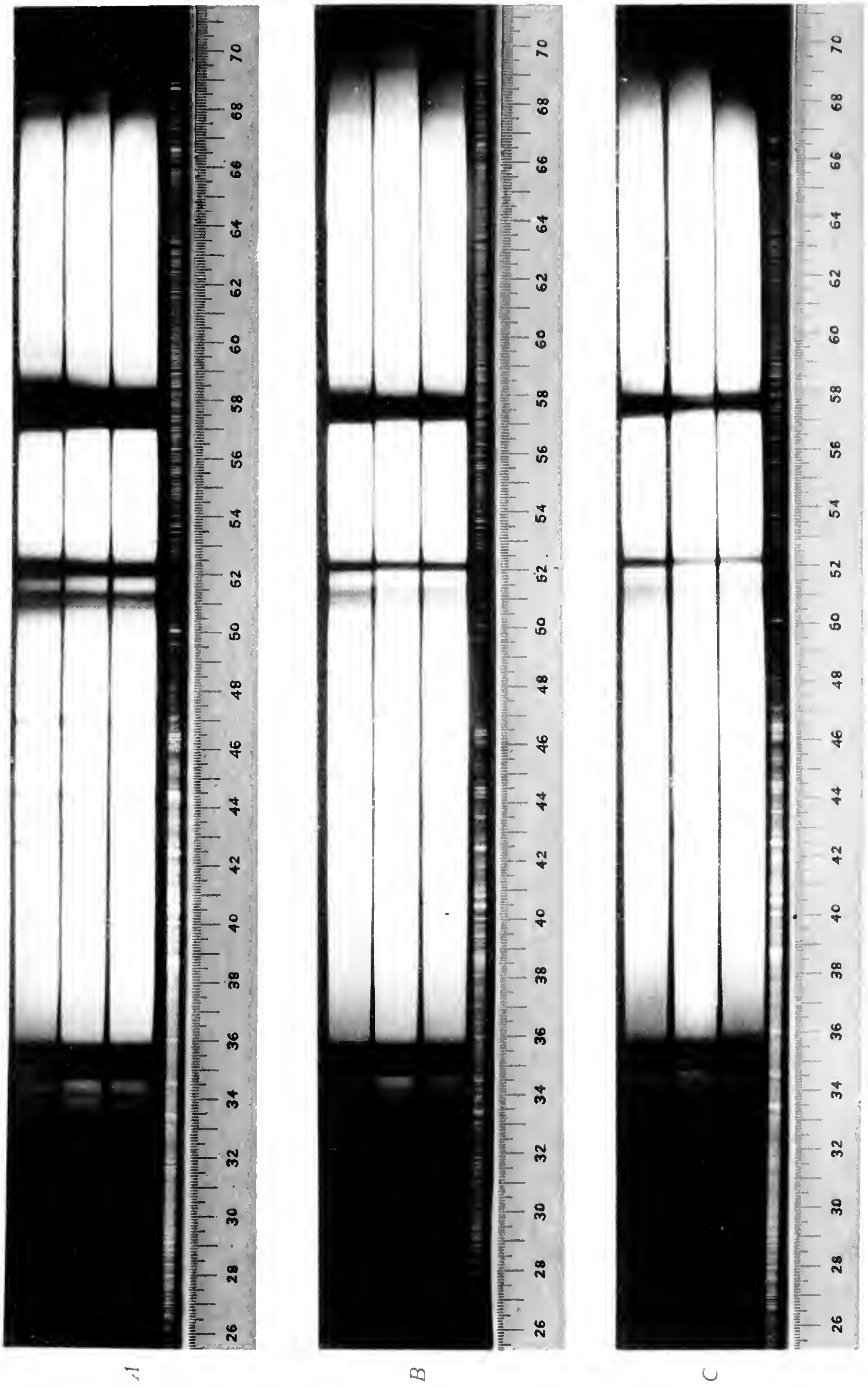
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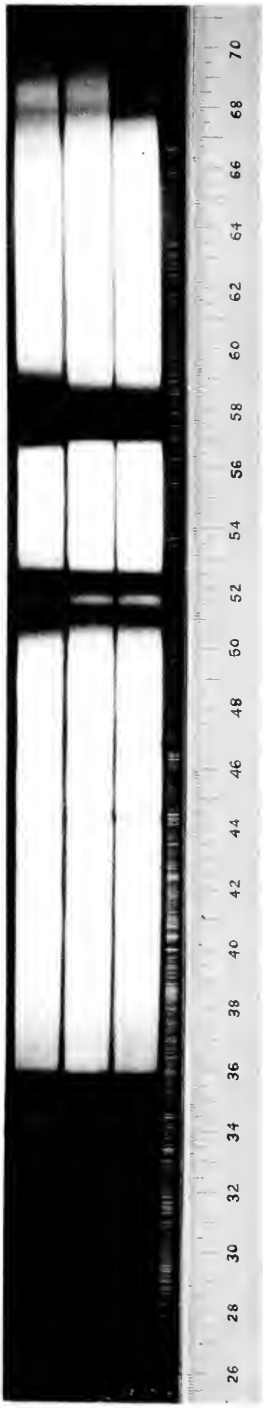
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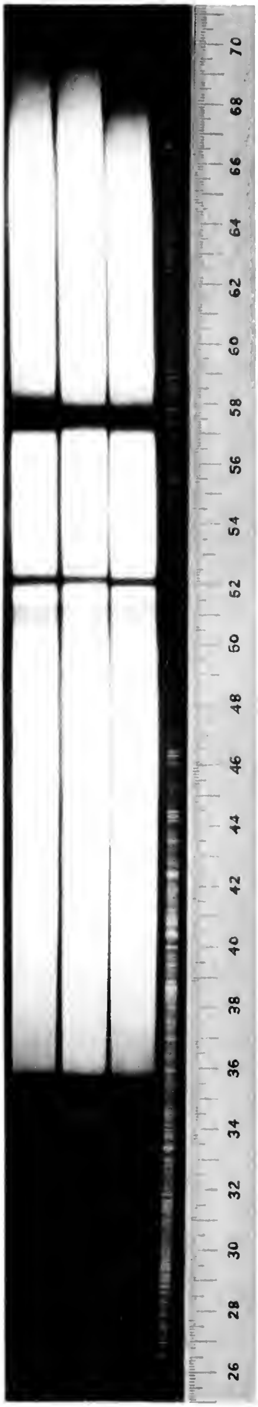
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FIGURE 1

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PLATE 1

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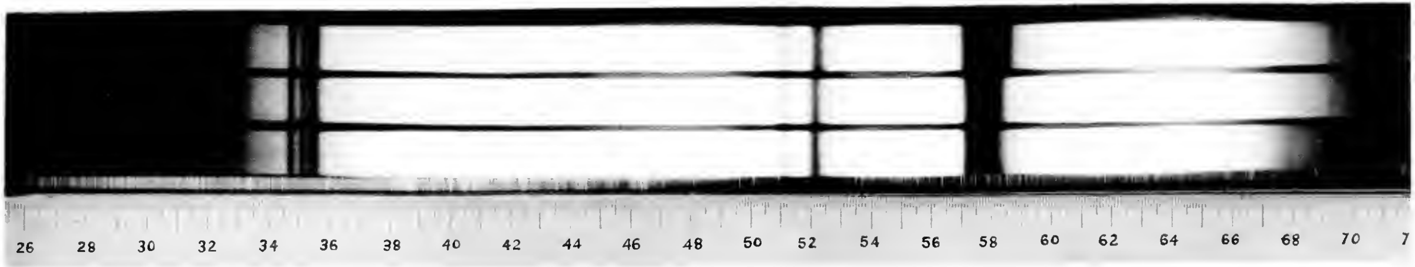
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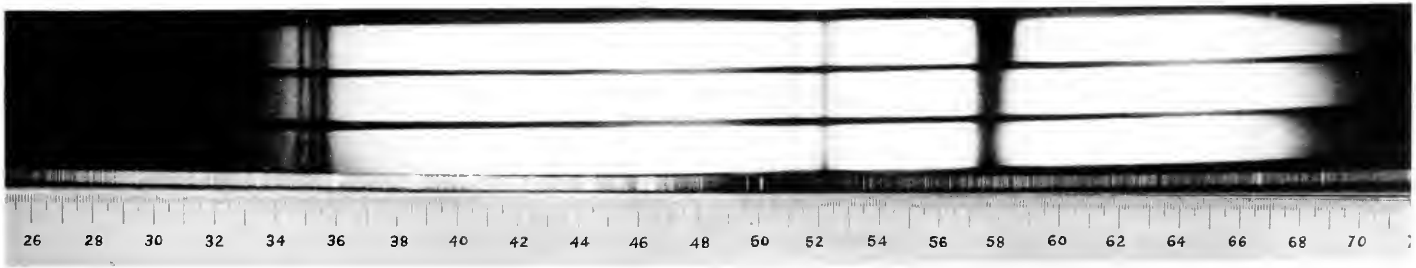
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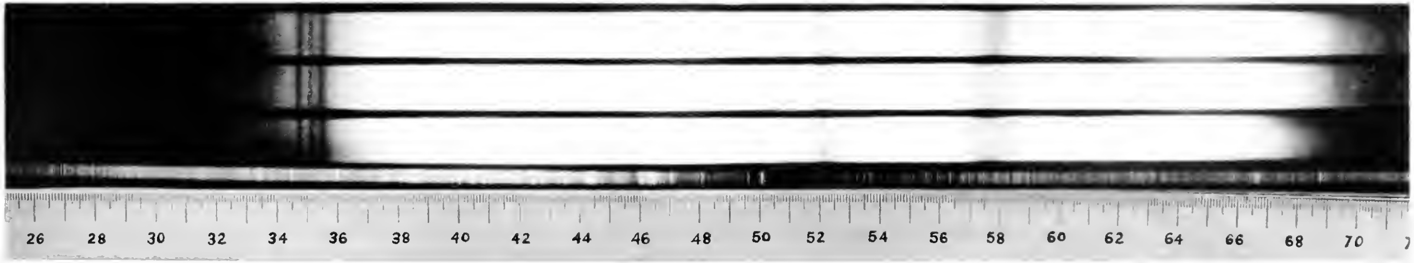
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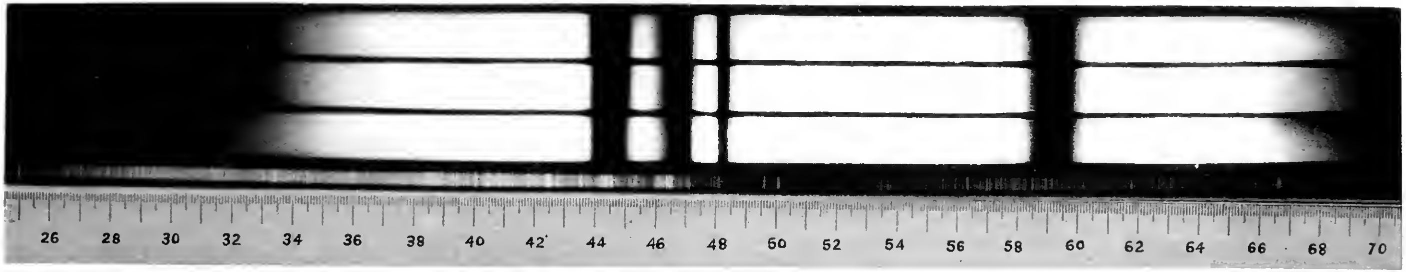
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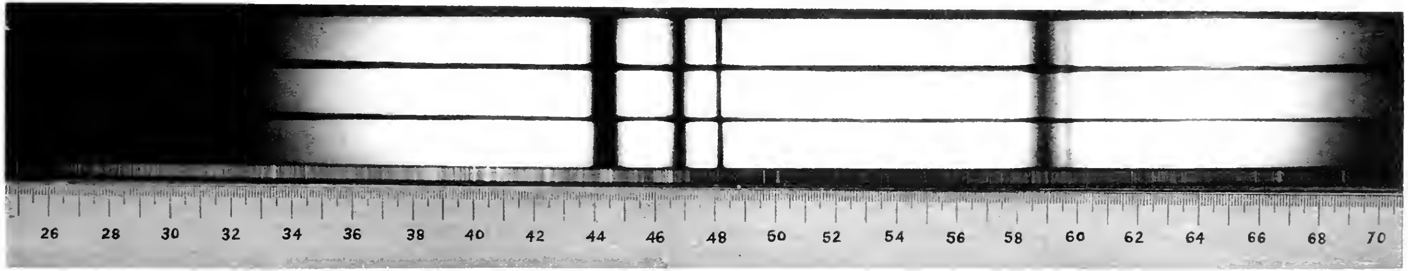
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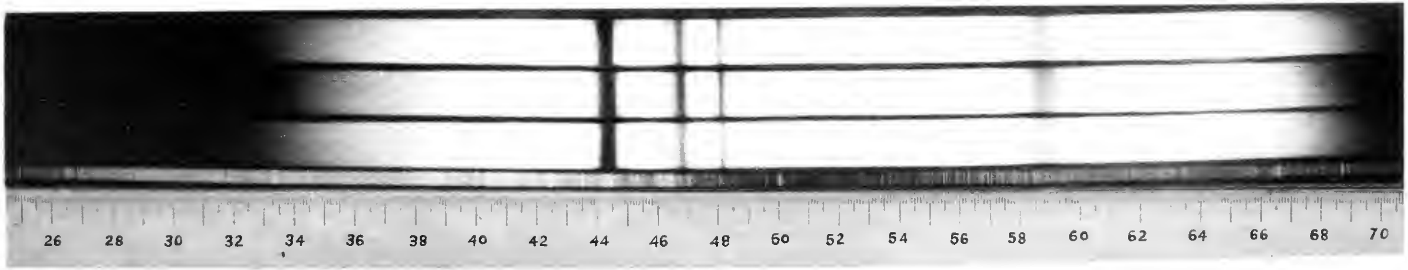
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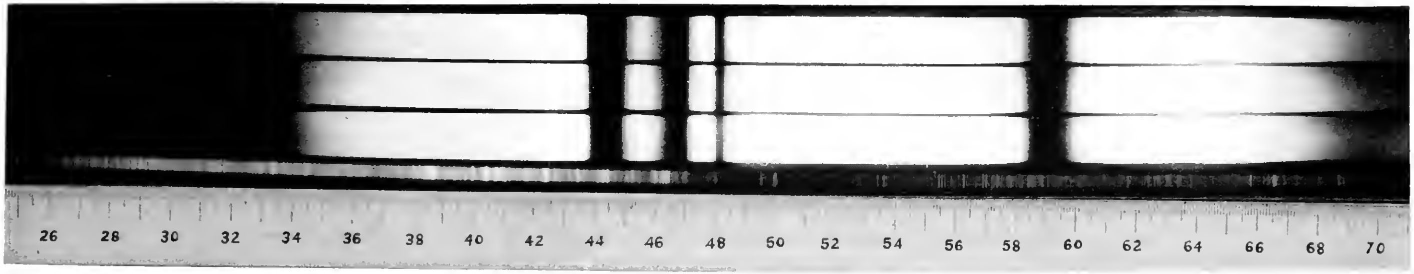
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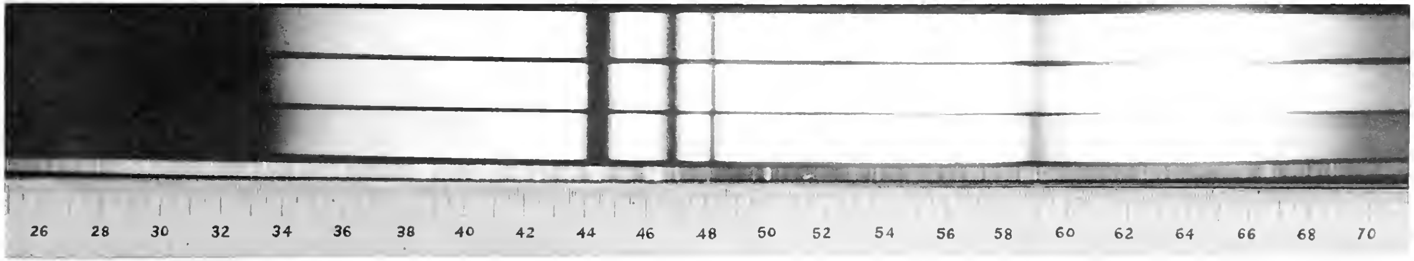
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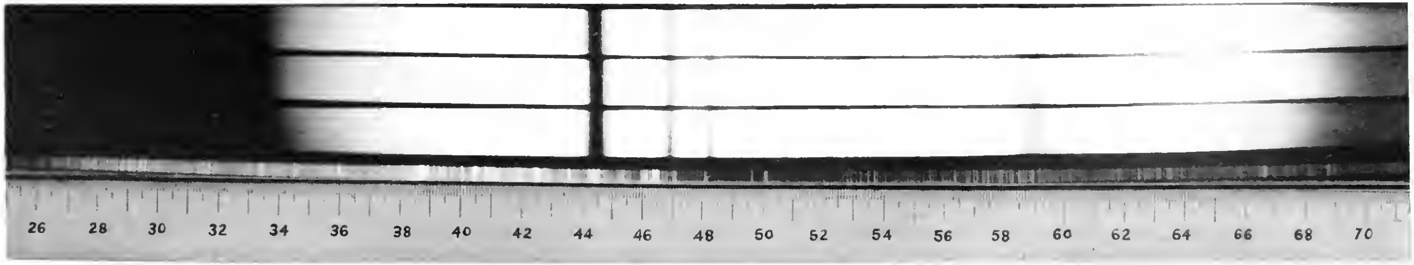
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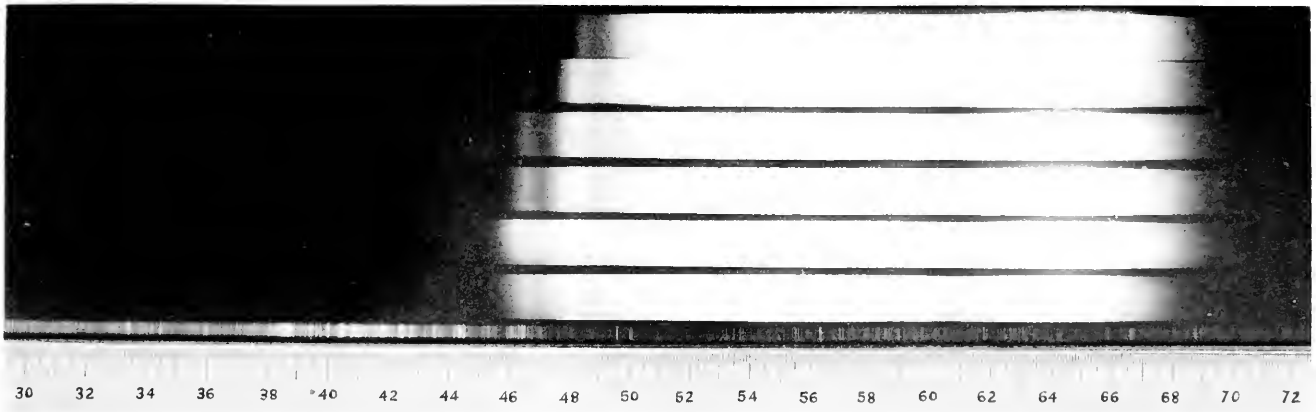
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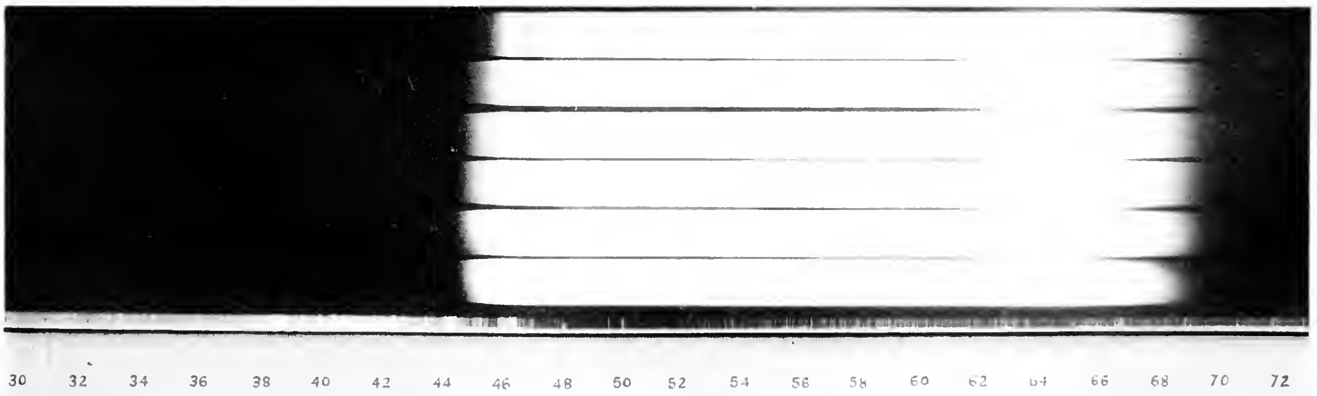
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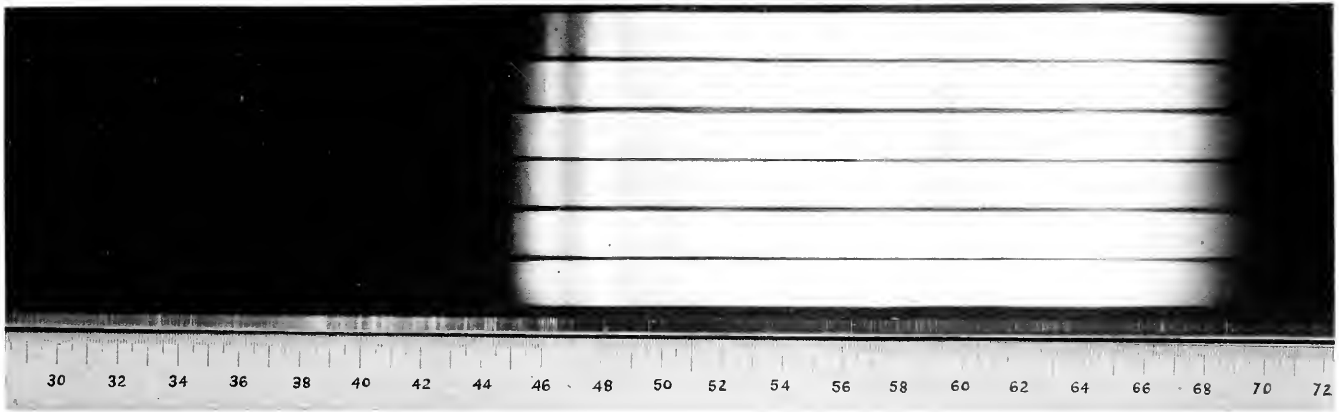
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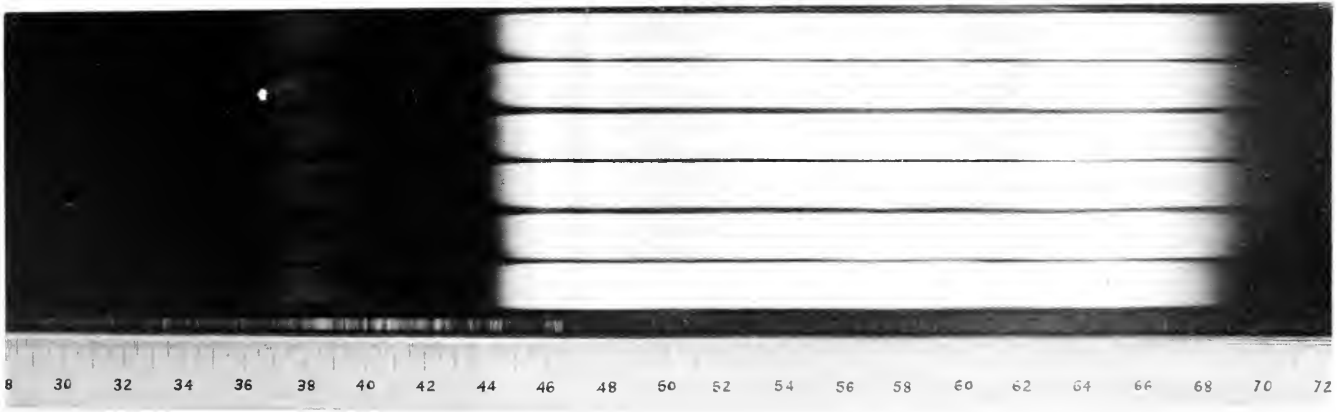
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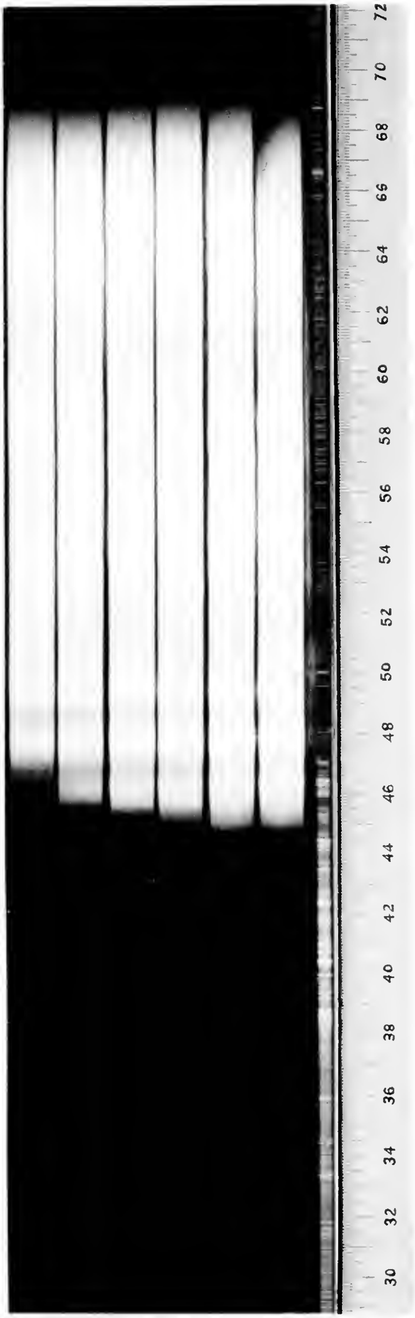
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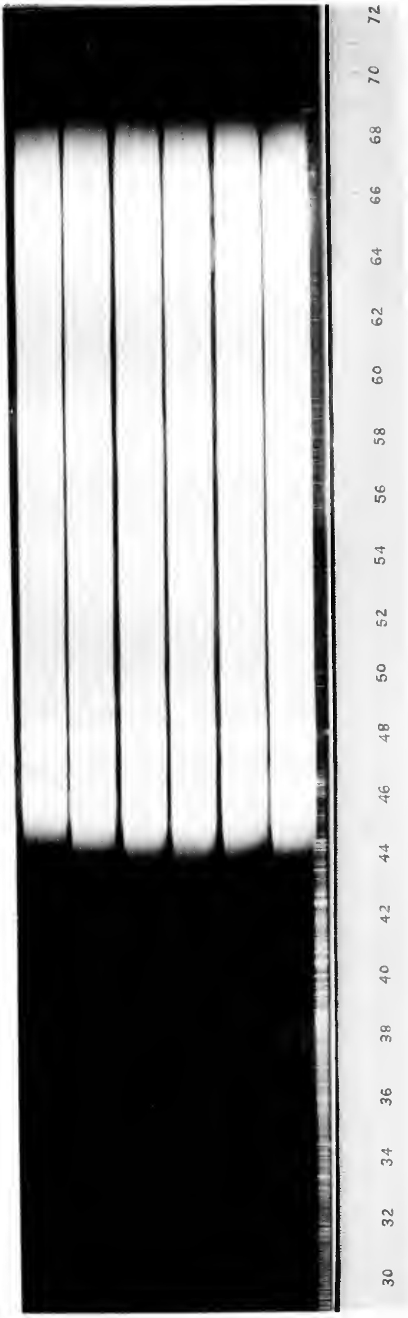
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CHAPTER IV.

ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF CERTAIN SALTS OF NEODYMIUM AS STUDIED BY MEANS OF THE RADIOMICROMETER.

The radiomicrometer is simply a thermo-element attached to a loop of thin copper wire suspended in a magnetic field. One of the greatest difficulties in constructing this element is to obtain copper wire free from all magnetic metals. If perfectly pure copper wire could be found, an instrument could be constructed of almost any desired sensibility.

A very good specimen of small copper wire was furnished us by Leeds and Northrup, of Philadelphia. This wire was dipped in dilute nitric acid and the exterior dissolved away until the wire was of proper size. The removal of the outside coating of the wire removed practically all of the magnetic material from it, this material probably being iron from the dies through which the wire was drawn.

It was not a simple matter to construct a satisfactory thermo-electric junction. The alloys used in making this junction were 90 parts bismuth and 10 parts tin, and 97 parts bismuth and 3 parts antimony. The method of making the thermo-electric junction and of soldering it on to the ends of the loop of copper wire we owe to Professor A. H. Pfund.[1] Fine strips of the alloys were obtained in the following manner:

A few grams of the alloy in question were fused in a vessel free from all magnetic material, and then thrown tangentially upon a clean and smooth glass plate. In this way strips of the metal were obtained of almost any desired thickness. Some were too thin to handle, those used being about 1 mm. wide, 0.01 mm. thick, and about 5 mm. in length.

The thermo-element was made by soldering an end of a strip of one of the above-named alloys to an end of a strip of the other, the whole having the form of a letter V. The two free ends of the V were soldered to the two ends of the loop of copper wire. The soldered surfaces were blackened to absorb the energy more completely. At the end of the loop of copper wire opposite the thermo-element a light glass rod is fastened. This carries the mirror and is suspended from above by a quartz fiber. The mirror employed was about 4 sq. mm. This entire system, consisting of thermo-element, loop of copper wire, and mirror, weighed about 20 mg. It was suspended by means of a quartz fiber so that the loop hung between the poles of a strong magnet.

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[1] Phys. Rev., **34**, 228 (1912). Phys. Zeit., **13**, 870 (1912).

This entire system was suspended in the interior of a glass tube, the tube being closed by a ground-glass stopper, and provided with suitable windows for exposing the junction and observing the mirror. The upright tube was provided with a side tube for evacuation, and by a method devised by Professor Pfund a very high vacuum could be obtained and maintained for any desired length of time. By suitably turning the ground-glass stopper in the top of the glass tube, the loop of copper wire, mirror, and, indeed, the whole system, could be made to occupy any position relative to the magnets, even after the entire system had been evacuated. The whole apparatus was supported upon a leveling stand and packed in cotton to protect it from external radiation, the thermal junction alone being exposed to the radiation in question.

The sensibility of the instrument used can be seen from the following data: It had a full period of 8 seconds, and with a candle at a distance of a meter gave a deflection of 15 cm. when the light was allowed to fall on the junction after passing through a glass window.

When the apparatus was pumped out and the radiomicrometer thus suspended in a vacuum, the deflection for a candle at a distance of a meter was 50 cm. Since glass absorbs just about half the energy emitted by a candle, our radiomicrometer, when provided with a rock-salt window and exposed to a candle at a distance of a meter, would give a deflection of about 100 cm.

How our instrument compared with the radiomicrometers constructed and used by other investigators can be seen from the following table, taken in part from the paper by Coblentz:[1]

TABLE 1.

Investigator.	Whole period in seconds.	Deflection in cm. per sq. mm.; candle 1 m. distance.
Boys, Phil. Trans. (A) 180, 159 (1889) ...	10	0.9
Paschen, Wied. Ann., 48, 275 (1893)	40	3.0
Lewis, Astrophys. Journ., 2, 1 (1895) ...	20	1.3
Coblentz, Bull. Bur. Stand., (1 Sept. 1907)	40	3.6
Coblentz, Bull. Bur. Stand., (1 Sept. 1907)	25	6.0
Jones and Guy	8	8.0
Jones and Guy	7	25.0 (*vacuo*)
Jones and Guy	7	50.0 (*vacuo*) rock-salt window.

The magnetic control due to small amounts of magnetic impurities in the copper wire was, of course, greater the more sensitive the instrument. For this reason the radiomicrometer was not used in a vacuum. The length of the quartz fiber was so chosen that a candle at a distance of a meter gave a deflection of 16 cm. The half period was 4 seconds. This sensibility was found to be quite sufficient for work in the red and infra-red, and even for wave-lengths as short as 4,500 A.U. The measurement could be carried out quickly and the magnetic disturbance was practically negligible.

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[1] Bull. Bur. Standards 4, No. 3.

When the thermo-junction was exposed to the radiation and the source of energy removed, the instrument returned to its original zero position to within 0.5 mm. In most cases several readings were made for a given amount of radiation, and these usually agreed to within 1 per cent. The source of energy was a Nernst glower attached to a storage battery, the amperage being 1.2 and the voltage 110. This was found to be very constant, successive readings in the same position of the spectra agreeing well with one another.

The vessels used for holding the solutions were made of brass and gold plated. They were about 4 cm. in diameter and of the desired thickness. The ends were made of the best optical glass. Vessels of the same thickness gave practically the same deflection both when empty and when filled with water.

METHOD OF PROCEDURE.

The light from a Nernst glower was rendered parallel by a lens, then passed through the vessel containing the solution, and allowed to fall on the slit of a Hilger spectroscope. The solution was first inserted into the path of the light, and then the pure solvent, this being done without disturbing the adjustment. By means of a movable framework, first the vessel containing the solution and then that containing the solvent were interposed in the path of the beam. A metal screen interposed between the Nernst glower and the vessel containing the solution allowed the light to pass through the solution only when an observation was being made. By this means the thermoelectric junction was exposed to the radiation only long enough to read the deflection of the mirror.

The light, after passing through the solution and the slit of the spectroscope, fell upon the prism of the Hilger spectroscope. A second slit was inserted in the spectroscope instead of the eye-piece. The light passed from the prism through this second slit, and was then focused on the thermal junction of the radiomicrometer.

The Hilger spectroscope contained a milled head, graduated so that the wave-lengths could be read off directly. By suitably turning this head any desired wave-length could be thrown upon the junction of the radiomicrometer.

The width of the slit used in the visible part of the spectrum was 0.4 mm. In the infra-red, where there is far more energy, the slit width was cut down to 0.22 mm. A series of readings was carried out as follows: The vessel containing the solvent was first placed in the path of the beam of light, the screen removed, and the deflection of the mirror noted. Then the vessel containing the solution was put in the same place that was formerly occupied by the vessel containing the solvent, the screen removed, and the deflection again noted. The prism was then turned slightly by means of the graduated and calibrated head, and a new wave-length allowed to fall on the junction. By repeating this procedure any wave-length could be allowed to fall on the junction. If we represent by I the deflection with the solution in the path of the beam of light, and by I_0 the deflection with the solvent in the path of the light beam, the percentage of light which passed through the solution would be represented by I/I_0. In tables 2 to 5 we have the ratio of I/I_0.

TABLE 2.—*Observed Transmission of Neodymium Chloride Solutions.*

λ	N.=3.43. D.=2.5mm.	N.=3.43. D.=5mm.	N.=0.857. D.=10mm.	N.=0.427. D.=20mm.	λ	N.=3.43. D.=2.5mm.	N.=3.43. D.=5mm.	N.=0.857. D.=10mm.	N.=0.427. D.=20mm.
486	72	67	80	70	676	71	62	63	57
492	83	72	82	74	678	78	67	61	. .
495	67	61	61	66	681	85	75	74	76
499	38	25	40	41	685	89	91	97	89
501	26	13	29	30	691	92	90	99	90
503	15	8	13	16	699	88	74	97	89
505	9	2	7	12	706	65	37	91	84
506	10	1	11	11	710	49	20	80	75
509	13	2	13	14	714	33	8	47	57
513	13	4	10	17	719	18	1	29	27
515	10	6	2	8	722	7	1	8	5
516	6	2	4	5	724	4	0	1	0
518	10	4	13	14	729	6	3	0	0
520	23	11	31	29	733	14	14	0	0
522	36	18	45	42	737	26	26	5	3
525	52	23	62	56	741	38	41	17	16
530	83	78	92	84	745	50	51	42	36
535	96	95	94	89	750	57	51	64	59
544	92	95	91	87	755	59	41	79	75
550	97	98	80	79	760	54	32	84	79
556	69	59	69	70	765	45	16	75	73
559	56	41	50	53	769	33	6	57	55
563	36	22	26	33	772	21	0	34	30
565	20	7	9	12	776	12	0	14	15
567	7	4	1	2	781	9	0	4	4
572	2	0	0	0	786	10	4	0	0
577	1	1	1	1	792	17	16	2	0
579	2	2	3	2	798	28	29	6	29
583	6	2	11	9	802	44	48	16	12
585	12	3	23	20	806	54	64	34	29
587	27	8	42	37	811	63	78	59	51
589	41	26	63	55	818	76	83	79	75
592	59	45	79	69	823	78	81	91	87
595	75	62	90	81	833	70	52	95	91
597	85	77	92	86	836	61	34	90	89
600	91	90	95	89	840	51	23	80	80
609	93	92	94	88	845	45	14	62	64
611	93	92	92	87	850	37	11	37	39
614	92	90	93	87	855	34	9	20	18
622	90	79	91	82	860	33	12	16	13
629	95	88	94	84	866	38	26	23	26
638	96	99	98	91	872	42	37	41	38
643	96	99	98	92	878	59	53	43	46
650	97	99	99	92	883	67	73	54	51
657	86	82	99	90	889	73	83	65	59
660	77	60	95	87	894	81	90	76	65
662	70	49	91	80	900	92	98	90	87
666	62	37	75	68	927	96	100	100	96
670	62	36	60	54	958	100	100	100	100
672	62	60	57	48					

TABLE 3.—*Observed Transmissions of Neodymium Bromide Solutions.*

λ	N.=1.66. D.=2.5mm.	N.=1.66. D.=5mm.	N.=0.415. D.=10mm.	N.=0.208. D.=20mm.	λ	N.=1.66. D.=2.5mm.	N.=1.66. D.=5mm.	N.=0.415. D.=10mm.	N.=0.208. D.=20mm.
486	64	44	84	83	672	71	52	69	67
492	64	46	81	84	676	67	57	68	70
495	60	35	73	76	678	67	73	75	76
499	38	22	54	53	681	71	77	83	80
501	29	11	45	43	685	82	89	87	90
503	2	9	33	26	691	95	92	92	93
505	17	7	21	25	699	82	80	95	92
507	15	4	26	25	706	72	60	93	91
509	17	9	30	29	710	55	45	88	83
513	18	6	28	25	714	38	28	72	67
515	13	6	21	14	719	21	11	48	39
516	9	4	11	10	722	12	6	19	8
518	16	7	28	25	724	7	2	6	1
520	28	12	39	41	729	10	5	1	0
522	43	19	55	51	733	19	11	2	1
525	53	32	66	73	737	32	21	8	12
530	71	54	89	86	741	45	30	26	25
535	79	57	100	93	745	59	40	49	49
544	84	65	100	94	750	67	49	73	69
555	77	48	95	93	755	67	50	92	80
556	69	47	86	77	760	62	47	100	83
559	57	37	73	62	765	51	37	95	79
563	42	23	51	39	769	40	25	82	65
565	21	12	26	17	772	28	16	59	44
567	9	3	10	5	776	18	9	37	24
572	3	2	2	1	781	18	6	17	8
577	3	1	3	3	786	15	7	5	1
579	6	2	9	10	792	21	12	3	1
583	6	5	17	21	798	33	21	10	9
585	24	11	29	36	802	46	27	23	24
587	39	23	47	51	806	57	35	44	42
589	55	34	63	67	811	69	45	64	63
592	69	53	72	77	818	76	62	83	82
595	75	61	86	81	823	80	66	98	91
597	78	65	91	89	833	77	58	94	94
600	83	73	93	95	836	68	53	91	91
605	87	73	92	94	840	58	44	82	82
614	86	74	94	92	845	50	34	69	70
622	88	76	85	84	850	47	28	48	46
629	88	78	90	86	855	43	24	33	25
638	91	83	92	93	866	47	27	35	38
643	92	98	94	94	872	53	34	48	52
650	91	90	94	92	878	61	42	56	60
657	88	83	93	94	883	69	48	63	64
660	81	72	90	91	889	75	57	70	71
662	79	62	87	85	900	87	69	87	92
666	74	56	78	78	958	97	84	98	100
670	68	50	70	65					

TABLE 4.—*Observed Transmissions of Neodymium Nitrate Solutions.*

λ	N.=2.95. D.=2.5mm.	N.=2.95. D.=5mm.	N.=0.736. D.=10mm.	N.=0.368. D.=20mm.	λ	N.=2.95. D.=2.5mm.	N.=2.95. D.=5mm.	N.=0.736. D.=10mm.	N.=0.368. D.=20mm.
486	....	80	95	80	672	67	53	61	61
492	....	71	93	76	676	75	51	60	61
495	....	61	74	60	678	78	71	65	64
499	25	39	49	45	681	85	77	76	77
501	16	23	38	37	685	88	82	86	84
503	11	14	25	17	691	88	87	92	90
505	4	7	25	7	699	81	78	94	91
507	9	4	19	11	706	64	51	86	86
509	17	4	23	14	710	36	33	80	78
513	11	4	21	14	714	26	16	65	65
515	13	2	16	6	719	11	8	35	39
516	7	3	10	4	722	6	2	14	10
518	13	4	12	8	724	4	1	2	3
520	28	5	27	26	729	8	1	0	0
522	41	7	43	37	733	17	4	0	0
525	53	15	55	54	737	33	11	3	3
530	83	39	83	79	741	42	21	11	12
535	86	72	91	92	745	52	25	29	30
544	87	85	88	87	750	56	40	50	50
555	75	82	78	78	755	56	42	68	66
556	58	67	69	71	760	45	34	78	75
559	35	54	54	55	765	35	26	76	74
563	15	38	32	35	769	23	15	61	61
565	3	25	14	16	772	13	7	40	39
567	1	12	5	3	776	8	3	20	23
572	0	6	2	0	781	7	2	8	15
577	0	2	3	0	786	12	3	1	2
579	3	2	3	1	792	19	7	1	1
583	4	0	7	6	798	33	14	3	5
585	12	1	13	16	802	48	26	12	11
587	26	1	27	26	806	59	41	27	27
589	44	7	43	44	811	61	54	47	46
592	64	14	62	62	818	75	70	71	65
595	81	27	75	77	823	74	74	88	81
597	89	42	84	85	833	63	64	98	92
600	92	58	89	92	836	52	54	98	89
605	98	82	88	91	840	42	40	82	75
614	85	87	88	91	845	39	29	76	69
622	85	86	87	84	850	36	22	48	46
629	86	85	91	86	855	39	18	28	23
638	89	....	97	94	866	53	28	30	25
643	94	92	98	96	872	59	37	41	36
650	93	90	95	95	878	66	45	52	45
657	78	85	95	100	883	75	58	59	53
660	71	85	90	91	889	82	67	68	62
662	67	74	84	83	900	88	81	91	83
666	62	67	73	74	958	95	100	100	100
670	64	60	61	61					

TABLE 5.—*Transmission of Neodymium Acetate; Transmission of Neodymium Sulphate.*

λ	N.=0.84. D.=2.5mm.	N.=0.84. D.=5 mm.	N.=0.118. D.=10mm.	λ	N.=0.84. D.=2.5 mm.	N.=0.84. D.=5 mm.	N.=0.118. D.=10mm.
486	86	93	89	672	87	83	91
492	88	90	95	676	88	84	92
495	93	85	98	678	90	88	94
499	83	65	97	681	94	93	95
501	73	50	86	685	96	90	95
503	67	39	78	691	98	94	96
505	55	29	72	699	93	88	97
507	57	31	72	706	89	67	98
509	53	40	73	710	72	47	97
513	57	35	80	714	52	27	94
515	52	26	62	719	35	12	83
516	39	12	55	722	21	3	58
518	36	19	67	724	14	4	42
520	44	33	79	729	22	14	31
522	59	53	89	733	34	28	31
525	72	70	92	737	49	42	40
530	83	91	100	741	64	60	59
535	96	96	100	745	79	74	78
544	98	96	100	750	86	78	89
555	94	93	100	755	88	74	94
556	88	81	100	760	87	64	96
559	85	69	95	765	76	47	97
563	66	39	85	769	59	32	94
565	46	21	63	772	42	17	86
567	27	5	38	776	28	8	75
572	12	0	28	781	22	9	50
577	4	0	29	786	25	17	29
579	3	1	42	792	26	29	25
583	8	3	55	798	51	43	40
585	19	12	69	802	63	59	53
587	32	23	81	806	77	72	74
589	48	40	93	811	86	83	84
592	62	50	97	818	91	88	92
595	76	73	100	823	95	89	95
597	85	90	100	833	94	87	96
600	91	98	100	836	95	65	96
605	97	97	98	840	77	53	95
614	99	96	97	845	68	46	94
622	99	96	94	850	63	46	83
629	94	95	97	855	65	47	71
638	98	93	100	866	73	63	71
643	96	92	99	872	78	74	81
650	99	93	99	878	82	82	85
657	93	87	98	883	90	87	88
660	91	80	98	889	93	90	89
662	89	80	98	900	96	96	90
666	88	82	93	958	98	100	99
670	86	80	93				

When we first began to investigate any given salt we made a preliminary survey of its spectrum, noting the approximate positions of the absorption lines and bands. We then made our observations very close together over the regions in which the preliminary survey had indicated the presence of lines and bands. The number of absorption lines and bands, as is well known, is very great in the case of neodymium compounds, and these lines and bands frequently have very sharp edges. This made the work with this substance very difficult. The proper width of slit and position had to be chosen or a considerable error would result. Given a slit width which was approximately the same as that of an absorption line, a very slight movement of the slit or prism would change very greatly the total amount of energy falling on the thermal junction.

Take the neodymium band λ4275, which is very intense but narrow. On both sides of this band there is a region of almost perfect transparency. If the slit width necessary to give the desired deflection was greater than the width of this band, light would pass through around the edges of the band, and an error, which might be of very considerable magnitude, would result. With substances which did not contain such fine lines and bands the work would be much simpler.

The entire spectrum from wave-lengths λ4000 to λ20000 was observed at intervals of from 20 A.U. to 50 A.U., except in the regions where the preliminary survey indicated the absence of absorption lines and bands.

An examination of table 2 will show at λ486 a transparency of 72 per cent, which rapidly decreases, reaching the first minimum at λ505. There the transparency amounts to only 2 per cent. The transparency then increases a little and quickly drops to 6 per cent at λ515. The transparency then increases, becoming nearly complete at λ535. We have here, then, a double band with greater absorption on the red side. Other minima appear at λ572, λ730, λ786, and λ860. Bands λ730, λ786, and λ860 do not appear on the photographic plate, and the last two seem never to have been detected before. The above wave-lengths are given as in the tables.

