THE
PHYSICAL REVIEW.

NEW GROUPS OF RESIDUAL RAYS IN THE LONG-
WAVE SPECTRUM.¹

BY E. F. NICHOLS AND WILLIAM S. DAY.

THIS paper contains an account of the measurement of the mean wave-lengths of residual rays from four substances, three of which have not been experimented with before. The apparatus used is also described, including a Nichols radiometer of recent pattern. The substances examined and the mean wave-lengths found are as follows :

Rock salt (sodium chloride),	$\lambda=52.3 \mu$
Ammonium chloride,	$\lambda=51.4 \mu$
Witherite (barium cabonate),	$\lambda=46.0 \mu$
Strontianite (strontium carbonate),	$\lambda=43.2 \mu$

APPARATUS.

The general method of making the measurements can best be explained by reference to the accompanying diagram, Fig. 1, which represents a horizontal plan of the arrangement of apparatus. *A*, the source of light, consisted of a number of Nernst glowers, usually five, held in a porcelain holder. The current was supplied at about a hundred volts by a storage battery. Each glower required from 0.7 to 0.8 ampere.

As the source of light and the entire apparatus were enclosed in the same glass case, it was necessary to remove some of the heat

¹ A paper read before the American Physical Society at the Washington meeting, April 25, 1908.

developed by the glowers by means of a cylindrical, double-walled water-jacket *B* through which a stream of tap-water flowed. The

Fig. 1.

dotted lines represent the path followed by the rays examined. M_1 was a concave silvered mirror. S_1 and S_2 were two surfaces of the substance whose residual rays were to be examined.

Between the silvered mirror and the first surface there was a shutter, not shown in the diagram, which was operated by an electromagnet. By means of it the radiations could be admitted or shut off at will. *C* was the first slit of a reflecting spectrometer of the Rubens type. A real image of the glowers was projected on the plane of the slit by the mirror M_1 after reflection from the surfaces

S_1 and S_2 as indicated. M_2 , the first spectrometer mirror, was so adjusted that the diverging rays from any point of the slit were rendered parallel after reflection. D was a transmission grating made of constantan wire, the axis of the wires being about 0.5 mm. apart. The diameter of the wire itself was about half the grating space, being 0.26 mm. This grating was made by winding the wire on a rectangular brass frame as on a reel, on the outer edges of which grooves had been cut by a screw-cutting lathe to receive the wire. The wires having been tightened by an adjustment in the frame for this purpose, were soldered in place and cut away at the back. M_3 was a plane silvered mirror standing vertically on the prism table of the spectrometer, the axis of the spectrometer lying in its reflecting surface. It was by the angular displacement of this mirror that the angular deviations of the diffraction spectra were measured. Since any angular displacement of a mirror makes a doubly great angular displacement of a reflected ray, it is necessary in measuring the angular deviation of a diffracted beam, to turn the mirror through an angle equal to only half the actual angular deviation, in order to throw the diffracted image on the second slit. M_4 was the second concave silvered mirror of the spectrometer and was adjusted to throw an image of the first slit upon the second. Both slits were maintained throughout the experiments at a constant width of approximately 6 mm.¹ After leaving the last slit the radiations fell successively on the plane silvered mirror M_5 and three surfaces S_3 , S_4 , S_5 , of the substance under examination, from which they diverged until they reached the concave silvered mirror M_6 which finally formed an image of the second slit on one vane of the radiometer R . The diagram shows another surface Q , attached to the mirror M_5 , an arrangement used in measuring the reflection coefficients of a number of substances, not mentioned in this paper.

There were two reasons why the surfaces examined were divided into two groups separated by the spectrometer, instead of being placed in one group, as has been usual heretofore. By this arrangement smaller surfaces could be employed, as they could then be

¹ Rubens and Aschkinass used slits of 1 cm. width in their experiments on rock-salt, and 1.6 cm. with sylvite. Wied. Ann., 65, p. 241, 1898.

placed nearer the points where the images were formed, and it was much easier to secure suitable specimens for the smaller surfaces required. The second reason was that the difficult process of adjusting the surfaces was in this way much simplified. After five successive reflections on surfaces as imperfect as some of those used in the present experiments, the visible light was so far diminished, after its passage through the spectrometer, that it was too faint to be seen. But by temporarily replacing S_1 and S_2 by silvered mirrors, the remaining surfaces S_3 , S_4 and S_5 were easily adjusted when the spectrometer was set for the central image of the grating. The visible image of the second slit could thus be accurately set and focused on the radiometer vane by the mirror M_6 . The silvered mirrors were then replaced by the surfaces S_1 and S_2 , which reflected a visible beam easily followed through the spectrometer to the second slit, making the complete adjustment a comparatively easy matter. Quite a number of screens not shown in the diagram were used to keep stray radiations from affecting the radiometer. To shield it also against chance drafts of air of varying temperature, which would make the zero unsteady, it was enclosed in a thin box with two openings, one to admit the beam from the spectrometer, the other to permit the observation of deflections.