The salts of neodymium were studied as far as λ20000, but beyond 1μ there seems to be complete transparency. The absorption of water is, as is well known, very great in the region λ12000 to λ20000.

DISCUSSION OF THE RESULTS.

The results are plotted in figs. 1 to 11. The abscissæ are percentage transparencies, the ordinates are wave-lengths. These curves, since they represent the transparencies of the solutions in question, are called *transmission curves*.

Figs. 1, 2, and 3 represent the transparency of solutions of neodymium chloride expressed in terms of Beer's law. If we represent the concentration by N and the depth of layer by d,

$$Nd = \text{constant}$$

The concentration represented in fig. 1[1] is 3.43 normal, in fig. 2 it is 0.857 normal, and in fig. 3 it is 0.427 normal. The depth of layer represented by fig. 1 is 2.5 mm., by fig. 2 it is 10 mm., and by fig. 3 it is 20 mm. The concentration and depth of layer were thus varied so as to keep Nd constant.

If the solvent plays no rôle in the absorption, the three sets of curves must fall directly over one another, *i. e.*, be identical, since the number of absorbing parts in the path of the beam of light is kept constant. A comparison of the curves shows that, in general, the more concentrated the solution the less the transparency and the broader the absorption bands. In the more dilute solution the intensity of the bands is greater. This comes out very clearly in the red and infra-red region, where there is greater accuracy of measurement.

Take the three absorption bands, λ730, λ785, and λ860. In curve 1 the minima of these bands are approximately 4, 9, and 33 per cent, while the minima in curve 2 are much less. In fig. 2 the bands λ730 and λ785 reach the abscissa, which means that there is no transmission. At this dilution the band λ860 has still considerable transparency, as will be seen by the fact that it remains a considerable distance above the abscissa. The band λ860 does not reach the abscissa even at the dilution represented in fig. 3.

All of the bands manifest the above phenomena, the change in intensity being greatest where the change in dilution is greatest, *i.e.*, from curve 1 to curve 2. With increase in dilution the position of the middle of the band is displaced toward the region of greater wave-length.

Similar results were obtained with neodymium bromide, and these are plotted in curves 4, 5, and 6. The concentrations and depths of layer were varied so that the product of the two remained constant. The work with the bromide was, therefore, done in terms of Beer's law. The concentrations used were 1.66 normal, 0.415 normal, and 0.208 normal, the corresponding depths of the solution being 2.5 mm., 10 mm., and 20 mm. We find here the same general changes in the intensities of the bands as with the chloride. The more dilute the solution the more intense and the narrower the band.

This is shown by comparing figs. 4, 5, and 6. In fig. 4, which represents the most concentrated solution of the three, the bands are the least intense. In fig. 5 the opacity of two of the bands has become complete, shown by the fact that these touch the abscissa.

Neodymium nitrate was also studied and the results are plotted in curves 7, 8, and 9. The concentrations used were 2.95, 0.736, and 0.368 normal. The depths of layer were 2.5 mm., 10 mm., and 20 mm.

Band λ570, curve 7, appears to be an exception to the general relation pointed out above, connecting intensity and width of band with dilution. This was the first band studied by means of the radiomicrometer, and comparatively small deflections were observed in this region of the spectrum.

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[1] Our attention was drawn to the existence of these bands in the infra-red by Pfund, who had already mapped them radiometrically for neodymium nitrate.

The remaining bands of neodymium nitrate, however, show the same relations that have been pointed out for the chloride and bromide; with increasing dilution the intensities of the bands increase and the centers seem to be displaced somewhat towards the longer wave-lengths.

We then have three salts, neodymium chloride, neodymium bromide, and neodymium nitrate, all of which show a marked increase in the intensity of the absorption bands with increase in dilution, when the product of concentration and depth of layer is kept constant, *i. e.*, when the conditions demanded by Beer's law are fulfilled.

POSSIBLE EXPLANATION.

It is well known that a resonator vibrates more strongly if excited by the vibrations from one single vibrating resonator of the same pitch than when set into vibration by a large number of resonators, one of which has the same period as its own, and the others slightly different periods. In other words, if several vibrators are near one another, every one exerts a certain influence on its neighbors. The result is that no one of them has exactly the same period as the original resonator.

The presence of one vibrator seems to exercise a damping influence on the other, and causes it to vibrate with a period slightly different from its normal period. We thus have less perfect resonance.

The absorption of light by solutions appears to be a resonance phenomenon. In a concentrated solution the vibrators are relatively close to one another and mutually affect one another. The result is an imperfect resonance, and consequently the absorption bands are less intense in the more concentrated solution.

The vibrators are farther removed from one another in the more dilute solutions, and in most cases are probably surrounded by large amounts of water of hydration. The damping effect would not be so pronounced, and a resonator would have greater freedom to vibrate in its own period. In such cases we would have a more nearly perfect resonance, and the resulting absorption bands would be more intense. This tentative explanation seems to account for the observed facts. Subsequent work has shown that a part of this effect can be explained as due to the fact that the slit width was not infinitesimal. Fig. 10 is plotted from the results for neodymium sulphate, and fig. 11 from those for neodymium acetate. The concentration of the sulphate is 0.118 normal, and of the acetate 0.84 normal. The length of the solution of the sulphate is 10 mm., and of the acetate 2.5 mm.

The absorption of the acetate, for a given concentration, is much greater than that of any other neodymium salt thus far studied. This agrees with the results obtained photographically.

The absorption of water beyond 1μ is very great, as has already been stated. If we are working with very concentrated solutions and use a "water" vessel of the same thickness as the "solution" vessel, it is obvious that the results would not be comparable. Take the 3.43 normal solution of neodymium chloride; it contains, for a given thickness, only about 90 per cent as much water as the same thickness of pure water. It is, then, obvious that in the longer wave-lengths a correction term must be introduced for this difference. This was practically negligible with salts of neodymium, since these do not seem to have any bands in the region where water has appreciable absorption.

Salts of praseodymium have bands in the infra-red, at least as far as 2μ. In such cases the above correction must be introduced. This correction can be introduced in either of two ways. We can take the specific gravity of the solution and from the concentration calculate the amount of water present. We can then use a "water" vessel of suitable thickness. For example, if the very concentrated solution in question contains only 90 per cent of water, and we use a vessel for the solution which is 10 mm. thick, we must use a vessel for the water which is only 9 mm. thick. In this way the beam of light is made to pass through the same amount of water both in the case of the solution and of the solvent, and the absorption due to water is, therefore, the same in the two cases.

The second method of procedure is to allow the "water" vessel and the "solution" vessel to be of the same thickness, and to apply mathematically the proper correction to the results obtained.

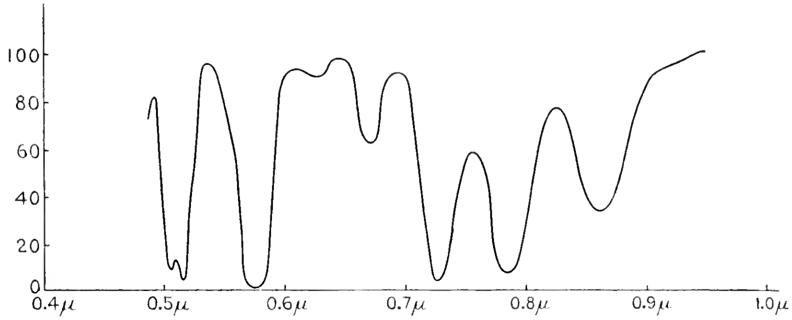

Fig. 1.

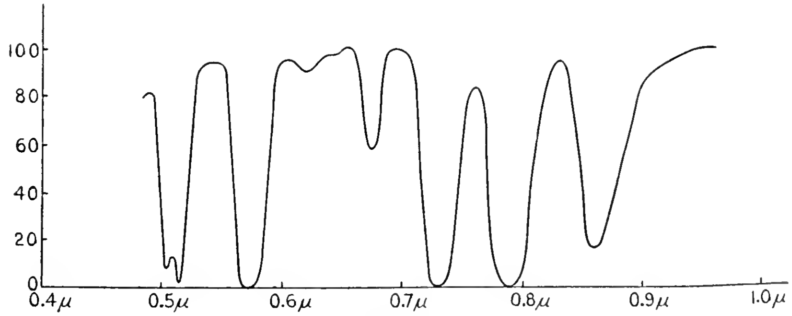

Fig. 2.

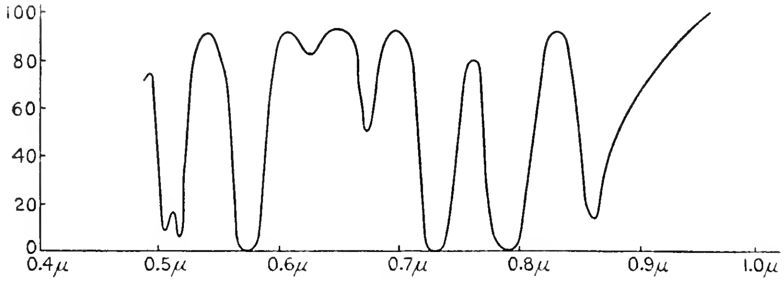

Fig. 3.

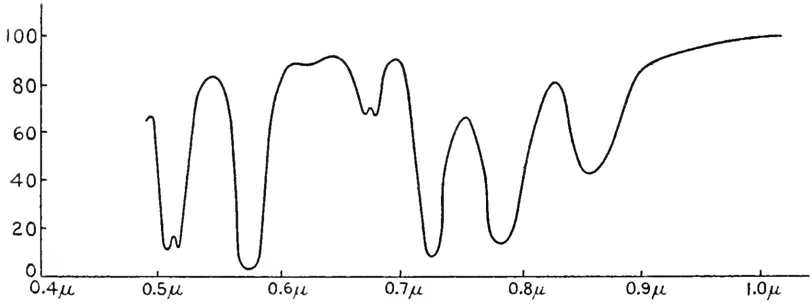

Fig. 4.

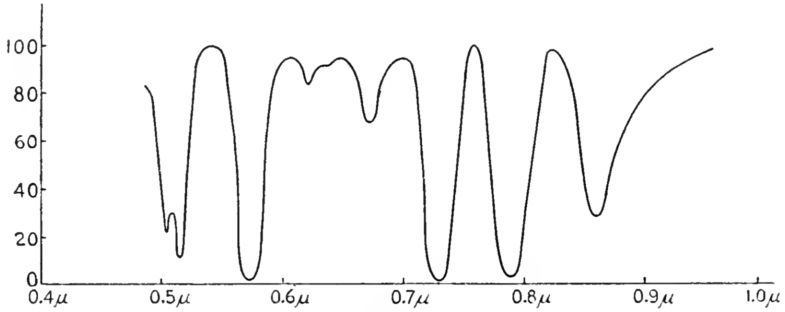

Fig. 5.

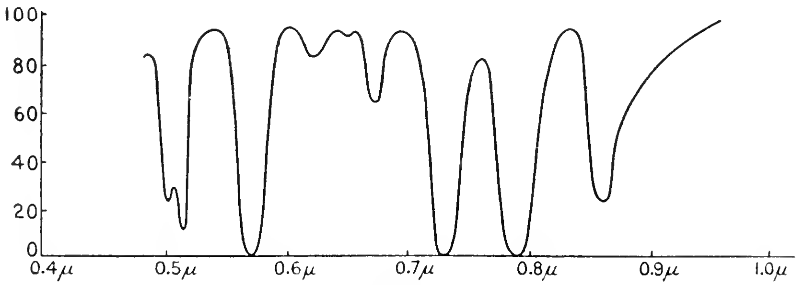

Fig. 6.

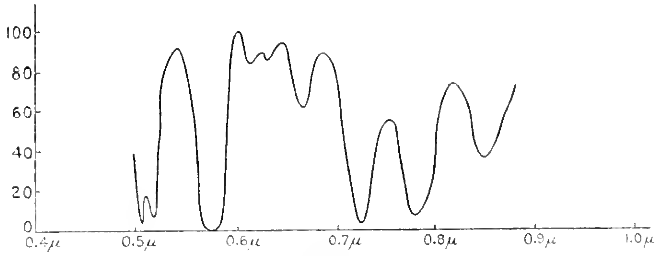

FIG. 7.

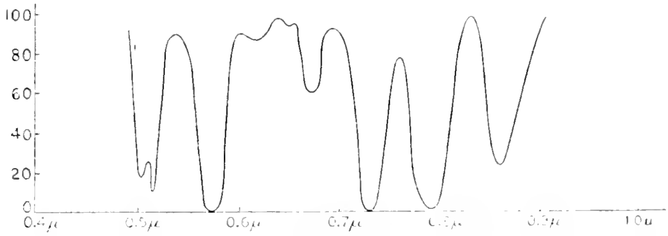

FIG. 8.

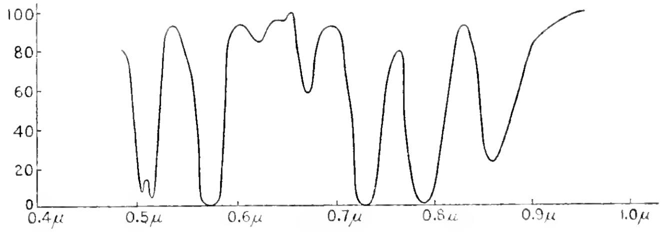

FIG. 9.

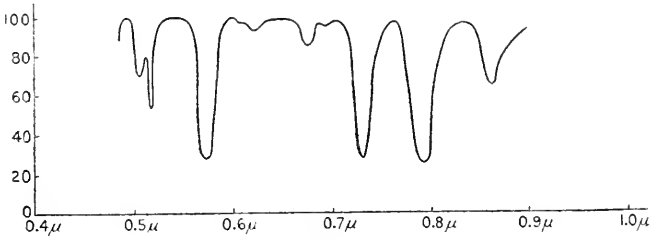

FIG. 10.

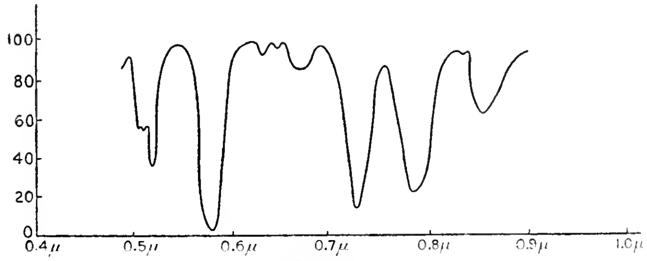

FIG. 11.

CHAPTER V.

THE ABSORPTION OF LIGHT BY WATER CHANGED IN THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER—NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION.

The use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy.[1] The radiomicrometer was used for studying the absorption spectra of solutions rather than the grating spectrograph and the photographic plate, because it enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensity; and also because it made possible the study of the absorption spectra of solutions over a much greater range of wave-lengths than the photographic method.

In building a radiomicrometer adapted to this work—that is, with sufficient sensibility and with a short period—one of the greatest difficulties, as already mentioned, was to obtain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero-point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds and Northrup of Philadelphia and of R. W. Paul of London. Both of these houses furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermo-electric junction already described, a most sensitive radiomicrometer was built, which at the same time had a very short period, and with this instrument work was done with salts of neodymium and praseodymium, the results of which were recorded in the Physikalische Zeitschrift.[2]

ABSORPTION OF FREE AND COMBINED WATER.

At the beginning of the academic year 1912–13 the absorption spectra of solutions of a large number of salts of different metals were mapped out and compared with the absorption of water, using the same depths of water as the water in the various solutions. The depth of water in the solution was determined from the concentration of the solution and from its specific gravity. It was soon found that the absorption of the solution was *less*, and in many cases *very much less* than that of the layer of water having a depth equal to the depth of the water in the solution.

The above result is directly at variance with everything that was known at the time. The dissolved substance could not have less than no absorption of light, the assumption having been made up to this time that in an

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[1] Phys. Zeit., **13**, 649 (1912).

[2] *Ibid.*, **13**, 651 (1912).

aqueous solution the water present absorbs just as much as pure, uncombined water.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance; since the water in the solution has very different absorption from an equal amount of pure, uncombined water.

We then carried out a number of experiments in cells whose depths could be easily and accurately adjusted, with different substances, in the following manner: The absorption spectra of a number of different substances were first measured, then the absorption spectra of water having the same depths of layer as the water in the solutions. For certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent. The percentage transmission—that is, the deflection of the radiomicrometer for the solution, divided by the deflection for water—for the first-named substances amounted to more than 100 per cent. Pure water had a different absorption from an equal depth of water in the solution, and since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflections for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

HYDRATED AND NONHYDRATED SUBSTANCES.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated are more transparent than pure water having the depths of the water in the solutions in question. Solutions of nonhydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution. It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure, uncombined water. To test this quantitatively the following procedure was adopted.

METHOD OF PROCEDURE.

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell set to a depth of say 21 mm. Some of the same solution was then placed in another cell set to a depth of say 1 mm. Light of a known wave-length was then passed through the one solution and the deflection noted. Light of this same wave-length was then passed at once through the other solution and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced by the shallower solution, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm.

This process was repeated for the different parts of the spectrum, changing the wave-length of light from reading to reading by only a small amount. The object of using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower. From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say 21 mm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep, could also be calculated. Water was then introduced into two cells, and the cells so adjusted that the difference in depths was exactly equal to the depth of the water in the layer of the solution, which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave-length of light, and then, at once, the deflection when the light was passed through the more shallow layer of water. The deflection for the deeper layer was divided by the deflection for the shallower layer. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in question.

RESULTS.

The above results for the solution are plotted as one curve and those for water having the same depth as the water in the solution as another curve, wave-lengths being abscissæ and transmission ordinates. A comparison of the two curves shows at once whether water in the free, uncombined condition or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the shallower, and, similarly, by those for water, are also given in tables 6 to 10. These are the data from which the accompanying curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light, and which are both colorless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

We selected for these substances with little or no hydrating power, salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. For the salts with large hydrating power, calcium chloride, magnesium chloride, and aluminium sulphate were used. These salts were shown, from our earlier work, to be among the most strongly hydrated substances with which we are familiar. Two depths of layer of each solution of every

TABLE 6.

λ	KCl, 4N. I/I_0	H_2O.	NH_4Cl, 4N. I/I_0	H_2O.	NH_4NO_3, 3.12 N. I/I_0	H_2O.
711	97	97	92	98	95	98
724	96	95	91	96	97	98
741	95	95	90	92	96	96
760	93	95	85	92	91	95
776	92	95	85	88	92	94
798	94	95	88	95	91	95
818	92	95	87	95	92	96
836	94	93	87	95	91	94
855	91	90	86	93	89	92
878	92	90	86	91	90	93
900	90	89	84	87	89	88
922	87	86	82	86	85	90
947	82	84	79	82	82	83
958	77	78	73	72	73	79
964	75	73	69	70	70	71
969	65	65	64	63	65	67
974	58	56	57	58	58	59
979	51	50	52	52	50	54
982	47	46	45	46	44	46
985	41	45	43	43	40	44
991	39	43	41	43	39	43
1,007	39	43	41	42	39	44
1,013	40	42	39	44	41	44
1,019	42	46	40	46	42	44
1,025	41	42	44	49	45	48
1,032	49	49	44	49	48	49
1,037	53	52	56	55	52	53
1,042	56	56	53	58	55	55
1,046	59	60	57	57	57	60
1,059	63	62	58	65	60	65
1,065	68	67	62	67	64	65
1,072	71	68	64	68	66	69
1,078	74	72	67	67	66	72
1,085	75	73	67	66	68	74
1,100	77	75	68	72	69	78
1,113	76	76	69	72	69	78
1,138	75	72	68	70	68	72
1,148	70	69	64	65	64	71
1,158	64	63	62	64	59	64
1,165	58	59	58	58	56	60
1,172	52	51	50	50	53	52
1,179	42	40	40	40	38	41
1,186	29	28	29	26	29	30
1,193	18	19	19	19	18	19
1,200	13	16	14	13	12	17
1,206	10	12	12	13	9	13
1,213	10	11	10	12	9	13
1,220	10	11	10	11	9	12
1,227	10	11	10	11	9	12

substance investigated were employed, in order to bring out the two most important water-bands in the region of the spectrum used. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water-bands would not bring the other out in the way desired. By using the two depths of solution, and studying them in the manner above described—that is, by the differential method— we were able to study both of the water-bands as produced, on the one hand by the pure solvent, and on the other by the solution.

In tables 6 to 10, under λ, are given the wave-lengths of light that were passed through the solution; and under I/I_0 the percentage of transmission, on the one hand, of the solution; and on the other, of water having a depth exactly equal to that of the water in the solution.

Table 7.

λ	KCl, 4 N. I/I_0	H_2O.	NH_4Cl, 4N. I/I_0	H_2O.	NH_4NO_3, 3.12 N. I/I_0	H_2O.
1,085	85	86	79	87	81	88
1,100	87	88	80	92	81	93
1,113	86	87	79	86	84	86
1,138	81	85	79	84	81	84
1,148	79	82	77	84	78	84
1,158	80	79	74	81	76	81
1,165	76	77	71	77	72	77
1,172	72	71	66	70	67	70
1,179	64	62	59	62	61	62
1,186	51	51	52	50	50	50
1,193	41	43	42	44	40	44
1,200	35	38	37	40	34	40
1,206	37	36	35	37	32	37
1,213	30	34	30	36	32	36
1,220	30	35	29	35	34	35
1,227	30	34	30	35	32	35
1,233	30	33	28	35	31	35
1,241	30	34	29	34	31	34
1,248	31	34	28	33	31	33
1,250	33	34	30	34	32	34
1,255	34	35	30	36	32	36
1,268	34	35	31	37	32	37
1,270	37	37	38	38	38	38
1,285	38	38	33	38	33	38
1,295	39	38	32	38	33	38
1,300	41	38	32	39	34	39
1,308	42	39	32	41	35	41
1,316	41	39	32	40	34	40
1,323	42	37	32	38	34	38
1,330	40	37	32	37	33	37
1,338	40	35	30	35	31	35
1,346	36	33	28	36	30	36
1,352	34	29	26	29	27	29
1,358	29	26	23	27	25	27
1,365	25	22	21	23	21	23
1,372	20	18	17	20	17	20
1,387	13	12	12	11	10	11
1,404	7	7	7	8	7	8
1,418	3	4	4	3	3	3
1,430	2	2	3	2	2	2
1,445	0	0	0	1	1	1

In table 6 the depth of layer of all the solutions was the difference between 21 and 1, *i. e.*, 20 mm. The depth of water was in every case the same as that of the water in the solution in question.

The depth of layer of the solutions given in table 7 was the difference between 11 mm. and 1 mm., *i. e.*, 10 mm., and was only half of that in table 6. The object of this was to bring out more prominently the second water-band. The depth of water used was in every case the same as that of the water in the solution.

TABLE 8.

λ	$CaCl_2$, 5.38 N. I/I_0	H_2O.	$MgCl_2$, 4.96 N. I/I_0	H_2O.	$Al_2(SO_4)_3$, 1.012 N. I/I_0	H_2O.
710	94	98	95	98	95	93
724	92	98	98	98	95	95
741	90	95	95	98	94	93
760	87	94	94	98	92	93
776	88	93	92	97	93	95
798	91	96	93	94	92	90
818	93	99	90	90	93	92
836	92	97	92	95	92	92
855	90	93	91	90	90	91
878	90	90	91	93	91	90
900	89	92	88	92	89	90
922	86	91	88	91	85	86
947	87	84	84	86	82	81
958	78	79	76	78	76	73
964	75	73	82	76	72	66
969	70	68	75	69	68	61
974	65	62	68	65	64	55
979	59	53	61	56	58	48
982	51	49	48	51	53	42
985	48	49	54	45	51	40
991	44	46	48	49	47	39
1,007	42	46	46	48	46	38
1,013	42	46	45	50	46	39
1,019	43	49	44	51	44	40
1,025	47	50	46	44	46	43
1,032	52	53	51	54	46	45
1,037	55	55	52	56	52	50
1,042	58	59	56	58	53	53
1,046	62	62	59	65	55	55
1,059	66	65	63	67	55	58
1,065	71	70	69	70	62	63
1,072	74	72	71	75	60	65
1,078	75	74	71	76	64	69
1,085	78	76	76	79	65	70
1,100	80	77	78	79	67	72
1,113	79	78	80	81	67	74
1,138	77	75	77	78	64	67
1,148	74	71	75	77	60	65
1,158	69	65	73	73	57	55
1,165	66	62	65	65	55	53
1.172	61	52	61	58	50	43
1,179	54	41	52	44	45	34
1,186	42	30	43	32	34	22
1,193	32	21	32	24	25	15
1,200	22	17	23	18	20	12
1,206	16	16	18	17	16	10
1,213	13	15	16	18	14	9
1,220	12	13	14	15	11	10
1,227	12	13	14	16	12	8

The depth of layer of the solutions given in table 8 was the difference between 21 mm. and 1 mm., *i. e.*, 20 mm. The depth of water used in every case was the same as that of the water in the solution.

In table 9 the depth of layer used was the difference between 11 and 1 mm., *i. e.*, 10 mm. The object of using the smaller depth of the solution was to bring out more clearly in the case of hydrated salts the second water-band.

When salts which are strongly hydrated in aqueous solution are not very concentrated, the difference between the transparency of the salt solution and that of water of the same depth of layer as the water in the solution is not so pronounced. This is what would be expected, since the total amount of water combined with the dissolved salt increases with the concentration of the solution. The data given in table 10 bring out this fact.

TABLE 9.

λ	$CaCl_2$, 5.38 N. I/I_0	H_2O.	$MgCl_2$, 4.96 N. I/I_0	H_2O.	$Al_2(SO_4)_3$, 1.02 N. I/I_0	H_2O.
1,085	84	84	82	84	79	82
1,100	84	84	83	84	78	81
1,113	84	86	83	84	78	84
1,138	86	85	82	83	77	83
1,148	82	83	79	80	75	80
1,158	80	79	77	77	73	77
1,165	78	76	77	75	70	73
1,172	76	72	74	70	66	69
1,179	72	65	71	64	63	58
1,186	63	55	62	52	55	48
1,193	54	45	56	46	49	39
1,200	45	40	48	42	43	34
1,206	38	39	42	40	38	30
1,213	35	39	39	38	36	29
1,220	33	36	37	38	34	28
1,227	32	36	36	38	32	28
1,233	31	35	34	37	32	28
1,241	32	35	34	34	31	28
1,248	32	35	34	37	31	28
1,250	33	35	34	38	31	28
1,255	33	37	34	38	31	28
1,268	35	38	33	38	30	29
1,270	37	39	34	39	30	30
1,285	38	40	35	40	30	31
1,295	40	40	35	40	30	32
1,300	42	41	36	41	30	32
1,308	42	41	37	42	30	33
1,316	45	41	39	42	30	33
1,323	47	40	39	41	28	33
1,330	46	39	40	40	27	32
1,338	45	37	38	38	27	30
1,346	42	35	38	36	24	27
1,352	40	32	34	33	22	24
1,358	37	29	33	30	20	21
1,365	33	25	29	26	18	19
1,372	29	21	25	22	15	15
1,387	19	13	18	15	10	9
1,404	12	10	12	11	7	5
1,418	7	6	7	9	4	3
1,430	3	3	4	3	2	2
1,445	2	1	1	1	1	1

The depth of layer of the different solutions for which the results are recorded in table 10 was the difference between 21 and 1 mm., *i. e.*, 20 mm. The results are, therefore, comparable with those recorded in table 8, the difference being a difference in the concentrations of the solutions used. The difference between the transmission of the solution and that of water at the same depth as the water in the solution is very much less for the more

TABLE 10.

λ	$CaCl_2$ 2.69 N. I/I_0	H_2O.	$MgCl_2$ 2.48 N. I/I_0	H_2O.	$Al_2(SO_4)_3$ 0.508 N. I/I_0	H_2O.
710	96	94	95	95	97	96
724	95	96	93	96	98	96
741	95	95	90	95	95	93
760	94	96	92	95	95	95
776	93	97	93	95	95	95
798	90	98	91	95	96	96
818	93	97	91	93	95	96
836	91	96	89	93	93	95
855	91	92	88	92	92	92
878	90	92	84	90	90	91
900	88	90	84	88	89	86
922	89	92	81	86	82	85
947	82	86	78	83	78	80
958	75	79	72	76	73	75
964	70	74	70	73	68	69
969	65	69	62	64	62	62
974	58	61	58	58	57	54
979	50	52	50	51	50	46
982	44	47	46	46	46	42
985	40	43	42	43	43	40
991	39	41	40	41	41	39
1,007	38	40	41	42	40	40
1,013	39	42	40	44	40	40
1,019	40	43	40	44	41	41
1,025	43	45	44	41	43	43
1,032	45	47	47	44	45	46
1,037	48	50	50	46	47	48
1,042	51	52	52	48	49	49
1,046	56	56	56	54	53	54
1,059	61	59	58	55	60	59
1,065	65	64	64	62	59	62
1,072	69	67	67	64	63	65
1,078	70	69	69	67	65	69
1,085	72	72	72	68	68	72
1,100	73	73	73	71	69	73
1,113	72	74	74	72	68	74
1,138	72	74	74	70	67	72
1,148	66	69	69	67	64	67
1,158	67	62	62	60	58	62
1,165	57	58	58	58	54	54
1,172	52	51	53	52	47	46
1,179	46	39	42	42	39	35
1,186	30	27	31	27	28	25
1,193	20	19	21	20	20	16
1,200	13	14	15	15	14	12
1,206	12	11	12	13	12	10
1,203	11	11	12	12	11	10
1,220	11	10	11	11	11	10
1,227	10	9	10	10	10	9

dilute than for the more concentrated solutions; this is what would be expected in terms of the solvate theory applied to the phenomenon in question.

Considerable work was done in *comparing directly* the transmission of a solution and that of water having the same depth as the water in the solution in question. The deflection of the radiomicrometer as given by the solution is in the column marked "Deflection of solution," and the deflection as given by water having the same depth as water in the solution is given in column "Deflection of water."

TABLE 11.

λ	Deflection of solution of $Al_2(SO_4)_3$.	Deflection of water.	Deflection of solution of KCl.	Deflection of water.	λ	Deflection of solution of $Al_2(SO_4)_3$.	Deflection of water.	Deflection of solution of KCl.	Deflection of water.
710	50	51	53	53	1,037	91	84	112	108
724	58	58	56	56	1,042	92	92	119	116
741	62	63	67	68	1,046	99	99	125	120
760	72	72	77	77	1,059	105	105	141	136
776	75	76	88	90	1,065	109	112	150	145
798	83	83	98	99	1,072	114	119	159	153
818	82	82	108	109	1,078	118	125	164	158
836	93	94	116	116	1,085	122	132	168	164
855	97	97	124	124	1,100	128	140	176	172
878	105	105	129	130	1,113	129	142	178	175
900	105	105	140	138	1,138	127	142	174	170
922	112	112	140	140	1,148	123	131	164	162
947	113	113	142	142	1,158	112	118	161	159
958	109	106	136	136	1,165	108	111	157	154
964	107	100	129	125	1,172	99	94	132	126
969	104	93	118	116	1,179	87	74	107	100
974	98	83	108	106	1,186	68	49	73	66
979	93	73	92	92	1,193	54	35	50	48
982	82	66	83	83	1,200	42	26	34	36
985	80	64	78	80	1,206	35	23	29	32
991	78	62	78	80	1,213	30	21	25	30
1,007	78	65	78	81	1,220	28	20	24	29
1,013	74	65	81	85	1,227	26	19	24	28
1,019	77	68	84	88	1,241	24	19	23	26
1,025	80	75	96	96	1,255	23	18	25	27
1,032	84	77	100	101					

The results obtained for aluminium sulphate having a concentration 1.02 N, and for potassium chloride 4 N are given in table 11. The depth of solution used was 20 mm., and the depth of water that of the water in the solutions in question.

Duplicate measurements were made with the radiomicrometer for nearly every solution of all the substances worked with at the various wave-lengths studied. It was found that readings for the different solutions of the same substance having the same concentration were, for a given wave-length, different from one another to the extent of somewhat less than 2 per cent. From this it seems fair to assume that the error in our work was not greater than 2 per cent.

DISCUSSION OF THE RESULTS.

An examination of the tables of data for potassium chloride, ammonium chloride, and ammonium nitrate—that is, for those substances which, in aqueous solutions, combined with very little water, as was demonstrated by the freezing-point method, shows that for all wave-lengths studied the solution, and water of the same depth as the water in the solution, have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent. When we began this work we supposed, as others had done, that the water in the solution, whether it was combined with the dissolved substance or not, would have the same power to absorb light as so much pure solvent water. We shall now see that such is not the case.

The results for the above-named substances were not plotted in the form of curves, since the curve for water and for the solution would practically coincide with one another, the dissolved substance having very little absorption over the region of wave-lengths studied in this investigation.

When we turn to the data in tables 8 and 9 very different relations manifest themselves. These are the data for calcium chloride, magnesium chloride, and aluminium sulphate, that is, for salts which, in aqueous solution, are strongly hydrated, as was shown by the earlier work in this laboratory.[1] The solution in these cases is often more transparent than the same amount of water that is contained in the solution.

That these relations may appear the more clearly, the results obtained for the above-named salts are plotted as curves in figs. 12 to 17. Fig. 12 is the curve for calcium chloride having a depth of 20 mm. This was obtained by dividing the deflection produced by 21 mm. of the solution by that produced by 1 mm. of the solution. On the same sheet we have the curve for water having a depth equal to that of the water in the calcium chloride. This curve for water was also obtained by the "differential" method, *i. e.*, by dividing the deflections produced by the deeper solution by those obtained with the more shallow solution, the difference in the depths of water in the two cases being just equal to the depth of water in 20 mm. of the solution in question. Fig. 13 is the curve for calcium chloride with a depth of layer of 10 mm. $(11-1)$. The data from which the curve was plotted are contained in table 9. The smaller depth of solution was used, so that the water-band between 1.2μ and 1.3μ would come out more distinctly. The results for this solution, like those for all the others, are compared with the absorption of a depth of water equal to that of the water in the solution. The absorption of the water, in this as in all other cases, was obtained by the "differential" method.

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[1] Carn. Inst. Wash. Pub. **60.**

Fig. 14 is the curve for magnesium chloride having a depth of $21-1=20$ mm., and the corresponding water-curve. The data from which these curves are plotted are given in table 8.

Fig. 15 is the curve for magnesium chloride having a depth of 1 cm., also obtained by the "differential" method. These data are taken from table 9.

Fig. 16 is the curve for aluminium sulphate having a depth of $21-1=20$ mm., and the corresponding absorption curve for water.

Fig. 17 is the curve for aluminium sulphate having a depth of $11-1=10$ mm., and the corresponding water-curve.

Fig. 12 shows the relative absorption of water and of the solution of calcium chloride having a concentration of 5.38 normal and a depth of 20 mm. The corresponding water-curve is marked throughout by the symbol H_2O. The solution is the more transparent from 0.9μ to nearly 1μ. The water then becomes the more transparent over a short region of wave-lengths. From 1.05μ to 1.2μ the solution is the more transparent. In this region the solution becomes as much as 25 per cent more transparent than the pure water, as can be seen by comparing the points on the "water" curve with the corresponding points on the curve for the solution which are vertically above the points on the water-curve. The water becomes appreciably more transparent only at and near the bottom of the "water-band" having a wave-length of approximately 1μ. This is the effect that we would expect to get if the dissolved substance exerted a "damping" effect on the absorption of light by water.

It will be recalled that the salts which do not form hydrates show, in aqueous solution, practically the same absorption as the corresponding amount of water. It would, therefore, seem reasonable to account for the differences in the case of nonhydrating and strongly hydrating salts as due to the water of hydration, or the water that, in this case, is combined with the calcium chloride.

The curves in fig. 13 are for a smaller depth of the same solution of calcium chloride. This figure brings out the same general relations as was shown in fig. 12. The water-curve in the region 1.25μ is above that of the solution, showing that water in this region for the shallower depths of solution is more transparent than the solution. The additional feature brought out by this figure is the water-band in the region 1.4 to 1.5μ. After the first-named water-band is passed the solution becomes more transparent than the water and remains so until the wave-length 1.42 is reached. Here both the solution and the water are practically opaque, as is shown by both the curves approaching the abscissas.

The curve for magnesium chloride having a depth of 20 mm. is almost exactly a duplicate of that for calcium chloride having the same depth. Practically the only difference worthy of mention is in the region from 1.0μ to 1.1μ. In the case of magnesium chloride the water remains the more transparent over this region of wave-lengths. In the case of calcium chloride the solution is the more transparent over this region. The difference in the transparency of the water and the solution throughout this region is, however, not very great. From 1.1μ towards the longer wave-lengths, as we come down the descending arm of the curve towards the second water-band, the water in the case of the magnesium chloride (as in the case of calcium chloride) becomes much more opaque than the solution, the differences here being of the same order of magnitude as those with calcium chloride.

Fig. 15 gives the results for magnesium chloride with a depth of layer of 1 cm., and the same relations hold as in fig. 14, for the relative transparency of the water and of the solution. The water becomes the more transparent from 1.22μ to 1.34μ. For the longer wave-lengths the solution becomes more transparent until the region 1.41μ is passed. For wave-lengths longer than 1.41μ the transmission of both solution and water is practically zero—that is, they both become opaque to the longer wave-lengths.

The results in fig. 16 bring out some new features of interest and importance. These are the results that were obtained with aluminium sulphate. The new feature shown by the curve for aluminium sulphate, as compared with those for calcium chloride and magnesium chloride, is that at the minimum of the curve corresponding to wave-length 1μ the solution is more transparent than the corresponding water. Beyond the wave-length 1.04μ the water becomes the more transparent with aluminium sulphate as with magnesium chloride. Beyond the wave-length 1.17μ the solution becomes more transparent in this case as with magnesium chloride and calcium chloride.

If we turn to fig. 17 the relations are as follows. In the region of 1.2μ the water is the more opaque. From 1.29μ to 1.36μ the water becomes the more transparent. From 1.36μ to the longest wave-length studied, the solution again becomes more transparent than the corresponding layer of water.

An examination of all the results thus far obtained bearing on this problem leads us to conclude that the greater transparency of the solution as compared with the water in the solution must be due to some action of the dissolved substance on the solvent water. The question remains, what is this action?

EXPLANATION OF THE RESULTS.

We have seen from our earlier work on the absorption spectra of solutions, which has been in progress in this laboratory continuously for the past eight years, that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first shown by Jones and Anderson,[1] and a large number of examples of this effect have since been found by Jones and Strong.[2] We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts which were brought to light for the first time by our investigations of the absorption spectra of solutions. Many of the phenomena which were thus explained, it seemed, could not be

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[1] Carn. Inst. Wash. Pub. **110**.

[2] Carn. Inst. Wash. Pubs. **130** and **160**.

explained in terms of any other suggestion that has thus far been made. In a word, the solvate theory of solution as proposed by Jones about a dozen years ago,[1] to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions which we use in the laboratory, and not simply a theory of ideal solutions as the theory of electrolytic dissociation alone must be regarded, has served good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions of dissolved substances.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution, is the same almost to within the limit of experimental error.

For those substances which have been shown to form complex hydrates, however, the absorption of light by their solutions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution—or, in other words, a solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence that water in the solution is different from pure, free water. This difference, it seems to us, can be readily accounted for by the theory that a part of the water present in the solution is in combination with the dissolved substance.

We have carried out similar investigations with aluminium nitrate, but the concentration of the strongest solution that could be obtained was not sufficiently great to show the phenomenon in question. We therefore do not incorporate the results obtained with this substance. That the solutions must be very concentrated to show clearly the phenomenon with which we are dealing is seen from the results given in table 10. Here the solutions of the three salts in question that were used are more dilute than those for which the results are tabulated in tables 8 and 9. An examination of table 10 will show that the phenomenon in question does not manifest itself to anything like the same extent as with the more concentrated solutions. This is exactly what we would expect in terms of the solvate theory of solutions. The more concentrated the solution the larger the total amount of the water present combined with the dissolved substance. If combination between water and the dissolved substance explains the facts recorded in this paper, then the larger the amount of water present that is combined with the dissolved substance the more pronounced the phenomenon in question.

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[1] Amer. Chem. Journ., **23**, 89 (1900).

The results obtained with aluminium sulphate bring out the same facts shown by calcium chloride and magnesium chloride, and also that water is more transparent in the region 1.1μ and more opaque at 1μ. That the sulphate should not agree throughout with the chlorides is really not surprising, since the sulphates show abnormal results in almost every particular. This is probably due, in part at least, to the large amount of polymerization which the sulphate molecules in general undergo in the presence of even water as a solvent. It should also be remembered in the present connection that while calcium chloride and magnesium chloride crystallize with only 6 molecules of water, and are therefore only largely hydrated, aluminium sulphate crystallizes with 18 molecules of water and is therefore very largely hydrated.

The results in table 11 are the radiomicrometer deflections for a solution of aluminium sulphate and those for water having the same depth as the water in the solution in question, and the corresponding data for potassium chloride. A comparison of the two columns for potassium chloride and its corresponding water shows that the two are almost equally transparent to all the wave-lengths studied.

A comparison of the aluminium sulphate with its corresponding water brings out the phenomenon that we are now discussing in a very pronounced manner.

One other relation of a general character should be pointed out. The curves (figs. 12 to 17) show that the addition of salt to water shifts the absorption towards the longer wave-lengths. This is analogous to what had already been found by Jones and Uhler,[1] Jones and Anderson,[2] Jones and

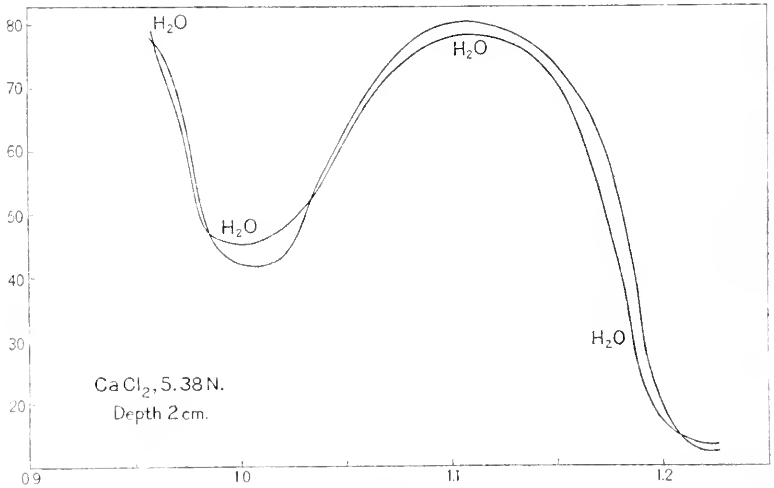

FIG. 12.

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[1] Carn. Inst. Wash. Pub. 60.

[2] Carn. Inst. Wash. Pub. 110.

Strong,[1] and Guy and Jones,[2] when the absorption of salts as affected by the water present was studied. It was found that rise in temperature and increase in the concentration of the solution both tended to shift the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and the increase in the concentration of the solution tended to simplify the hydrates in combination with the particles of the salt. The resonator within this simplified system seems to vibrate so as to shift the absorption bands towards the red.

The effect of the salt on the absorption of the water is the same as that of rise of temperature and increase of concentration on the absorption of the dissolved substance. We would naturally look for a similar explanation of the two sets of phenomena. It has been suggested by Dr. Guy, that the effect of the salt on the absorption of light by water may be due to the breaking down of the associated molecules of water by the dissolved substance. This would be in keeping with the fact established by Jones and Murray,[3] that one associated substance when dissolved in another associated substance diminishes its association.

In terms of this explanation, however, it is a little difficult to see why nonhydrated salts, such as were used in this work, do not also diminish the association of water and cause a shifting of its absorption bands towards the longer wave-lengths. It may be that the effect of the dissolved substance in breaking down the association of the water is pronounced only in the case of water of hydration or the water that is combined with the dissolved substance, and that the explanation offered above is fundamentally correct.

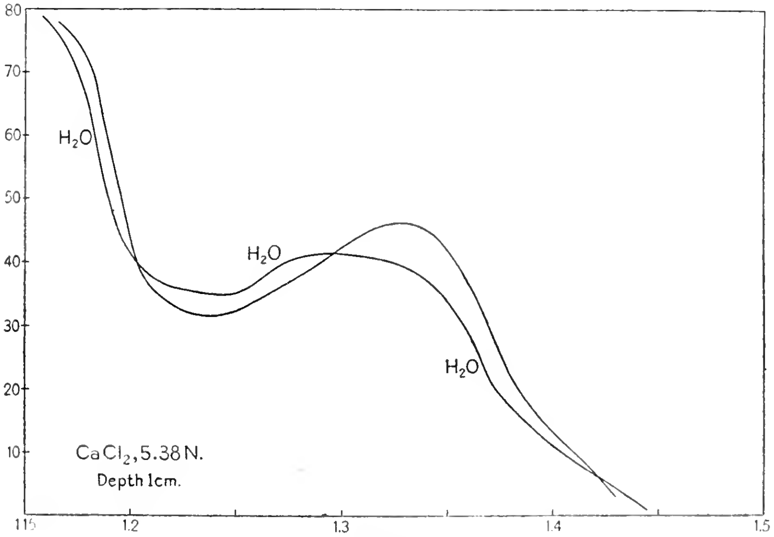

Fig. 13.

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[1] Carn. Inst. Wash. Pubs. **130** and **160**.

[2] Amer. Chem. Journ., **49**, 1 (1913).

[3] Amer. Chem. Journ., **30**, 193 (1903).

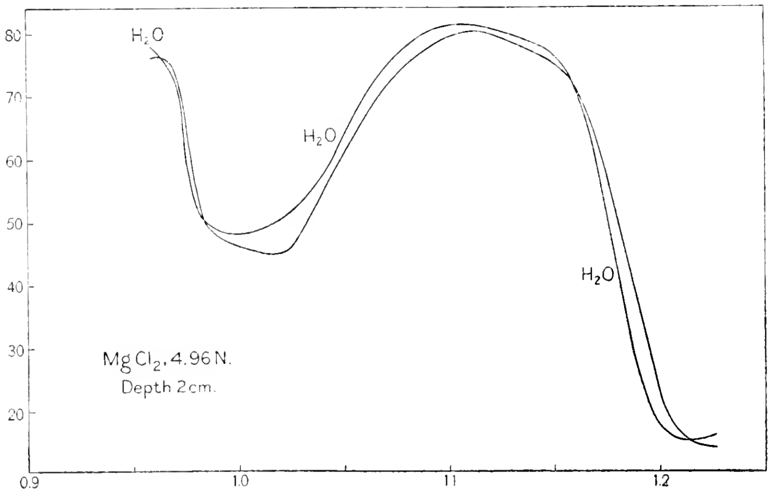
80
70
60
50
40
30
20
0.9
1.0
1.1
1.2
H_2O
H_2O
H_2O
$MgCl_2$, 4.96 N.
Depth 2cm.