The whole apparatus except the spectrometer stood on a wooden shelf, 75 cm. by 150 cm., supported by brackets from the brick wall of the laboratory. The spectrometer was supported on a stand which rested on the floor of the laboratory. Holes were cut in the shelf for those parts of the spectrometer which projected above it. By means of sheet rubber, oil-silk and rubber cement, the openings were made secure against the admission of water-vapor. The prism table could be rotated and the divided circles could be read from the outside. The glass case referred to above was a show case of the same length and breadth as the shelf, and 75 cm. high. Its location is indicated in Fig. 1 by the heavy border line, the light line representing the edge of the shelf. It was mostly supported by a cord with pulleys and a counterweight, so that it could be raised or lowered with little effort. The purpose of this case was to exclude water-vapor from the path of the rays and from the surfaces, as the experiments of Rubens and Aschkinass showed that

water-vapor absorbs very strongly radiations of long wave-length. The air under the case was kept dry by trays of calcium chloride, and leakage between the case and the shelf was prevented as far as possible by oil-silk cushions stuffed with cotton.

Fig. 2.

RADIOMETER.

The metal work of the radiometer was made by Wm. Gaertner & Co. of Chicago from the designs of one of the writers. Fig. 2 shows its main features. It consisted of four distinct parts, the

suspended system with its adjusting mechanism, the main body of the instrument, the glass cover, and the tripod stand. The construction of the suspension and the reasons underlying it have undergone no essential modification since the first radiometer of this type was built.¹ The dimensions of the vanes aa' , their distances from the rotation axis, and the choice of the black material with which they are coated, depend upon the special purposes for which the radiometer is to be used. The suspension in the present experiments carried vanes about 5 mm. long by 1.5 mm. wide, their centers lying about 2.2 mm. from the axis of rotation. The vanes were coated with black iron oxide, which is a far better absorber for very long waves than lamp-black.

The body of the radiometer consisted of a rectangular brass block of square section, 18 cm. high, and 7 cm. broad and long, with a hollow cylindrical boring extending axially from the top nearly to the bottom. Outside underneath was a cylindrical stud, which rested in a corresponding socket in the tripod base B , and was held in place by a screw and washer underneath. This allowed an adjustment in azimuth after the tripod was permanently fixed. The tripod base was provided with leveling screws. The top of the brass body was ground plane and was covered by a glass bell also ground, from which went the tube to the mercury air-pump. Near the bottom of the radiometer were three openings. The lower one C was opposite the mirror of the suspended system, and was covered by a piece of plate glass cemented on. The angular deflections of the suspended system were observed through this window by means of a telescope and scale. The plane of the window was tilted so that the reflections of the scale from its surface should not interfere with the reflections from the mirror. Above this window, but on the two sides adjacent to it, were two opposite openings D in front of the vanes, and E behind them. Through the front opening passed the radiations to be examined, and through the other the vanes could be inspected and the visible radiations adjusted so as to fall on one of them. This second opening was covered by cementing a piece of plate glass over it. The front opening, as shown at D in Fig. 2, was arranged so as to be near the

¹ E. F. Nichols, *PHYS. REV.*, 4, p. 297, 1897.

vanes, which hung in the center of the instrument. A glass, rock-salt, fluorite, or other plate, was fastened as shown at the inner end of a short tube or thimble, suitable rubber washers being used to keep the joints air-tight. This thimble was screwed into the radiometer and could be removed without disturbing the packing of the transparent plate, and another like it with a different plate already mounted, could be readily substituted. In these experiments a quartz plate 0.5 mm. thick was used, and the thimble in which it was fitted had a vertical cross-bar in the center to support the plate against the atmospheric pressure.

The adjustments adopted for the suspended system are these :

1. Raising or lowering the suspended system.
2. Changing the sensitiveness and the period by lengthening or shortening the fiber.
3. Changing the zero.
4. Changing the distance of the vanes from the window.