FIG. 14.

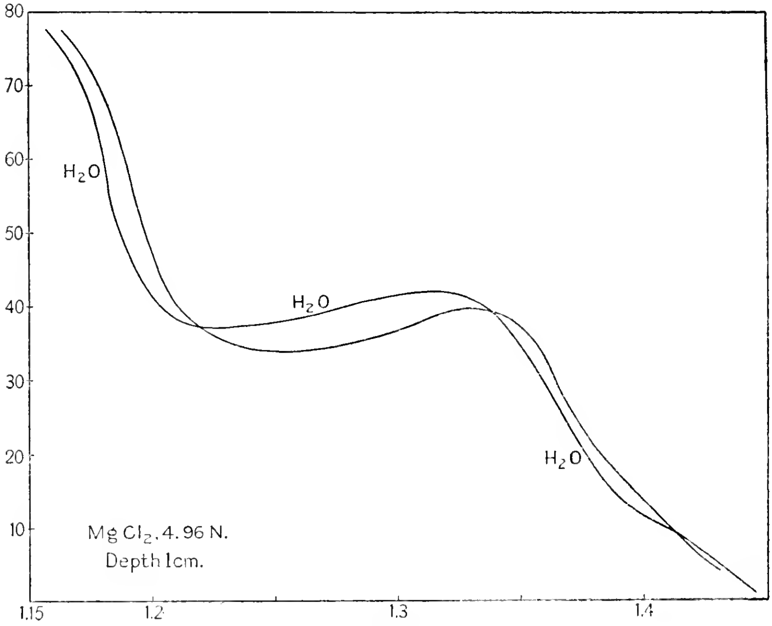
80
70
60
50
40
30
20
10
1.15
1.2
1.3
1.4
H_2O
H_2O
H_2O
$MgCl_2$, 4.96 N.
Depth 1cm.

FIG. 15.

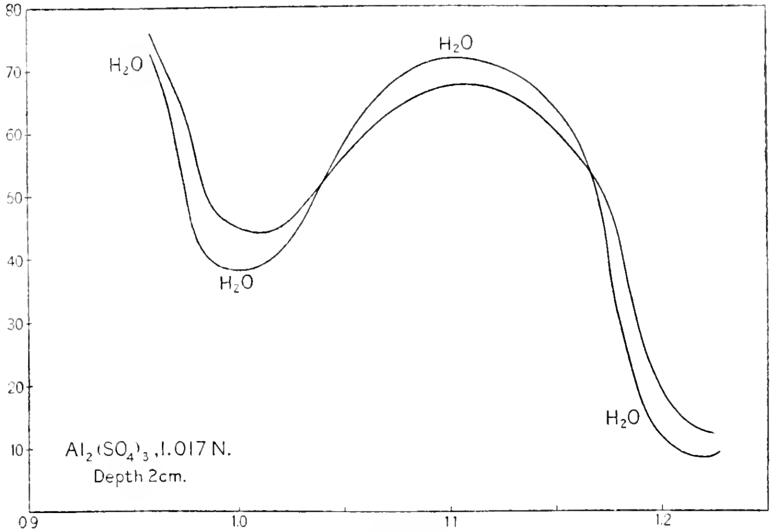
80
70
60
50
40
30
20
10
0.9
1.0
1.1
1.2
H_2O
H_2O
H_2O
H_2O
$Al_2(SO_4)_3$, 1.017 N.
Depth 2cm.

FIG. 16.

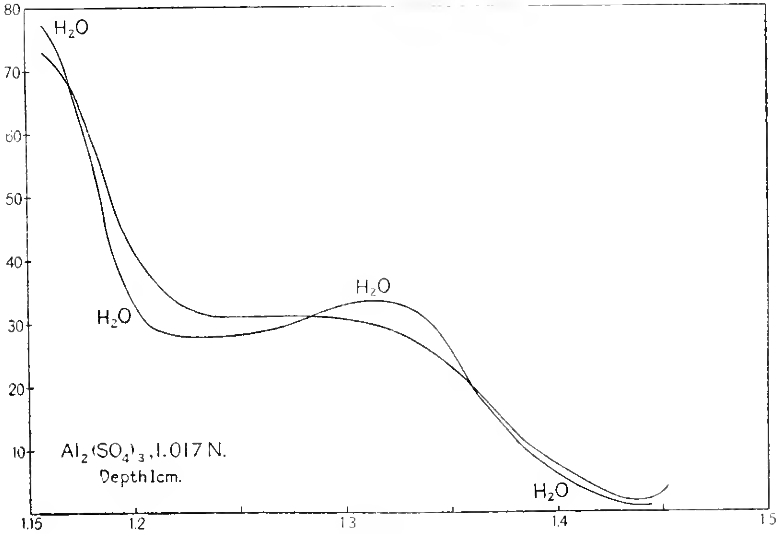
80
70
60
50
40
30
20
10
1.15
1.2
1.3
1.4
1.5
H_2O
H_2O
H_2O
H_2O
$Al_2(SO_4)_3$, 1.017 N.
Depth 1cm.

FIG. 17.

CHAPTER VI.

ABSORPTION SPECTRA OF A NUMBER OF SALTS AS MEASURED BY MEANS OF THE RADIOMICROMETER.

The results tabulated and discussed in Chapters IV and V, which are concerned with the energy measurements of the absorption spectra of solutions by means of the radiomicrometer, were made by comparing the intensity of a given source of light (after passing through the solution) with the intensity of the same source of light after passing through an equal depth of water. In a word, the depths of cells in each case were the same. As has already been stated, a cell whose depth was 1 cm. was filled with the solution and placed in the path of the beam of light and the deflection of the instrument noted; then a cell of the same depth was filled with the solvent and interposed in exactly the same position as the former cell, and the deflection of the instrument again noted. Denoting the former by I and the latter by I_0 we get the ratio I/I_0, which represents the percentage transmission of the solution as compared with water. Such a procedure was repeated at frequent intervals throughout the spectrum, locating a series of points through which the transmission curves could be drawn.

Certain phenomena presented themselves throughout the course of this investigation, which suggested a more careful study of some of the absorption bands located in the infra-red portion of the spectrum; and at the same time it was thought advisable to map the absorption spectra of some of the more common salts of cobalt, nickel, etc., in terms of Beer's law; since up to the time of this investigation no satisfactory quantitative study of the infra-red spectrum of these salts had appeared.

In order to make a careful study of the exact intensity of the various portions of any given bands, it is clear that we are dealing with a much more complex and intricate problem than simply with the location of the band; and on this account it was necessary to improve our apparatus and at the same time to exert more care, if possible, in carrying out any given operation.

It was early found that if we desired to study that region of the infra-red spectrum in which water had considerable absorption, we must not compare our solutions with an equal depth of layer of water, as noted above; but with a depth of layer equal to the water in the solution, which in the most concentrated solutions was much less than the actual depth of the cell containing the solution—a part of the cell's depth being occupied by the dissolved substance. Even when such a correction was made, it was found that for a given wave-length, in the water absorption bands, the solution gave greater deflections than did the solvent, *i. e.*, that in such regions the solution was actually more transparent than an equivalent depth of water.

Remembering that the solutions with which we were then working, *i. e.*, solutions of salts of neodymium and praseodymium, were strongly hydrated, it was thought that in view of the fact that at least a part, and in the concentrated solutions a considerable part of the water present was there as water of hydration, it would be advisable to study the effect of colorless hydrated salts upon the absorption of water.

This chapter of our work has been sufficiently discussed elsewhere in this monograph, and will be taken up here only to state that these experiments showed clearly that there were many variables to be considered. We have, first, the effect of the solvent on the absorption of the solute; and, secondly, the effect of the solute upon the absorption of the solvent. In addition to these, there was, of course, the absorption of the solvent and the solute independently. Such being the case, we would not be obtaining comparable results for various dilutions of any solutions in terms of Beer's law, even if we did compare each dilution with an equivalent amount of water. It is clear that by so doing we would not be getting comparable ratios, since the solvent and the solute were mutually affecting each other's absorption; and this effect would not be the same for the different dilutions of the same salt.

MODE OF PROCEDURE.

It is, however, possible to get the exact transmission of a given depth of solution by a method of differentiation. If we placed in cell A 11 mm. of a solution and in cell B 1 mm. of the same solution, the ratio representing the respective deflections of the instrument, when these cells are alternately placed in the path of the beam of light, should give the absorption or transmission of $(11-1)$ or 10 mm. of the solution.

Since, if we let A be the percentage absorption of a unit's depth of layer of the solution, and I_0 the initial intensity of the light impinging upon the surface, we get

$AI_0 =$ amount of light absorbed by first unit layer of the solution. Then,

$$I_0 - I_0A = I_0(1-A) = \text{ light incident upon surface of second unit layer.}$$

Denoting this by I_1, we get

$$I_1 = I_0 - I_0A = I_0(1-A) \text{ or } \frac{I_1}{I_0} = 1 - A$$

Considering again the third unit layer, we get, by similar reasoning,

$$I_1 - I_1A = \text{ amount of light incident upon its surface.}$$

Denoting this by I_2, we get

$$I_2 = I_1 - I_1A = I_1(1-A)$$

but $I_1 = I_0(1-A)$; therefore, $I_2 = I_0(1-A)^2$; hence $I_n = I_0(1-A)^n$. We can then, by this process, obtain transmissions for given depths of solution and for varying concentrations. This was the method adopted throughout this chapter of the work.

DESCRIPTION OF CELLS USED.

In all cases where we were dealing with different depths of layer, it was necessary to use cells adjustable in length. A very satisfactory form of cell was devised and used throughout the latter part of this work. It consisted essentially of two brass cylinders telescoping neatly into each other. The external diameter of the outside cylinder was about $2\frac{1}{2}$ inches, and the thickness of the walls was in every case about 2 mm., which was sufficient to withstand handling without danger of changing the shape of the cell. Into the ends of each cylinder there was sealed, by means of Wood's metal, a glass plate about 1 mm. thick, made of the very best optical glass. In all cases the glass plates were so nearly parallel as to show interference fringes; and both cells gave the same deflections, either when empty or filled with the same solution and placed in the path of the light before the radiomicrometer.

After adjusting the glass ends and fixing them securely by means of Wood's metal, the entire cell was first plated with silver, being taken out of the plating-bath from time to time and polished to a bright surface with the finest crocus paper. On top of this silver coating a heavy plating of gold was deposited. The distance between the glass plates fastened to the ends of the telescoping cylinders, which determined the depth of layer of solution used, was in all cases fixed by gold-plated washers, whose thickness had been accurately measured to 0.001 inch by means of a vernier caliper.

Before any series of readings was made, the positions of the two cells was so adjusted in the sliding carriage as to give equal deflections, when alternately placed in the same position before the radiomicrometer, in that part of the spectrum where neither the solute nor solvent had any absorption; and from time to time throughout the experiment duplicate readings were made on this point to see that the cells had not changed their relative positions. In case any change was noted, a duplicate series of readings was always made. Such readings upon the same cell usually agreed to about one division of the scale, which corresponded to about 1 to 2 per cent, depending upon the throw of the instrument. In the midst of the very intense absorption bands,where the deflections of the instrument were small, reaching zero at many points, the error resulting from any drift in the instrument or reading of the scale was greater than the mean error given above.

In nearly all cases new solutions were made up and the results duplicated, so that the tables and curves below represent a mean of several series of readings. In most cases the agreement was very satisfactory, usually the difference not being over 3 per cent.

Since any change in the position of the prism was a determining factor in the portion of the spectrum which fell upon the thermo-junction, and since in the very intense, sharp bands of the neodymium salts any slight change in the position of the prism would make a great difference in the final results, great care had to be exerted in setting the head reading of the spectroscope. Such difficulties were not met with in solutions where the absorption bands were broad and diffuse, as in salts of cobalt, nickel, etc.

In studying the changes which might occur in any band, it is of course necessary that all conditions be as nearly as possible the same. One of the most important factors here is that of the width of the slits of the spectroscope. With those solutions whose absorption bands are broad and diffuse, not having such well-defined edges as with the salts of neodymium and praseodymium, this is not such a determining factor. Should the band be very narrow—say approaching that of the width of the slit necessary to be used in order to secure reasonable deflections of the instrument—it is seen that any slight change in the slit will make a large difference in the amount of light falling on the thermal-junction.

Considering a concrete example, let us suppose that the slit-width is just equal to that of the absorption band, under a given dispersion. If, now, the band and the slit exactly coincide, it is evident that no light will be falling upon the junction, this being indicated by zero deflection of the instrument. If, on the other hand, the slit is slightly wider than the band, some light will enter around the edges of the band; and, though the narrow band may actually have complete absorption at a given point, it would not be indicated by the instrument, since some light is entering around the edges of the band.

Denoting the deflection of the instrument for a cell of 2 mm. depth of a solution of x concentration by A, and the same for 1 mm. of the same solution by B, we get, by the differential method discussed above, the ratio A/B for the intensity of the light transmitted by $(2-1)$ or 1 mm. of the solution in question.

By a similar reasoning we get the ratio A'/B' for the value of the transmission of a solution of concentration $\frac{x}{20}$, using absorbing layers 21 mm. and 1 mm., respectively. While such a method is theoretically and mathematically correct for infinitely narrow slit-widths, and practically so for bands which are wide in comparison with the necessary slit-widths, yet in the case of very sharp, narrow neodymium bands it has been found not to give comparable results. The reason for this is clearly seen in the light of the facts discussed above.

Let us consider the ratios A/B and A'/B'. In the first case we are dealing with concentrated solutions, where the absorption bands are broad; hence B is small, and, in case the slit-width is comparable with the width of the absorption band, B will be very much smaller than B', since B' is only 1 mm. of an $\frac{x}{20}$ concentration solution. In a word, B, which is 1 mm. of the more concentrated solution, has 20 times the number of absorbers as has an equal depth represented by B', and a decrease in the denominator of the fraction means an increase in its value.

While the ratios A/B and A'/B' give the transmissions for 1 mm. of a solution of concentration x, and 20 mm. of a solution of concentration $\frac{x}{20}$ respectively, provided the slits are narrow; yet in the visible part of the spectrum, where such wide slits had to be used on account of the small amounts of energy in this region, these ratios are not comparable.

For this reason we have confined the larger part of our work on neodymium compounds almost entirely to wave-lengths greater than 0.7μ. In all the following tables and curves representing these data, constant slit-widths of 0.2 mm. have been used. This was the minimum width which could be employed, in order to get reasonable deflections throughout the spectrum from 0.7μ to 1μ. Experiments have shown that any error resulting from slit-widths would not amount to more than 3 or 4 per cent throughout this region.

The source of light was, as in the previous chapters, a Nernst glower carrying about 1.2 amperes, and the current kept constant by means of an adjustable slide-wire resistance. The source of current was a large number of storage cells, and this was never allowed to vary over 0.01 ampere. Great care was exerted in keeping the current constant while obtaining a single ratio, since this is really the only time in which a slight change in current density was dangerous.

DISCUSSION OF TABLES AND CURVES.

NEODYMIUM CHLORIDE IN WATER.

Table 12 gives the observed transmissions of solutions of neodymium chloride in water. In all the tables the following four dilutions have been studied, the depths of cell being, generally, 2.5, 5, 10, and 20 mm., respectively; and the concentrations being made so as to keep $n \times d = k$. In column 1 of each table there is given λ, taken at such intervals as the solution in question required. In those portions of the spectrum where the transmission was complete, or very nearly so, these intervals were greater than in those regions where there were absorption bands.

Reading from left to right in this table, beginning with column 2, there are given the absorptions for solutions of the following concentrations: 2.141, 1.07, 0.535, and 0.267 normal, respectively; the corresponding depths of absorbing layer being 2.5, 5, 10, and 20 mm., respectively. In every case the transmission was obtained from the ratio $\frac{x+1}{1}$, where x is 2.5, 5, 10, and 20 mm., respectively.

In all cases the concentrated mother-solution was carefully made up, its concentration determined by a gravimetric precipitation of the metal, and the succeeding solutions made by diluting measured parts of the mother-solution.

Observations are given here over only that portion of the infra-red spectrum from $\lambda 6800$ to $\lambda 10000$. It is in this region that the most pronounced neodymium bands occur. It was thought advisable not to go further into the infra-red, since beyond 1μ the general absorption due to the solvent is very marked. This would, of course, interfere with a quantitative study of any band occurring in this region, since it is impossible to separate the two absorptions, previous work having shown that they are not additive.

The work in the visible region of the spectrum was limited by the slit-widths necessary to be used, which has been mentioned and discussed above. We have rather chosen a limited portion of the infra-red, over which we could work without altering either the intensity of the light or the slit-width, which was in all cases 0.2 mm.

The curves representing table 12 are given in figs. 18 to 21 inclusive. The percentages of transmission are plotted as ordinates, while the wave-lengths are given as abscissæ. An examination of these curves shows three pronounced minima, representing the three absorption bands, with their centers near λ7300,[1] λ7950, and λ8700, and less-marked bands near λ7150 and λ9000. The latter of these small bands is possibly due in part to the absorption of the solvent; but since its intensity does not increase markedly with dilution, it is more probably a doublet. Considering the curves representing all four dilutions, we see that the λ7300 and λ7900 bands show complete absorption over a considerable range of wave-lengths, and any change in intensity could not be very noticeable. The λ8700 band, however, has its minima gradually lowered as we pass from curve 18 to curve 21, *i. e.*, in the direction of increasing dilution. This phenomenon has been noted elsewhere in this monograph, and a possible explanation of it based upon a theory of resonance suggested. A closer and more exact study has shown that, although the phenomenon is a real one, yet it is probable that it may

TABLE 12.—*Percentage Transmission of Neodymium Chloride Solutions.*

λ	D.=2.5mm. C.=2.141N.	D.=5mm. C.=1.071.	D.=10mm. C.=0.535.	D.=20mm. C.=0.267.	λ	D.=2.5mm. C.=2.141N.	D.=5mm. C.=1.071.	D.=10mm. C.=0.535.	D.=20mm. C.=0.267.
686	93	88	88	86	800	15	10	8	6
693	95	95	95	94	805	24	23	22	18
698	96	96	96	94	809	40	39	38	37
704	96	96	98	94	814	58	58	58	53
708	96	93	95	92	819	80	78	78	76
712	92	93	95	88	825	89	91	91	82
716	88	89	88	85	830	93	92	93	88
720	81	78	81	81	834	94	95	95	88
723	64	62	63	56	839	93	93	93	87
726	32	31	25	23	845	91	92	91	86
730	7	7	5	6	850	87	86	87	78
733	0	0	0	0	856	75	73	71	66
737	0	0	0	0	861	54	46	43	40
741	5	2	1	2	867	29	21	18	16
746	18	14	12	5	872	28	24	23	18
751	36	39	29	28	877	40	39	40	34
755	54	55	52	49	882	53	48	52	47
759	75	74	72	68	888	69	59	60	53
763	85	85	83	81	894	61	59	61	56
767	84	86	85	83	900	67	66	66	59
770	79	81	80	76	906	80	78	79	71
774	67	73	65	61	912	90	92	89	79
779	47	45	45	40	917	96	93	94	86
783	29	27	26	24	923	98	97	96	86
787	22	10	10	7	928	98	96	96	84
791	0	0	0	0	933	98	96	96	81
796	0	0	0	0	938	98	94	90	75

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[1] The wave-lengths in the above and following tables are given, in general, to only three places.

in part be due to the combined effect of the slight water absorption and, even a more important factor, the slit-widths, as discussed above.

The regions of maximum transmission occur near λ7600 and λ8400, and solutions of neodymium chloride become almost completely transparent beyond 1μ, except for the general absorption of the solvent. Slight absorption bands occur in this region, one near 1.5μ, but they are so masked by the intense water absorption that it was found impossible to make a quantitative study of them.

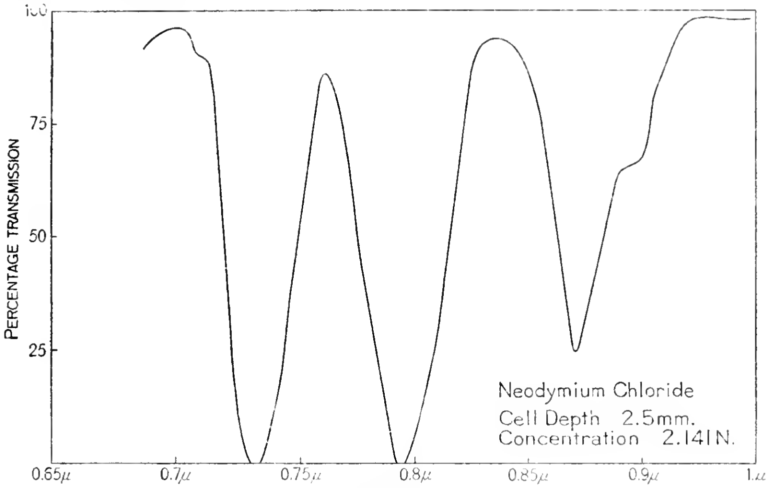

FIG. 18.

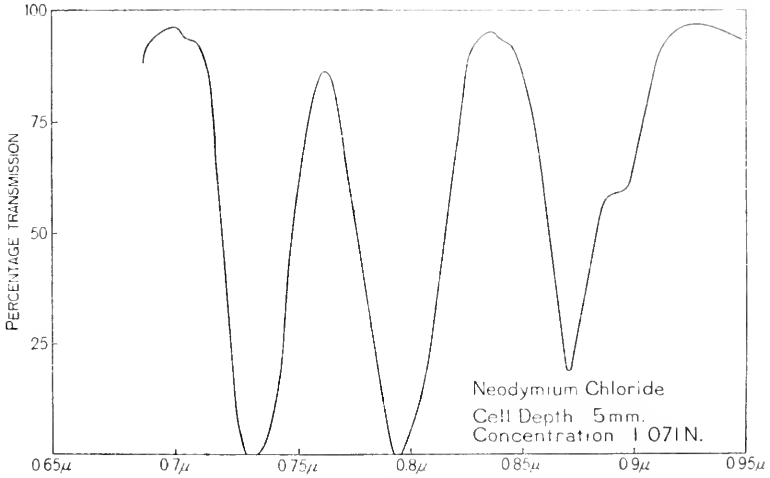

FIG. 19.

From a comprehensive study of the four curves representing the absorption spectra of concentrated solutions of neodymium chloride, it seems probable that Beer's law holds quantitatively for the infra-red region, except for such slight changes as have been fully discussed above.

Since, as mentioned above, the absorption bands with their centers near λ7300 and λ7950, in solutions of such concentrations as are given in table 12, reach complete absorption, and as in such cases it would not be easy to detect any change in their intensity, it was thought advisable to make a study of a series of more dilute solutions of the same salt.

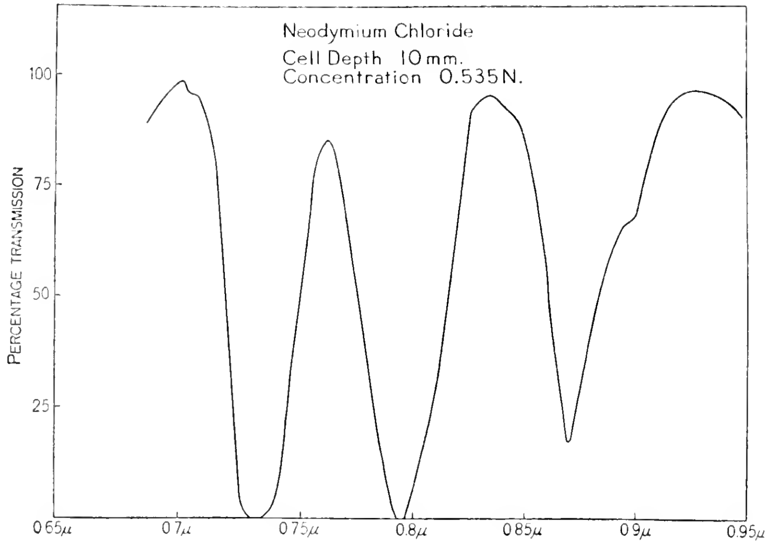

Fig. 20.

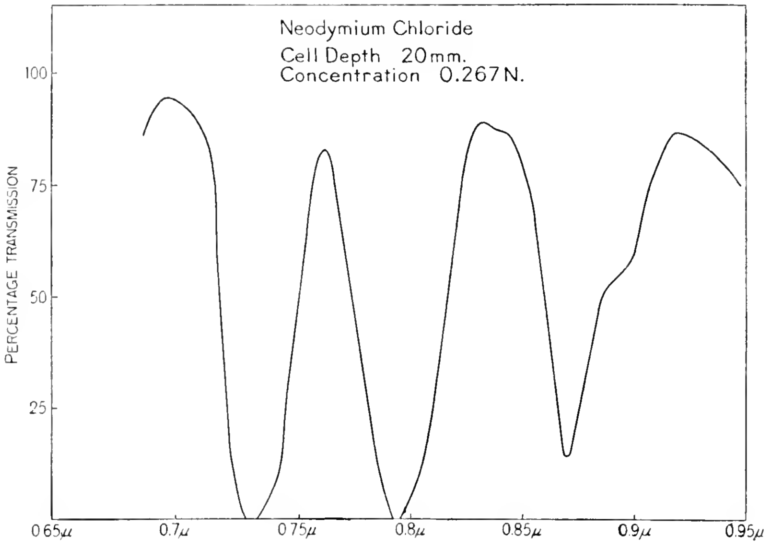

Fig. 21.

The results of this experiment are given in table 13. Reading from left to right, the concentrations are 0.536, 0.267, 0.133, and 0.067 normal, respectively, the corresponding depths of absorbing layers being 2.5, 5, 10, and 20 mm., respectively. Here again it is seen that the conditions of Beer's law are adhered to. The results are graphically represented in figs. 22 to 25, inclusive. These curves show minima in about the same positions as did the curves representing the more concentrated solutions, but since the solutions are more dilute, they are accordingly more transparent; hence the minima in the curves are not so pronounced. The maximal absorption occurring near λ7300 and λ7900 are at about 25 per cent.

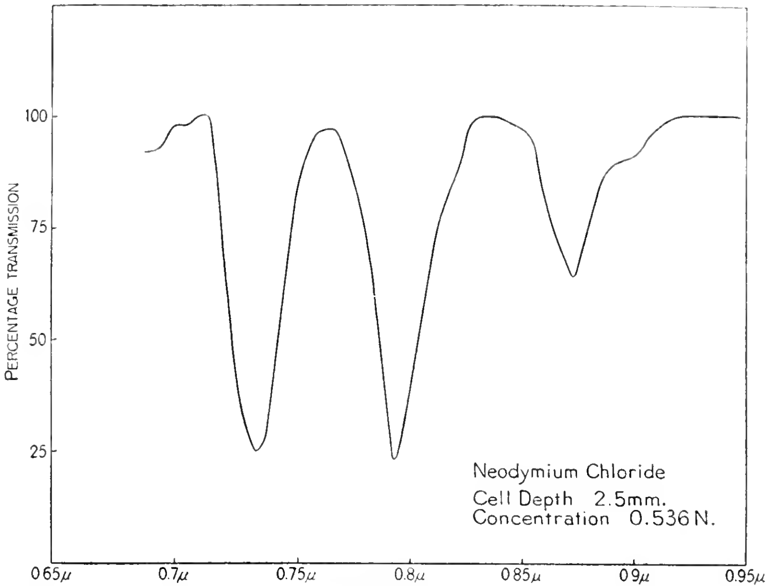

Fig. 22.

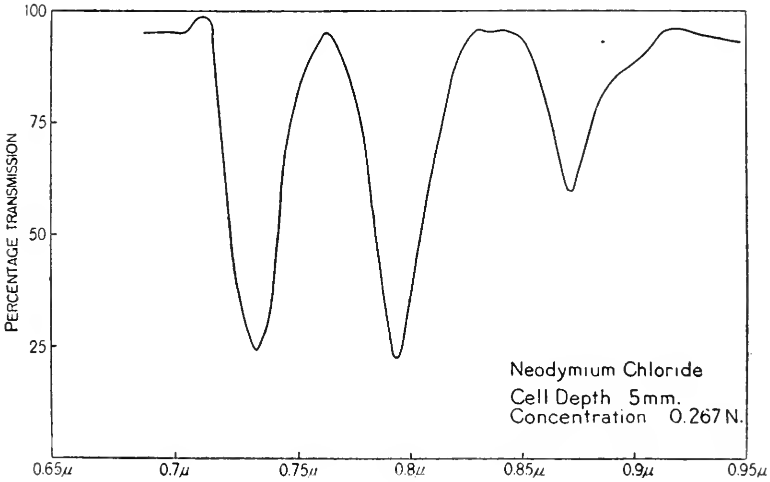

Fig. 23.

It will be noticed that beyond 0.9μ all of the curves drop sharply with dilution, which is due entirely to the increasing absorption of the water.

Figs. 22 to 25, inclusive, show just what might be anticipated from figs. 18 to 21, a lowering of absorption maxima as we pass towards the more dilute solutions. This change is most marked in the λ8700 band, and it is in this region that the absorption of the water is most pronounced, although a 20 mm. layer of water in this region has at no point over 10 per cent absorption. The change in the intensity of the absorption band is greater than this amount, but it seems probable that this, together with the added correction for the slit-widths, may account for the phenomenon, and that Beer's law holds for the dilute solutions of neodymium chloride.

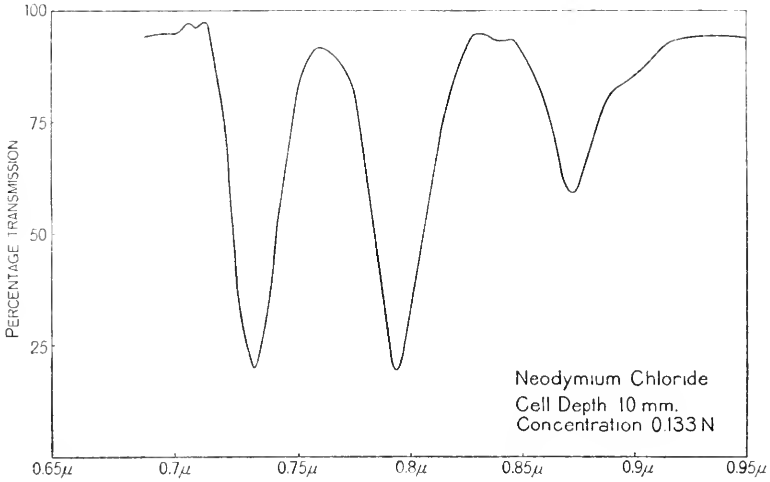

FIG. 24.

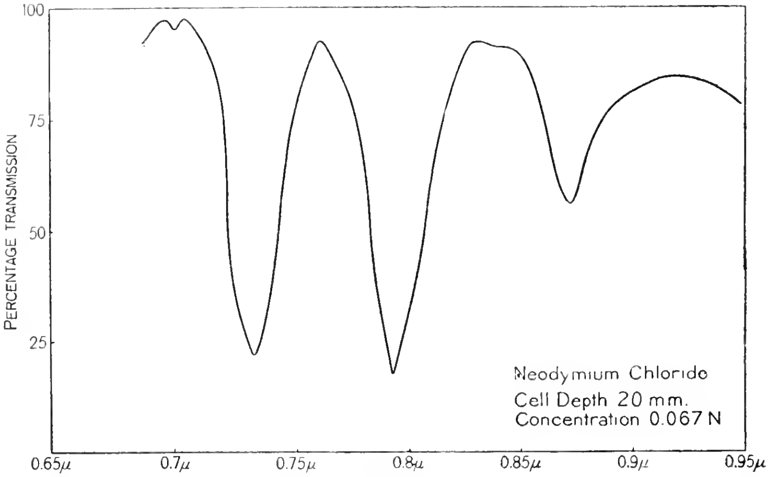

FIG. 25.

TABLE 13.—*Transmission of Neodymium Chloride Solutions (Dilute).*

λ	D.=2.5mm. C.=0.536N.	D.=5mm. C.=0.267N.	D.=10mm. C.=0.133N.	D.=20mm. C.=0.067N.	λ	D.=2.5mm. C.=0.536N.	D.=5mm. C.=0.267N.	D.=10mm. C.=0.133N.	D.=20mm. C.=0.067N.
686	92	95	94	92	800	45	39	38	39
693	93	95	95	97	805	64	59	57	57
698	97	95	95	97	809	78	72	71	70
704	98	95	96	97	814	85	84	82	82
708	98	95	97	98	819	92	91	88	88
712	100	98	96	96	825	100	94	94	94
716	100	98	98	92	830	100	96	94	93
720	96	94	89	89	834	100	94	94	92
723	85	84	83	84	839	100	96	93	91
726	59	54	58	53	845	98	95	94	91
730	42	41	40	34	850	97	94	90	89
733	31	29	26	25	856	92	87	84	83
737	25	24	20	22	861	78	77	74	70
741	28	29	29	29	867	70	64	62	60
746	47	44	51	44	872	64	60	59	56
751	69	65	65	60	877	74	71	68	66
755	85	82	82	78	882	84	80	76	75
759	93	86	90	86	888	89	84	82	78
763	97	90	92	92	894	90	84	83	79
767	97	95	90	92	900	91	88	86	81
770	97	93	90	89	906	95	90	87	83
774	91	86	87	84	912	98	95	90	84
779	79	76	78	74	917	100	96	92	85
783	69	61	59	56	923	100	96	93	84
787	47	39	38	34	928	100	95	92	84
791	23	24	20	18	933	100	94	94	83
796	28	25	23	23	938	100	94	95	78

TABLE 14.—*Transmission of Neodymium Nitrate Solutions.*

λ	D.=2.5mm. C.=2.010N.	D.=5mm. C.=1.05 N.	D.=10mm. C.=0.525N.	D.=20mm. C.=0.262N.	λ	D.=2.5mm. C.=2.010N.	D.=5mm. C.=1.05 N.	D.=10mm. C.=0.525N.	D.=20mm. C.=0.262N.
686	86	88	85	78	800	12	10	6	6
693	93	96	91	89	805	21	19	14	15
698	93	96	93	93	809	35	33	30	30
704	96	94	93	91	814	49	49	47	47
708	95	96	96	88	819	63	67	65	64
712	89	90	94	89	825	79	80	79	77
716	84	88	88	82	830	82	88	89	82
720	78	79	78	78	834	92	92	93	85
723	80	63	61	58	839	96	94	94	89
726	40	33	30	28	845	92	91	91	85
730	14	14	10	9	850	87	84	85	77
733	0	0	0	0	856	76	70	72	65
737	0	0	0	0	861	61	57	53	47
741	11	4	0	0	867	43	36	35	32
746	12	15	6	6	872	30	27	26	22
751	22	23	22	17	877	31	30	28	25
755	38	39	40	38	882	43	42	41	36
759	60	60	62	55	888	55	52	51	48
763	75	75	74	70	894	65	60	59	61
767	80	80	83	79	900	68	66	66	62
770	75	75	79	75	906	77	75	75	67
774	64	66	68	62	912	86	84	83	75
779	47	47	48	44	917	94	90	97	83
783	32	32	29	26	923	98	92	90	84
787	16	10	13	9	933	100	96	88	86
791	11	8	2	5	938	100	96	83	77
796	0	0	0	0					

NEODYMIUM NITRATE.

Table 14 gives the percentage transmission for solutions of neodymium nitrate. Column 1 gives the respective wave-lengths at such intervals as the solutions required. Reading from left to right, we find the percentage transmissions for the following concentrations: 2.010, 1.050, 0.525, and 0.262 normal, respectively, the corresponding depths of absorbing layers being 2.5, 5, 10, and 20 mm. Figs. 26 to 29, inclusive, represent these results, the abscissæ being wave-lengths and the percentage transmissions being given as ordinates. It is seen that the absorption bands in the nitrate solutions, as with those of the chloride discussed above, show three minima at λ7300, λ7950, and λ8750. The nitrate bands are not as intense as those

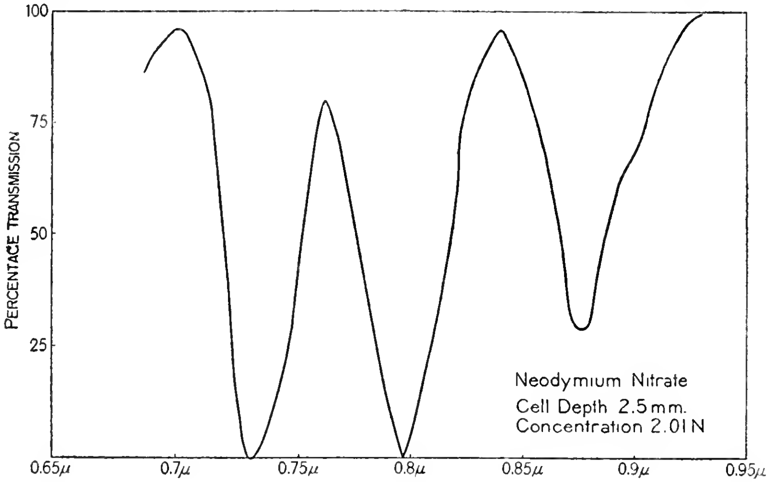

Fig. 26.

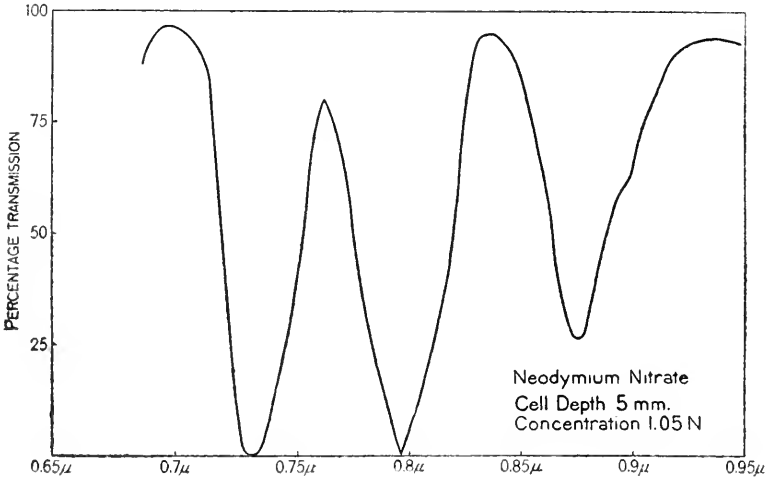

Fig. 27.

of the concentrated solutions of the chloride given in figs. 18 to 21. This is what we should expect, since the concentrations of the nitrate solutions are not so great. However, two of the absorption bands reach zero transmission. A comparative study of any of these bands in the succeeding curves shows that, just as was found with the chloride bands, they become more intense with dilution. The decided decrease in the transmission in the regions of the spectrum beyond 1μ is undoubtedly due to the increasing absorption of water as the solution becomes more dilute. The other slight deviations from Beer's law are not greater than could be accounted for by the corrections mentioned under the discussion of the chloride curves.

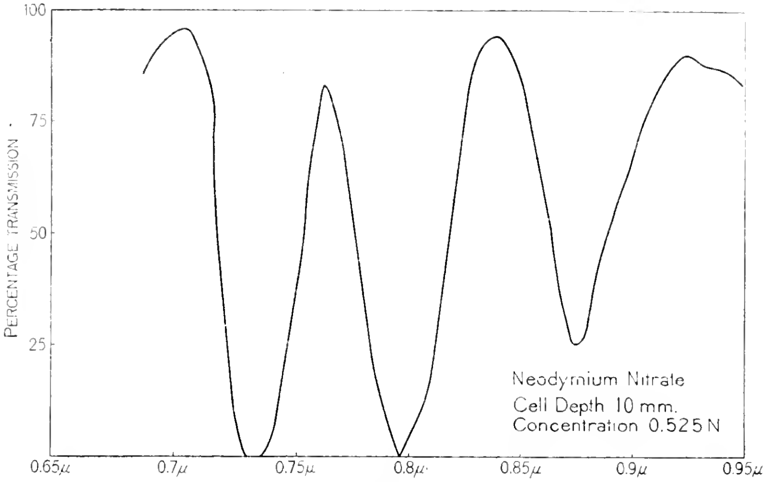

FIG. 28.

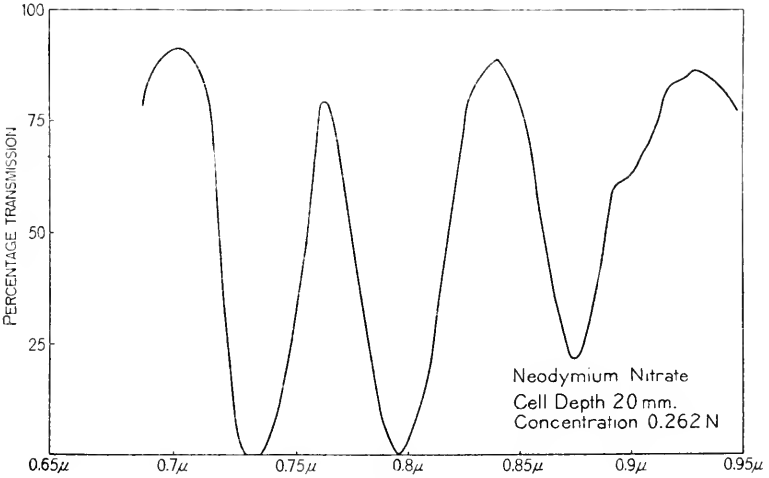

FIG. 29.

NEODYMIUM ACETATE.

Table 15 gives the results obtained for solutions of neodymium acetate in water. The concentrations, reading from left to right, were 0.617, 0.308, 0.154, and 0.077 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10, and 20 mm., respectively. The results in this table are plotted in figs. 30 to 33, inclusive. The percentage transmission and wave-lengths are represented, respectively, by the ordinates and abscissæ of the curves.

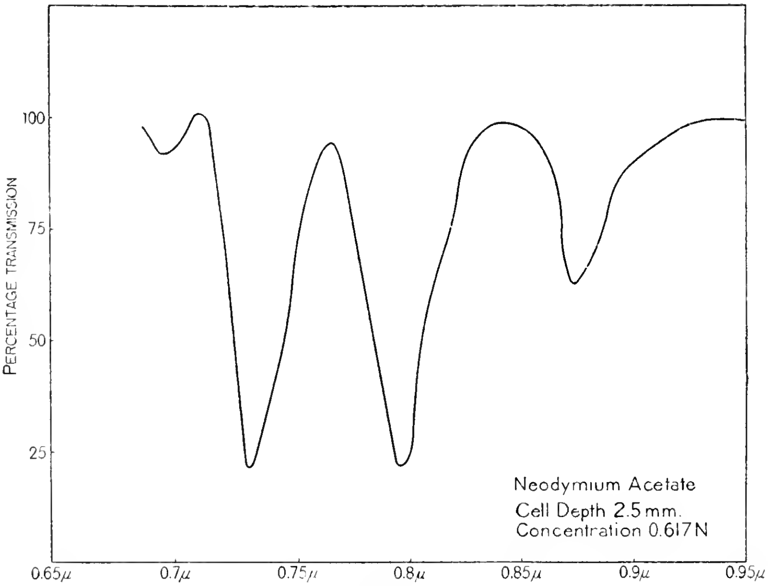

Fig. 30.

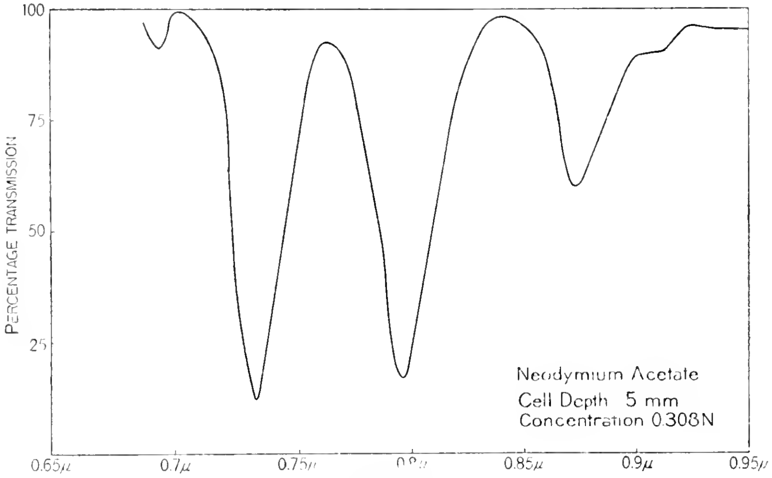

Fig. 31.

The minima of transmission fall at approximately the same positions as with the chloride and nitrate solutions discussed above, *i. e.*, at λ7300, λ7950, and λ8750. As indicated by the photographic method, the solutions of neodymium acetate have greater absorbing powers for a given concentration than either the chloride or nitrate.

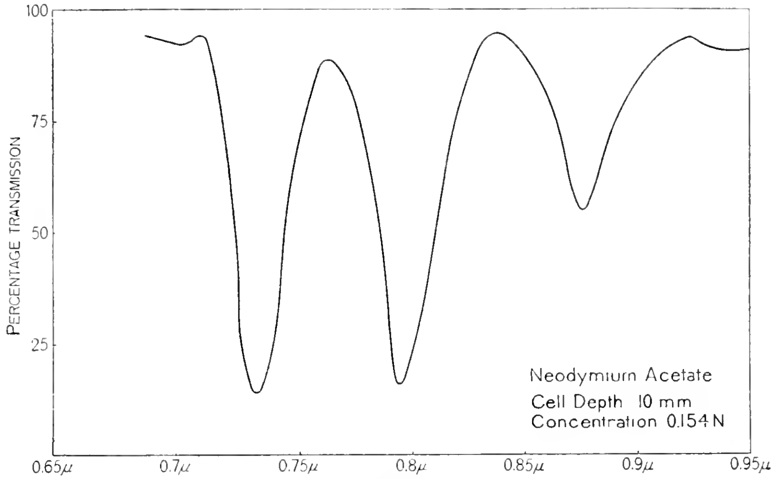

FIG. 32.