These adjustments were all provided for in the improved radiometer, and could be made after the system was in position before the glass cover was put on. The suspension could be raised or lowered by sliding the split brass tube *F*, Fig. 2, up or down in its sheath, or by turning the milled head *G*, which by means of an endless cord turned the pin *H*. On this pin the quartz fiber was wound on a groove at the center. By making use of both these methods of changing the height of the suspension, the length of the fiber could be changed, and thus the sensitiveness and period of the instrument, without changing the position of the vanes in front of the window. The zero could be changed by rotating the tube *F*. The block *J*, which held the tube, had a forward and backward motion in a slot, and was moved by the milled head *K* which rotated a pinion engaging a ratchet attached to the movable block. In this way the suspension could be moved so as to bring the vanes to any required distance from the window. The whole apparatus for adjusting the suspension rested on the ledge *L*, and could be taken out at will.

In the bottom of the radiometer a small quantity of some low-grade radioactive salt was scattered. This was for the purpose of removing any static charges on the suspension caused by accidental contact with the window or other part of the instrument.

The radiometer was continuously connected with a mercury air-pump throughout the experiments, and the pressure kept at from 0.04 mm. to about 0.08 mm. of mercury while observations were being made.

The flange of the glass cover and the stop-cocks were smeared with Ramsay's preparation made by melting together equal parts by weight of vaseline, paraffine and soft rubber.¹

OBSERVATIONS AND MEASUREMENTS.

The wire transmission grating already referred to, was calibrated optically with sodium light, and also by linear measurements on a dividing engine. In the optical calibration the grating was placed on a spectrometer and adjusted. Proceeding outward on either hand from the central image, only spectra of the odd-numbered orders at first appeared. Later the even-numbered spectra of higher orders were seen, at first faintly but with increasing intensity, until after the eleventh order, spectra of even orders were more intense than those of the odd. For purposes of optical calibration the deviation of the spectrum of the 16th order was employed. The grating constant deduced from these observations was 0.5081 mm. The grating was afterward placed on a dividing engine and the space occupied by 40 wires measured. The grating constant thus deduced was 0.5083 mm. A mean value, 0.5082 mm., was used in the computations.

In making a measurement of the mean wave-length of residual radiations, after the spectrometer and surfaces had been adjusted as previously described, measurements of the energy of radiation as indicated by the radiometer were made, first with settings of the spectrometer in the neighborhood of the central image at intervals of about 10' or 15' as read on the divided circle. A single observation consisted of three readings, first a reading of the scale when the radiometer suspension was at rest, then, the shutter being held open until the full deflection was reached, a second reading was taken and the shutter closed; finally the point to which the index returned was noted as the third reading. The deflection corresponding to these three readings was taken to be the difference between the second reading and the mean of the first and third. The number

¹ Any grease or wax surface is rendered much more impervious to the passage of air if glazed by passing a hot rod over it.

thus obtained was considered as a single observation, and the mean of several such observations gave the ordinate of a point on the energy curve, as shown in the curves in Figs. 3 and 4.

After obtaining points in this way for the central image, the approximate location of the maxima of the two spectra of the first order was determined by preliminary observations, and then a series of observations was made in the neighborhood of each of the diffraction images beginning either at the maximum and taking points alternately on opposite sides about 10' apart until the base of the image was reached, or beginning similarly at the base and approaching the maximum by taking points alternately on opposite sides. From each set of observations of this kind for any one substance, curves were drawn as shown in Figs. 3 and 4. The curve representing the central image and the location of its maximum were of comparatively small importance. In drawing the curves representing the distribution of energy in the diffraction spectra, the observed points were plotted and connected by a smooth curve, the position of the maximum of which was taken as the position of maximum energy. The positions of these maxima are however subject to a possible correction owing to the increasing transmission with increasing wave-length of the quartz window of the radiometer in this region of the spectrum. Quartz is known to be quite opaque between $4.5\ \mu$ and $24.4\ \mu$. Farther out it becomes more and more transparent for increasing wave-lengths. This changing transmission may have the effect of distorting to some extent the shape of the curves by shortening the ordinates on the short wave side. The effect of such an error would be to shift the maxima to longer wave-lengths. Measurements of the transmission of a thin quartz plate, which was about 79 per cent. for $\lambda = 52\ \mu$, 71 per cent. for $\lambda = 46\ \mu$ and 61 per cent. for $\lambda = 43\ \mu$, show that this error is small.

The difference between the spectrometer readings of the diffraction maxima on each side of the central image was taken as the true deviation, on account of the doubling due to the plane mirror already referred to. In this way the wave-length was calculated by means of the formula

$$n\lambda = a \sin \theta,$$

where n = the order of the spectrum, in this case always 1,

λ = the wave-length,

a = the grating constant = 0.5082 mm.,

θ = the angle of deviation.