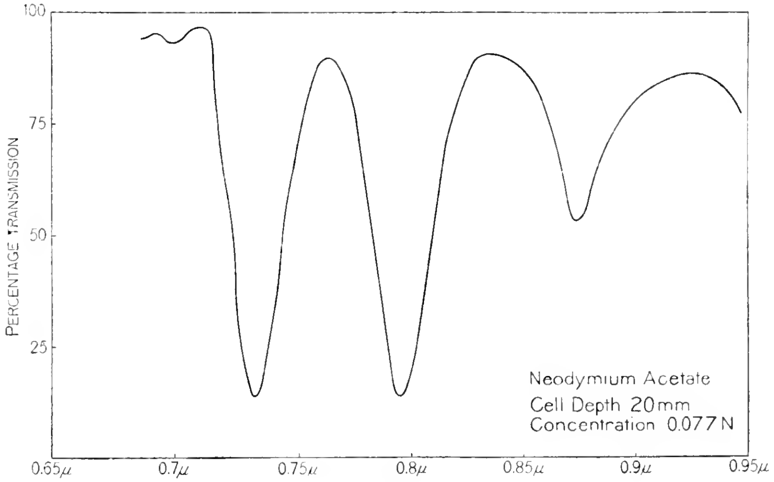

FIG. 33.

The small band near λ7000 appears slightly more intense with the acetate than with equal concentrations of the other salts; and the more intense bands λ7300, λ7950, and λ8750 show the same general tendency to have their minima lowered with increasing dilution. This set of curves shows in a marked way the rapid increase in the absorption near λ9500, which is due to the water present in the solution and illustrates the difficulty that is met with when working with aqueous solutions at greater wave-lengths than 1μ. Even over the range of wave-lengths at which we have worked, it is seen that the absorption due to water is a disturbing factor.

TABLE 15.—*Transmissions of Neodymium Acetate Solutions.*

λ	D.=2.5mm. C.=0.617N.	D.=5 mm. C.=0.308N.	D.=10 mm. C.=0.154N.	D.=20mm. C.=0.077N.	λ	D.=2.5mm. C.=0.617N.	D.=5 mm. C.=0.308N.	D.=10mm. C.=0.154N.	D.=20mm. C.=0.077N.
686	98	97	94	94	800	27	28	27	28
693	92	91	93	95	805	57	46	44	46
698	97	97	96	93	809	69	63	62	64
704	98	100	92	93	814	74	76	73	75
708	96	98	92	96	819	90	83	83	82
712	100	96	94	96	825	92	89	86	87
716	100	94	90	94	830	92	93	92	91
720	94	90	90	94	834	98	98	92	91
723	87	87	79	76	839	96	97	94	90
726	69	64	60	57	845	97	97	90	88
730	44	36	32	30	850	95	96	90	87
733	22	22	18	21	856	95	94	84	83
737	24	17	14	15	861	91	83	77	71
741	30	23	22	25	867	72	69	65	67
746	41	39	34	35	872	62	60	56	53
751	52	55	52	55	877	66	67	58	57
755	71	71	65	67	882	71	72	66	66
759	81	84	81	82	888	83	82	76	75
763	90	91	87	88	894	87	84	81	78
767	93	93	89	87	900	91	88	84	79
770	94	90	87	89	906	92	90	87	83
774	89	88	83	84	912	94	90	90	82
779	72	74	74	75	917	96	93	89	85
783	62	63	59	55	923	97	96	94	86
787	45	40	37	32	933	99	95	91	83
791	24	21	17	18	938	99	95	92	77
796	22	17	17	14					

PRASEODYMIUM CHLORIDE.

Solutions of praseodymium salts are not of great interest from our standpoint, in those regions beyond the visible part of the spectrum. It was found that such solutions were transparent in the infra-red end of the spectrum as far as 1.5, except two very weak bands which fall just in the midst of the intense water-bands. Since, at this point, a very thin layer of water is almost completely opaque, it is evident that it would be impossible to study aqueous solutions in this region, especially dilute solutions.

As shown by the photographic plate, praseodymium salts possess two groups of bands in the visible spectrum, one in the green near λ4600 and another near λ5900. Since the amount of energy at the former wave-length is so very small, the width of slits necessary to be used was too large to give satisfactory results. Such bands could, of course, be detected, but the deflections of the instrument at this part of the spectrum are very small, and, hence, relatively large errors would occur in making the readings.

For these reasons we have confined our attention to a careful study of the one band which has its center near λ5900. Table 16 gives the observed transmissions for the four dilutions of solutions of praseodymium chloride.

In column 1 there is given λ taken at such intervals as the graduated head of the spectroscope would permit. Reading from left to right, the respective concentrations were 1.377, 0.688, 0.344, and 0.177 normal, the corresponding depths of absorbing layer being 2.5, 5, 10, and 20 mm., respectively.

TABLE 16.—*Percentage Transmissions of Praseodymium Chloride Solutions.*

λ	D.=2.5mm. C.=1.377N.	D.=5 mm. C.=0.688N.	D.=10 mm. C.=0.344N.	D.=20 mm. C.=0.177N.	λ	D.=2.5mm. C.=1.377N.	D.=5 mm. C.=0.688N.	D.=10 mm. C.=0.344N.	D.=20 mm. C.=0.177N.
506	100	100	100	100	587	60	59	55	56
518	100	98	100	100	589	45	46	40	40
530	100	98	100	100	592	35	35	32	33
544	99	99	99	98	595	35	34	34	33
556	99	99	99	98	597	43	43	42	42
563	100	98	100	98	600	56	56	56	56
565	99	99	98	97	602	69	69	68	69
567	97	100	98	97	605	81	82	81	81
572	97	99	95	97	607	90	92	88	88
577	96	98	93	95	611	93	94	93	94
579	91	92	90	92	614	97	99	95	97
583	85	86	84	80	629	98	100	97	98
585	77	76	70	72					

In terms of Beer's law, the curves representing these tables should be identical. Such curves are represented by fig. 34. Beginning with the curve nearest the left and proceeding towards the right, the succeeding curves represent the four dilutions of praseodymium chloride as given in the preceding paragraph.

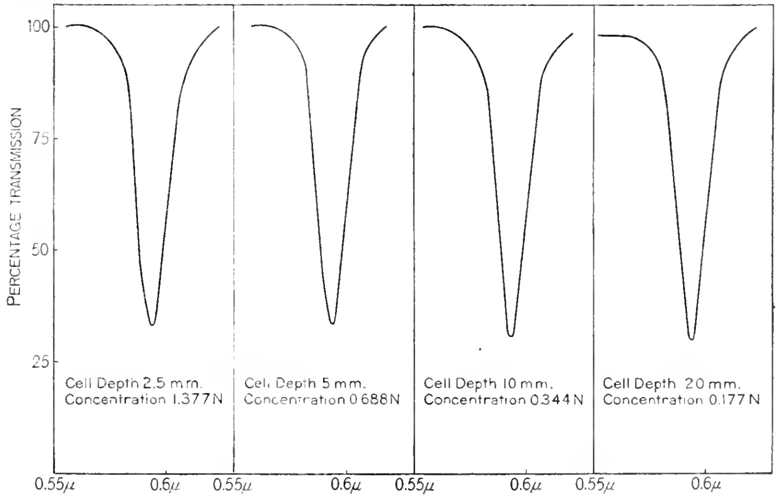

FIG. 34.

The curve representing the most concentrated solution is nearest the left of the figure. It is seen that these curves are identical to within the limits of experimental error; the slight increase in the absorption with dilution is to be attributed to the slit-width correction. The slit-width was in every case 0.4 mm. Water has no absorption in this region.

The results recorded in these curves are in agreement with previous photographic results. The minimum in transmission, which in each case is about 30 per cent, occurs near λ5900. The total deviation from Beer's law over the dilution studied is not over 3 per cent, which is well within the experimental error in this portion of the spectrum.

PRASEODYMIUM NITRATE.

Corresponding results for solutions of praseodymium nitrate are given in table 17. The concentrations of the solutions, beginning on the left and reading towards the right, were 1.282, 0.641, 0.320, and 0.160 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10, and 20 mm., respectively.

TABLE 17.—*Percentage Transmission of Praseodymium Nitrate Solutions.*

λ	D.=2.5mm. C.=1.282.	D.=5 mm. C.=0.641.	D.=10mm. C.=0.320.	D.=20mm. C.=0.160.	λ	D.=2.5mm. C.=1.282.	D.=5mm. C.=0.641.	D.=10mm. C.=0.320.	D.=20mm. C.=0.160.
506	100	100	99	100	587	62	60	60	58
518	98	98	100	100	589	48	46	46	45
530	100	100	99	99	592	40	40	38	36
544	99	98	100	100	595	37	36	36	36
556	99	98	100	98	597	44	44	44	42
563	99	99	98	97	600	56	56	56	54
565	96	100	98	96	602	68	67	68	67
567	98	100	98	97	605	79	82	79	80
572	95	97	96	95	607	87	89	89	88
577	93	92	94	93	611	91	92	94	92
579	90	92	90	91	614	95	95	97	96
583	83	86	85	83	629	98	98	99	98
585	73	74	72	72					

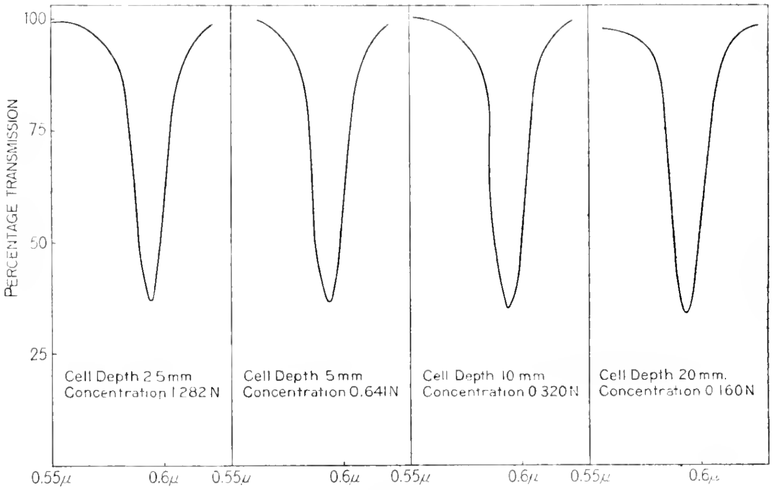

FIG. 35.

The results are plotted in fig. 35. Reading from left to right, there is shown the effect of increased dilution on solutions of praseodymium nitrate and such concentrations and depths of absorbing layers as were mentioned above, the most concentrated solution being nearest the left of the figure.

As with the curves representing the solutions of praseodymium chloride, these curves show that Beer's law holds quantitatively for solutions of the nitrate. Neither the position nor the intensity of the band is altered more than the limits of error of our work for the range of dilution studied. It may be recalled that this is in exact agreement with the photographic results recorded elsewhere in this monograph.

SALTS OF NICKEL.

Table 18 gives the percentage transmission of the nickel salts studied. Beginning at the left of the table, column 1 gives λ, taken at such intervals as the solutions required, and reading towards the right are the results for the following salts: nickel chloride, depth of cell 3 mm., concentration 2.74 normal; nickel nitrate, depth of cell 5 mm., concentration 1.68 normal; nickel sulphate, depth of cell 5 mm., concentration 1.108 normal, respectively.

Curves representing these results are given in figs. 36, 37, and 38.

TABLE 18.—*Percentage Transmissions of Solutions of Nickel Salts.*

λ	Nickel chloride. D.=3 mm. C.=2.74 N.	Nickel nitrate. D.=5 mm. C.=1.68 N.	Nickel sulphate. D.=5 mm. C.=1.108 N.	λ	Nickel chloride. D.=3 mm. C.=2.74 N.	Nickel nitrate. D.=5 mm. C.=1.68 N.	Nickel sulphate. D.=5 mm. C.=1.108 N.
544	71	69	81	796	16	20	33
556	64	69	79	805	18	24	40
563	62	65	76	814	22	31	44
565	60	61	73	825	28	36	49
577	56	57	68	834	32	40	55
583	52	50	66	845	36	46	58
587	47	46	61	856	41	48	64
592	40	40	60	867	46	51	66
597	34	33	40	877	49	52	68
602	26	28	43	888	51	56	69
607	22	22	37	900	53	56	68
614	17	17	33	912	54	56	67
618	12	12	26	923	52	51	64
625	10	9	23	933	50	48	62
632	8	6	18	938	47	44	59
638	5	6	15	955	42	38	52
643	3	4	12	966	36	30	44
650	0	4	12	978	30	24	38
662	0	3	10	990	26	20	33
676	0	2	10	1002	22	16	28
693	0	9	11	1012	20	14	24
755	7	8	10	1023	15	9	22
770	7	8	18	1035	13	8	20
779	11	13	20	1047	9	4	17
787	14	17	30	1060	6	4	14

NICKEL CHLORIDE.

Fig. 36, the curve for nickel chloride, shows an increasing absorption from 70 per cent transmission at λ5200 to complete absorption at λ6300. From this point there is complete absorption to the regions λ7200, and then a gradual increase in transmission, reaching a maximum of 53 per cent near λ9000, then decreasing again to zero transmission at λ10000.

As has been shown photographically, the visible spectrum of salts of nickel consists of intense broad absorption bands both in blue and red, showing a single region of transmission, extending to about λ6500 in the red. It is interesting to note that by means of the radiomicrometer we are able to study another region of transmission which reaches a maximum near λ9000. From this point the absorption rapidly increases until the region of water absorption is reached. It was not possible to determine whether the solution again became transparent beyond this point, on account of the water absorption.

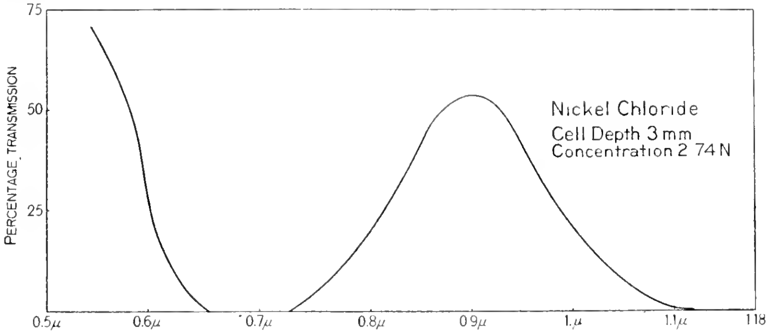

Fig. 36.

NICKEL NITRATE.

Fig. 37, which represents the second column of table 18, gives the transmission, as observed, for a solution of nickel nitrate, concentration 1.68 normal and 5 mm. absorbing layer. This figure is almost exactly analogous to the curve for nickel chloride, just discussed in the preceding paragraph, and shows maxima at λ5400 and λ9000. There is complete absorption in the region λ7000 and beyond 1.1μ. Figs. 36 and 37 represent approximately equal amounts of the chloride and nitrate respectively, and are very similar.

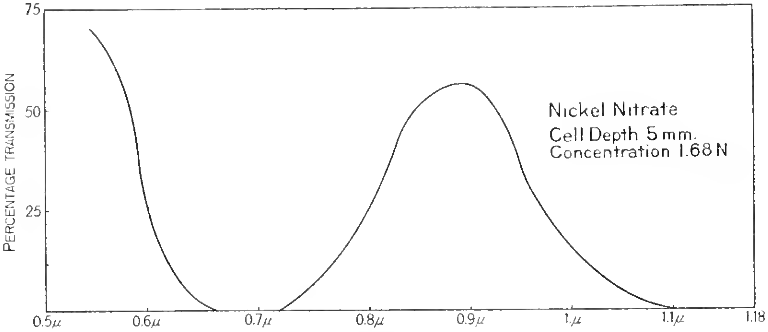

Fig. 37.

NICKEL SULPHATE.

The curve representing the last column of this table is given in fig. 38. The concentration of nickel sulphate was 1.108 normal, and the depth of absorbing layer was 5 mm. It will be seen that this solution is slightly more dilute than the other two solutions of nickel salts studied; and that in no region does the curve representing the transmission reach complete absorption. Maxima in transmission appear near λ5400 and λ9000 and minima of about 8 per cent at λ6900 and λ11000. Readings were not made at greater wave-lengths with any of the nickel salts, on account of the intense water absorption slightly beyond this region.

No striking or characteristic difference is noted in the absorption as shown by the three curves representing the three salts of nickel studied. Each of them shows maxima and minima in about the same region of the spectrum.

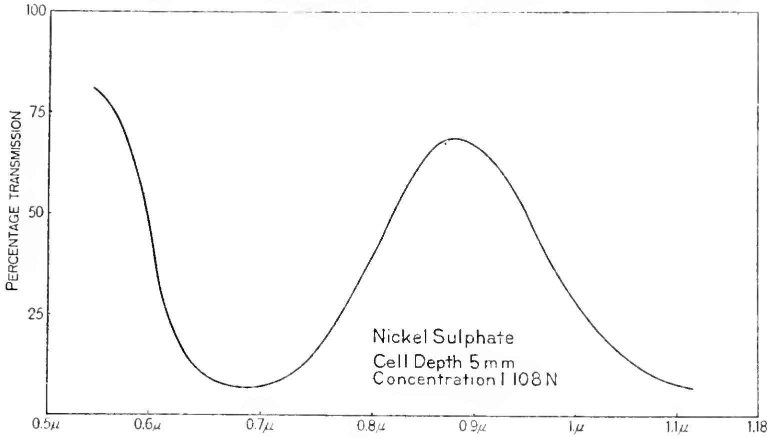

Fig. 38.

SALTS OF COBALT.

The photographic plate shows that in the visible region salts of cobalt have a strong ultra-violet absorption, a band in the orange near λ5000, and increasing transmission from the center of this band toward the longer wave-lengths. It was interesting to see whether solutions of cobalt salts were completely transparent beyond the limit of sensibility of the photographic plate, or if such solutions again showed absorption bands in the infra-red. It was also of interest to know whether equal concentrations of the different salts showed the same or different absorption bands. With this idea in view, the solutions of five salts of cobalt were studied. In each case the concentration was 0.347 normal, and the depth of absorbing layer 10 mm.

The results are given in table 19. Beginning at the left are given, in their respective order, the observed transmissions for 10 mm. of solution of the following salts: cobalt chloride, cobalt bromide, cobalt nitrate, cobalt sulphate, and cobalt acetate.

The results of table 19 are plotted as transmission curves in figs. 39 to 43, inclusive. A study of these curves shows that they are very similar, all having maxima of transmission at the following points: λ5950, λ7800, λ9100, and λ10,600. In general, for all the salts of cobalt studied, the transmission curves rise rapidly from λ5000 to λ5900, where the transmission reaches about 65 per cent. The curves show a broad but slight absorption over the region near λ6500, and reach a maximum transmission over the region near λ7000 to λ8000. The curves then descend, showing a series of small absorption regions near λ8400, λ8900, and λ9800. The last of these absorption bands shows a fairly sharp edge toward the shorter wave-lengths. Beyond λ10,500 the absorption increases rapidly until the region is reached where water is practically opaque.

Table 19.—*Transmissions of Cobalt Solutions.*

λ	Cobalt chloride. D.=10 mm. C.=0.347 N.	Cobalt bromide. D.=10 mm. C.=0.347 N.	Cobalt nitrate. D.=10 mm. C.=0.347 N.	Cobalt sulphate. D.=10 mm. C.=0.347 N.	Cobalt acetate. D.=10 mm. C.=0.347 N.
544	12	21	20	14	15
556	19	33	31	26	31
572	39	50	35	48	53
583	48	61	64	57	59
589	59	68	68	62	69
592	63	74	73	67	72
605	68	74	77	67	72
614	70	74	77	68	74
622	72	74	79	68	75
632	72	75	84	69	76
640	72	75	76	70	77
650	73	76	79	71	76
660	73	78	81	72	80
667	74	78	82	74	83
678	79	82	85	77	84
686	80	84	88	79	85
693	81	85	90	88	88
708	84	87	91	81	89
720	84	89	91	82	92
730	85	87	92	83	89
741	88	88	88	82	91
755	87	89	89	83	91
767	87	92	89	82	92
779	88	89	89	84	90
791	90	89	89	83	90
805	91	89	87	84	89
819	88	88	84	83	90
834	87	87	83	83	86
850	88	86	76	80	86
867	88	95	95	80	85
882	84	84	82	79	83
900	84	81	77	76	84
917	83	82	79	77	82
933	78	77	79	73	78
949	70	69	70	66	70
966	58	55	56	54	56
984	51	49	50	47	52
1,002	49	48	50	47	49
1,018	51	50	50	47	52
1,035	51	50	53	50	52
1,053	48	50	56	49	52
1,072	46	46	50	44	48
1,091	41	41	46	40	41
1,109	34	35	39	34	36
1,123	29	31	35	30	32
1,136	24	25	23	24	25
1,147	17	21	14	16	19
1,162	12	12	13	11	12
1,174	9	10	11	10	10
1,187	9	9	10	9	9
1,202	8	8	9	8	10

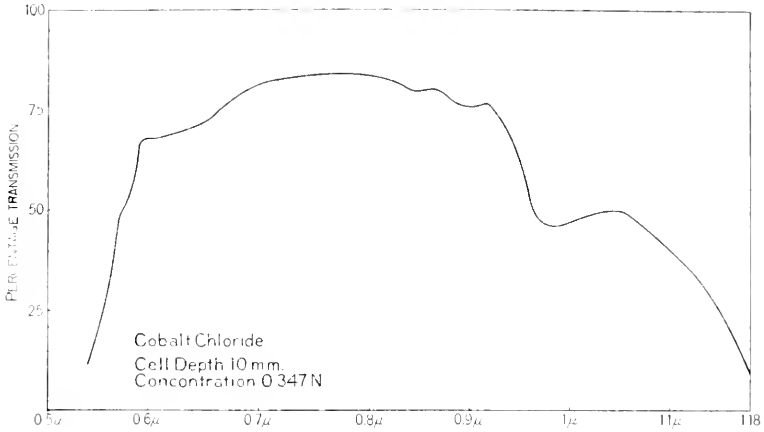

FIG. 39.

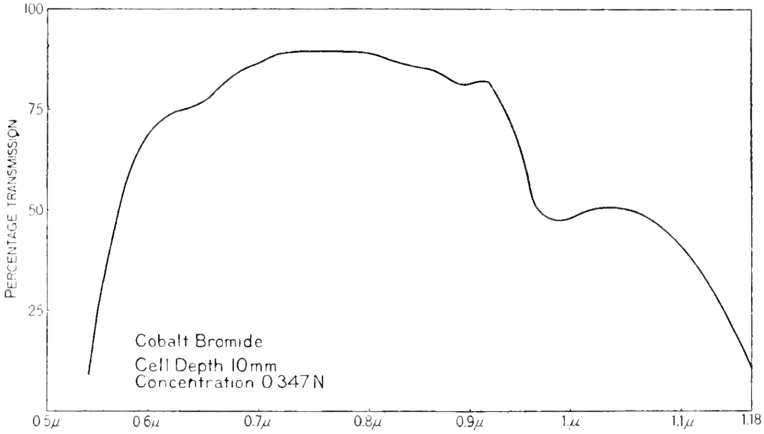

FIG. 40.

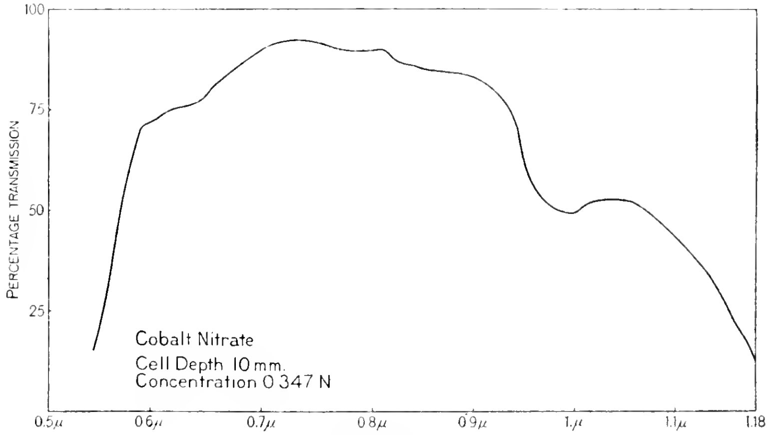

FIG. 41.

Fig. 42, representing the curve of transmission of cobalt sulphate, appears slightly different from the curves of the other salts of cobalt, having better-defined bands in the region of λ8000.

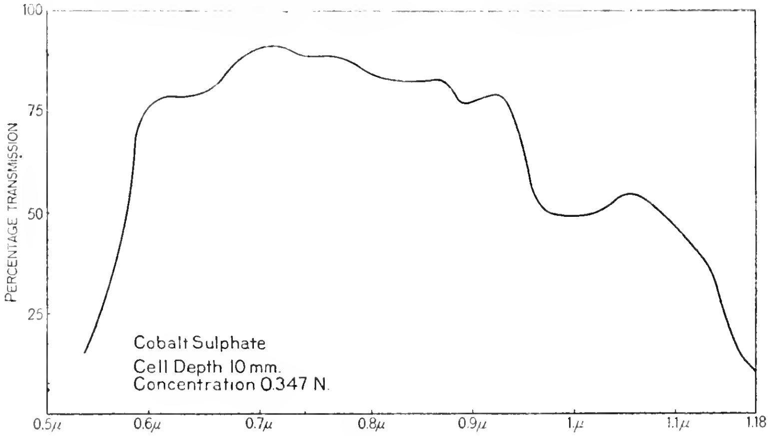

FIG. 42.

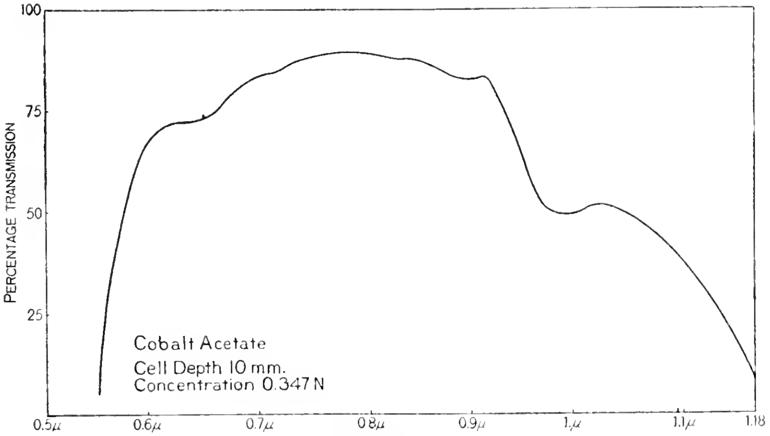

FIG. 43.

CHAPTER VII.

GENERAL SUMMARY OF RESULTS.

The work on *the effect of temperature* on the absorption spectra of solutions was extended to aqueous solutions, the range in temperature being from ordinary temperatures up to about 200°. For this purpose a special form of apparatus was constructed, made of brass and lined on the inside with gold. This was for the purpose of preventing the hot vapor under high pressure from coming in contact with any metal except gold.

With this apparatus the absorption spectra of aqueous solutions could be studied up to 200°, just as well as the spectra of nonaqueous solutions in the apparatus used by Jones and Strong, and described in Publication of the Carnegie Institution of Washington No. 160.

With neodymium chloride the following bands remain unchanged by temperature over the range from 20° to 200°: λ3800, λ4025, λ4200, λ4325, λ4440, λ4600, λ4690, λ4750, λ4820. The double band λ5050 to λ5270 changes very slightly. The bands λ4275 and λ5800 show marked changes, the red edge widening and becoming more diffuse. The λ5800 band widens as much as 50 A.U. toward the red, the violet edge remaining sharp.

With the neodymium bromide, as with the chloride, only λ4275 and λ5800 show any marked changes with rise in temperature. The band λ5800 widens for the bromide 60 A.U. from 20° to 190°.

The λ4275 band, for neodymium nitrate, shows a marked change, widening towards the red. The λ4425 band widens about 15 A.U. from 15° to 165°. The bands λ5125 and λ5800 show marked changes towards the red. The change was greatest in the most concentrated solutions, although the total number of absorbers in the path of light was kept constant.

The bands λ4275 and λ5800 for neodymium acetate show marked changes on the red side, the latter widening as much as 80 A.U. The acetate bands, for a given concentration of salt, are the most intense of all the neodymium bands. When the solution was cooled down, the absorption spectra went through exactly the reverse changes as when the temperature was raised. Since the acetate band, λ5800, is more intense for the same concentration than for neodymium chloride or nitrate, and since the acetate is less dissociated than the neodymium salts of the strong acids, it appears probable that this band is in some way connected with the molecules.

The sulphate of neodymium shows the same temperature effect as the other salts of this element.

The effect of temperature on the absorption spectra of cobalt chloride is very slight.

There is a slight widening of the band of praseodymium chloride whose center is near λ4825. The λ5900 band undergoes slight change with temperature, but from 20° to 160° it changes less than 25 A.U. There is no appreciable change with temperature of the bands whose centers are near λ4425, λ4650, and λ4820.

The above-described temperature changes take place only in concentrated solutions. In very concentrated solutions all of the praseodymium bands show a slight widening with rise in temperature. We shall see that increase in dilution affects the bands of praseodymium salts only when the solutions are fairly concentrated. Thus, rise in temperature and increase in concentration produce the same effect on the absorption spectra of solutions of praseodymium nitrate.

The effect of rise in temperature on the absorption spectra of solutions of uranyl nitrate is a general widening of the bands, with a slight shift of the center towards the red. The general absorption ending near λ3500 moves rapidly towards the red with rise in temperature. All of the eleven bands between λ3500 and λ4600 become more diffuse and broader with rise in temperature, the λ4180 band being most affected. The red edge of this band shifts as much as 25 A.U. from 40° to 120°.

The uranyl sulphate bands λ4175 and λ4325 have their centers shifted towards the red about 25 A.U. for a temperature range of from 20° to 185°. The band λ4750 remains unchanged, while the red edges of λ4325 and λ4550 shade rapidly towards the red. All bands below λ4500 become very diffuse as the temperature is raised, and at the highest temperatures are a single, broad, hazy absorption band extending from λ4000 to λ4400.

The most marked widening is in the uranyl sulphate bands λ4100, λ4200, and λ4350, the center of each of these bands being slightly shifted towards the red. The broad, hazy bands λ5100, λ5600, and λ6200 are not appreciably affected by changes in temperature.

None of the uranyl acetate bands seems to undergo change with dilution; all of the nine bands on the plate undergo change with rise in temperature, becoming more diffuse.

While some of the absorption bands of solutions are practically unaffected by temperature, many of them widen as the temperature is raised. The effect of rise in temperature is not to produce a symmetrical widening of the bands, but most of the widening is towards the red. The violet edge of the band usually remains pretty sharp. The red edge widens out, becoming more hazy and diffuse.

The effect of dilution on the absorption of light by solutions was early studied by Ostwald and others, especially in connection with the theory of electrolytic dissociation. It was known that both molecules and ions in solution absorb light, and the question was whether they have the same or different absorption. It was not possible to answer this question satisfactorily by means of the prism spectroscope. It has been possible to solve this problem by means of the grating.

Jones and Anderson had shown that if molecules and ions absorb differently, the difference is slight. We therefore worked over a wide range in dilution, comparing the absorption of a concentrated solution with one 500 times as dilute.

The neodymium chloride bands λ3400, λ3450 to λ3600 are not affected by change in dilution. The sharp band λ4275 is more intense in the most concentrated solution. The bands near λ5100, λ5200, and λ5800 are markedly affected by dilution, the former two appearing as distinct bands in the most dilute solution. The broadening of these bands with concentration is fairly uniform, both towards the red and the violet ends of the spectrum. The intense band from λ5690 to λ5850 is greatly affected by concentration, widening almost entirely towards the red. This widening is about 50 A.U. When a more dilute solution was used to start with, the broad band λ5700 to λ5825 is the only one which widens with increase in concentration, the widening being about 25 A.U. When a still more dilute solution is used as the starting-point, there is no appreciable change in any of the bands with increase in concentration.

With neodymium bromide, with increase in concentration there is a slight increase in the intensity of λ4275. The bands λ5090, λ5120, and λ5210 narrow uniformly with dilution. The greatest change is in band λ5750, which widens towards the red as much as 30 A.U., the violet edge remaining practically unchanged. When half the concentrations were used, the only band affected by dilution is the one near λ4800, which widens with the concentration as much as 20 A.U. When all of the dilutions were again doubled, there was practically no difference between the absorption spectra of the various dilutions.

The effect of dilution on the absorption spectra of neodymium nitrate is probably greater than on any other neodymium salt. Then bands λ5090 and λ5125, in the most concentrated solution, have so broadened as to become one band. The band λ5220 widens uniformly towards both the red and violet with increase in concentration probably as much as 70 A.U. Starting with a different concentration, the λ5750 band widens as much as 40 A.U. as the concentration is changed. When the original solution was still more dilute, only the λ5750 band changed appreciably.

The band λ5750 of neodymium sulphate widens with concentration as much as 25 A.U. It remains unchanged if the initial solution of neodymium sulphate is more dilute.

A number of the bands of neodymium acetate change with the dilution. The λ5210 band narrows about 10 A.U. with the first change in dilution, and then remains unchanged with further increase in dilution. The broad band λ5750 changes about 55 A.U. with the change in dilution studied. When only half the initial concentrations were used, only the bands λ5220 and λ5750 underwent change. With neodymium acetate further increase in dilution produced still further narrowing of the absorption bands. When one-fourth the initial concentration was used, the band λ5750 underwent change, narrowing about 20 A.U. This is the only salt of neodymium in which a change in a band was noted at such a high dilution.

The λ4675 band of praseodymium chloride narrows towards the violet about 20 A.U. with increase in dilution, while the broad band λ5900, under the same conditions, shows a narrowing of about 25 A.U. When more dilute solutions are employed, none of the bands shows any change with dilution. The changes in the two bands λ4675 and λ5900 with dilution are much less than with the corresponding bands of neodymium.

The two bands λ4450 and λ4650 of praseodymium nitrate widen about 20 A.U. with increase in concentration in very concentrated solutions. In the more dilute solutions there is no change.

The λ4700 band of uranyl chloride shows marked widening with increase in concentration, especially towards the red end of the spectrum. The λ4900 band also shades off rapidly towards the red end of the spectrum. When more dilute solutions were used, both λ4600 and λ4700 gradually widen with increase in concentration.

The λ4700 band of uranyl bromide widens uniformly with increase in the concentration. When a more dilute solution was employed as the starting-point, none of the bands changed with dilution.

The absorption of concentrated solutions of uranyl nitrate is complete to λ4500. With increase in concentration this gradually recedes towards the red, amounting to as much as 100 A.U. The λ4700 band widens under the conditions about 20 A.U. The sharp band λ4875 widens slightly with increase in concentration.

In the more concentrated solutions of uranyl salts many of the bands change with change in the dilution, while in the more dilute solutions there is scarcely any change at all.

The introduction of the *radiomicrometer* into this work converted it into a quantitative study of the absorption spectra of solutions. The grating spectroscope and photographic method were very efficient in locating the positions of the absorption lines and bands from wave-lengths λ2000 to about λ7600; and the photographic method gave some approximate idea as to the intensities of the various lines and bands. This method is, however, only roughly quantitative, and is very limited in the range of wave-lengths to which it can be applied.

The radiomicrometer provides us with a quantitative method for studying the intensities of the various lines and bands, and also greatly extends the range of wave-lengths that can be studied. In the earlier work with the radiomicrometer much time and labor were expended in perfecting the instrument, especially in constructing a sensitive radiomicrometer with a short period. Dr. Guy accomplished this very successfully.

The earlier work was practically limited to the study of the absorption spectra of solutions of neodymium salts—neodymium chloride, bromide, nitrate, and acetate.

The results were plotted in what is known as transmission curves, which express the percentage transmission for the different wave-lengths. Solutions of different concentrations of a given salt were studied, the depth of layer of the solution varying inversely as its concentration. The product of the depth of layer times the concentration is a constant. If the solvent plays no rôle in the absorption, then the transmission curves for the different concentrations of any given salts must fall directly over one another—the different curves would be the same curve.

We found that, in general, the more concentrated the solution the less the transparency and the broader the absorption bands; this is exactly what we obtained with the grating spectroscope and the photographic method. But in the more dilute solution the intensity of the bands was greater. We observed further, that with increase in dilution the middle of the band is displaced towards the longer wave-lengths.

The same general changes with dilution in the absorption spectra of solutions of neodymium bromide were observed as with the chloride; the more dilute the solution the narrower and more intense the bands.

The bands of neodymium nitrate, in general, show the same changes with dilution as those of the chloride and bromide. With increase in dilution the intensities of the bands increase, and their centers are displaced somewhat towards the longer wave-lengths.

The three salts of neodymium, then, all show an increase in intensity with dilution. A possible explanation of this phenomenon, based upon resonance, has been offered. It is a well-known fact that a resonator, when excited by vibrations from a single vibrating resonator having the same pitch, vibrates more strongly than when set into vibration by a large number of resonators, one of which has the same pitch as its own and the others slightly different periods. In a word, if several vibrators are near together, every one exerts a certain influence on the others. The result is that no one of them has exactly the same period as the original resonator. Each resonator damps the other and we have less perfect resonance.

In a concentrated solution the resonators are relatively close together and mutually affect one another. The result is imperfect resonance and the absorption bands are less intense in the more concentrated solution.

In the more dilute solution the vibrators are farther removed from one another and are surrounded by large amounts of water of hydration. The damping effect would thus be diminished. In such cases we would have more perfect resonance and the resulting absorption bands would be more intense.

Subsequent work has, however, shown that a part of this effect can possibly be explained as due to the fact that the slit-width used was not infinitesimal.

It was found by the radiomicrometer, as with the grating spectroscope and photographic plate, that for a given concentration the acetate absorbs much more than any other salt of neodymium.

One of the most interesting facts thus far established by means of the radiomicrometer is the *effect of the dissolved substance on the absorption spectra of water.* We noted that aqueous solutions of hydrated salts were often more transparent than pure water. This is obviously a very remarkable fact, and we at once took up its careful study. We compared the absorption of aqueous solutions of strongly hydrated salts with the absorption of a layer of water equal in depth to the water in the solution through which the light was passed. We then carried out similar experiments with salts which, in the presence of water, combine with only a small amount of it. In a word, we compared the absorption of light by water with the absorption of an equal depth of water in aqueous solutions of strongly hydrated salts, and the absorption of light by water with an equal depth of water in aqueous solutions of salts which are scarcely hydrated at all.

The nonhydrated salts with which we worked were potassium chloride, ammonium chloride, and ammonium nitrate. It was necessary in all of this work to choose salts which themselves have little or no absorption in the region in which water absorbs, *i. e.*, in the infra-red. It was found that aqueous solutions of the above-mentioned compounds showed the same absorption of light as water having the same depth as the water in the solutions in question. This is exactly what would be expected. The dissolved substance and the solvent do not combine with one another to any appreciable extent, and it would be very difficult to see how either could appreciably affect the absorbing power of the other.

When we turn to the strongly hydrating salts, very different relations manifest themselves. The salts of this class that were studied were calcium chloride, magnesium chloride, and aluminium sulphate.

In the case of a 5.3 normal solution of calcium chloride, the solution is the more transparent from 0.9μ nearly to 1μ. The water then becomes the more transparent for a short distance. From 1.05μ to 1.2μ the solution is the more transparent, becoming as much as 25 per cent more transparent than the pure water. The water becomes more transparent than the solution only at and near the *bottom of the "water-bands"* at approximately 1μ. This is what we should expect if the solute exerts a damping effect on the absorbing power of water. When a smaller depth of the solution of calcium chloride is used, the water in the region 1.25μ is more transparent than the solution. From this band on to the longer wave-lengths the solution becomes more transparent than the water until 1.42μ is reached, when both solution and water are practically opaque.

The results for magnesium chloride are essentially the same as those obtained for calcium chloride. The main difference is that from 1.0μ to 1.1μ, in the case of magnesium chloride, the water is more transparent; while for calcium chloride in this region the solution is the more transparent. The difference between water and the solution of magnesium chloride in this region is, however, not great. For wave-lengths longer than 1.1μ, the solution of magnesium chloride, like the solution of calcium chloride, is more transparent than the water, the difference for the two salts being of the same order of magnitude.

When a smaller depth of layer of the solution was used, the water was the more transparent from 1.22μ to 1.34μ. For the longer wave-lengths the solution was the more transparent.

The curve for aluminium sulphate brings out this new feature; at 1μ the solution is more transparent than the water. Beyond 1.04μ the water is transparent to 1.17μ, beyond which the solution is the more transparent, as with magnesium and calcium chlorides.

In the region 1.2μ water is the more opaque when a shallower layer of solution is used. From 1.29μ to 1.36μ, water is the more transparent; beyond 1.36μ the solution is the more transparent.

The explanation of these remarkable results is that they must be due to some action of the dissolved substance on the solvent. That the solvent can affect the absorption spectra of the solution was first shown by Jones and Anderson;[1] and a large number of examples of this same action has since been found by Jones and Strong.[2] The action was satisfactorily explained as due to a combination of the solvent with the dissolved substance, and this explanation accounted for many facts which could not be otherwise satisfactorily explained. This theory of solvation in solution has aided us in explaining many phenomena which the theory of electrolytic dissociation alone could not account for, as has frequently been pointed out.

The same solvate theory of solution seems to aid us in explaining the facts just discussed. Those substances that do not form hydrates when in the presence of water show normal results as far as absorption spectra are concerned. Their solutions have the same absorption as so much pure water, the substance itself showing no absorption.

It is the hydrated salts, and only these, which give the abnormal results herein recorded. *The combined water seems to have less power to absorb light than free or uncombined water.* This would account for all of the facts observed.

It should be noted that the presence of the salt shifts the absorption of the water towards the longer wave-lengths. It was earlier observed that rise in temperature and increase in concentration shifted the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and of increase in concentration is to simplify the hydrates existing in the solution. This simplified resonator shifts the absorption towards the red. The effect of the salt on the absorption of the water is the same as rise in temperature and increase in the concentration of the solution on the absorption of the dissolved substance. It may be that the dissolved substance diminishes the association of the solvent and thus simplifies the resonator. This may be true especially with the water of hydration or the water combined with the dissolved substance.

This new line of spectroscopic evidence bearing on the solvate theory of solution is regarded as probably the most direct that we have or can hope to obtain in favor of the view that there is combination between solvent and solute.

In studying the *absorption spectra of salts,* the intensity of the light after passing through the solution of the salt in question, was compared with the

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[1] Carn. Inst. Wash. Pub. **110**.

[2] *Ibid.,* **130** and **160**.

intensity of the light after passing through a depth of water equal to the water in the solution in question.

The absorption spectrum of neodymium chloride shows three pronounced minima representing the three absorption bands with their centers near λ7300, λ7950, and λ8700, and less pronounced bands near λ7150 and λ9000. The latter may be due in part to the solvent; for all four dilutions studied the λ7300 and λ7900 bands show complete absorption over a considerable range of wave-lengths. The minimum of band λ8700 is gradually lowered with increasing dilution.

The maximum transmission of solutions of neodymium chloride occur near λ7600 and λ8400, these solutions becoming almost completely transparent beyond 1μ, except for the absorption of the solvent of this region. It seems that Beer's law holds, in general, for the infra-red absorption of solutions of neodymium chloride.

The minima in the curves for the more dilute solutions of neodymium chloride are in about the same positions as those in the more concentrated solutions, but the solutions being more dilute are more transparent; hence the minima are not so pronounced. The maximal absorption occurs near λ7300 and λ7900. The λ8700 band has a minimum transmission of 64 per cent. There is complete transmission in the regions λ7200, λ7600, λ8300, and λ9300. The drop in all of the curves beyond 0.9μ is due to the absorption of the water.

With further increase in the dilution of the solution, there is a lowering of the maxima. The change is most pronounced in the λ8700 band, and here the absorption of the water is the most pronounced. The absorption of the water together with the correction for slit-width may account for this change, and Beer's law may hold for the dilute solutions of neodymium chloride almost as well as for the more concentrated.

Neodymium nitrate shows three minima at λ7300, λ7950, and λ8750. The nitrate bands are not as intense as those of the chloride, the solution of the nitrate not being as concentrated as that of the chloride. The nitrate bands, like those of the chloride, become more intense with increase in dilution. The absorption of water becomes more and more pronounced beyond 1μ.

The minima for solutions of neodymium acetate fall at approximately the same positions as with the chloride and nitrate.

Solutions of neodymium acetate, as indicated by the photographic method, show greater absorbing power than those of either the chloride or nitrate. The λ7000 band is slightly more intense in the acetate. The more intense bands λ7300 and λ7950 show the same tendency to have their minima lowered with increasing dilution. There is a rapid increase in the absorption near λ9500, due to the water present in the solution.

Solutions of praseodymium salts are transparent in the infra-red as far as 1.5μ, except two very weak bands which fall in the midst of the intense water bands. Praseodymium salts have two groups of bands, one in the green near λ4600 and another near λ5900. We have limited our investigations to the latter band, on account of the small amount of energy transmitted at λ4600. The curves representing the absorption of different concentrations of praseodymium chloride are identical to within the limits of possible experimental error. The results obtained with the radiomicrometer are in accord with those found by the grating and photographic plate. The minimum in each case occurs near λ5900. The total deviation from Beer's law, as shown by solutions of praseodymium chloride, is within the limits of experimental error.

The curves for praseodymium nitrate show that Beer's law holds here as well as for the chloride.

Solutions of nickel chloride show an increasing absorption from λ5200 to λ6300, where it is complete. Complete absorption extends to λ7200. Transmission increases to λ9000, then decreases to zero at λ10000. The visible spectrum of salts of nickel consists of intense broad absorption bands in the blue and red, having a single region of transmission in the red, extending to about λ6500. By means of the radiomicrometer we could study the region of transmission near λ9000. Beyond this we could not go because of the absorption of the water.

The absorption of nickel nitrate closely resembles that of the chloride. There is maximal absorption at λ5400 and λ9000. There is complete absorption in the region λ7000 and beyond 1.1μ.

The solution of nickel sulphate studied is slightly more dilute than the chloride and nitrate. In no region is there complete absorption. There is maximal transmission near λ5400 and λ9000, and minima at λ6900 and λ11000. Readings were not extended beyond this region on account of the intense absorption of the water. The three salts of nickel studied have just about the same absorption spectra, the curves showing maxima and minima in just about the same regions of the spectrum.

Salts of cobalt in the visible region have a strong ultra-violet absorption. There is a band in the orange near λ5000, and increasing transmission towards the red. The infra-red absorption of solutions of cobalt salts was studied, and the absorption of the chloride, bromide, nitrate, sulphate, and acetate compared. The transmission curves for all of these salts have maxima at λ5950, λ7800, λ9100, and λ10600.

The transmission curves for all of the salts of cobalt studied rise rapidly from λ5000 to λ5900. The curves show a broad, slight absorption over the region near λ6500, and reach a maximum transmission from λ7000 to λ8000. There is a series of small absorption regions near λ8400, λ8900, and λ9800. Beyond λ10500 the absorption increases rapidly to the region where water is practically opaque.

The curves for cobalt sulphate are slightly better defined than those for the other cobalt salts.