Three complete sets of measurements were made with rock-salt, the first two with an earlier arrangement of apparatus that had no provision for the exclusion of water-vapor from the path of the radiations. The three values of the mean wave-length obtained were 51.7μ , 52.9μ and 52.4μ . The mean of these values was

Fig. 3.

52.3μ . The third observation should be given the greatest weight as a better arrangement of the apparatus gave more than twice the radiometer deflection obtained in the first two. The mean of the first two, however, happens to be very close to the third.

Rubens and Aschkinass with an arrangement less favorable for getting good deflections, and with a slit width in the spectrometer of 1 cm. found 51.2μ for the mean wave-length of these residual rays.

Three sets of experiments were made with the mineral witherite, which is barium carbonate. The first set was made with the preliminary arrangement of apparatus mentioned above, but the other two after the adoption of the glass case covering the whole apparatus. The values obtained for the mean wave-length were $45.0\ \mu$, $46.8\ \mu$ and $46.2\ \mu$, the mean of the three being $46.0\ \mu$. It is probable that more weight should be given to the last two sets. The mean of these two alone is $46.5\ \mu$. Witherite has at least one other group of residual rays beside the one given above, and for this reason the central image has a very large amount of energy compared with that in the diffraction spectrum of the first order, as is shown in the curve in Fig. 3, which represents a single set of observations. It would be even greater than is shown by the curve if it were not for the heavy absorption by the quartz radiometer window at this point.¹ The curve shows indications of the diffraction spectrum of the third order for these other residual rays at $6.86\ \mu$ measured by L. B. Morse.² The presence of much shorter wave-lengths in the central image is shown by the fact that about 58 per cent. of the energy of the central image, so far as is indicated by the radiometer, is transmitted through a sylvite plate 5 mm. thick. In the diffraction image the total amount of energy was so small that the percentage transmitted by the sylvite plate could not be determined, but if there were any it was less than 8 per cent. This was to be expected from the known absorption of sylvite which is heavy beyond $20\ \mu$.

Four sets of observations were made with ammonium chloride, all under the improved arrangement of apparatus. The surfaces were prepared from the large solid masses of crystals of commercial sal-ammoniac. The values obtained for the mean wave-length were as follows: $51.2\ \mu$, $51.7\ \mu$, $51.4\ \mu$, $51.4\ \mu$. The mean value is $51.4\ \mu$. The energy of the central image was mostly in waves of this wave-length as only about 13 per cent. of it was transmitted through a sylvite plate 5 mm. thick.

Three sets of observations were made with the mineral strontianite (strontium carbonate). The values obtained for the mean wave-

¹ E. F. Nichols, *PHYS. REV.*, 4, p. 297, 1897.

² L. B. Morse, *Astroph. Jour.*, 26, p. 225, 1907.

length were: $43.1\ \mu$, $43.7\ \mu$, $42.7\ \mu$, the mean of the three being $43.2\ \mu$.

Attention should be called to the fact that the three chlorides whose residual rays are known, potassium chloride, sodium chlo-

Fig. 4.

ride, and ammonium chloride, have bases whose atomic weights, 39, 23 and 18, lie in the same order as the wave-lengths, $61.1\ \mu$, $52.3\ \mu$ and $51.4\ \mu$. In the light of recent experiments by Pfund,¹ Coblentz² and Morse³ this series points to chlorine as the active ion in the long-wave spectrum of the chlorides, and casts doubt upon Aschkinass's⁴

¹ A. H. Pfund, *Astrophys. Jour.*, 24, p. 19, 1906.

² W. W. Coblentz, *Jahr. d. Radioakt. u. Electron.*, 4, pp. 7-78, 1907.

³ L. B. Morse, *Astrophys. Jour.*, 26, p. 225, 1907.

⁴ E. Aschkinass, *Ann. Phys.*, 1, p. 42, 1900.

earlier surmise which made sodium and potassium the active ions in sodium and potassium chlorides in this remote region of the infra-red spectrum. The wave-lengths of the residual rays from strontium and barium carbonates also lie in the order of the atomic weights of the respective bases.

The writers take pleasure in acknowledging their indebtedness to Dr. S. R. Williams and Mr. C. S. Brainin for their assistance in helping with some of the observations, and to Mr. Ernst Werndl for the drawings of the radiometer.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY, NEW YORK, June, 1908.