THE EFFECT OF ULTRA VIOLET LIGHT AND X-RAYS ON THE STABILITY OF MATTER.

ARTHUR L. FOLEY, Indiana University.

Some fifteen years ago the writer began an investigation having to do with the question of the transformation of matter. At that time the subject was beclouded with conflicting theories and speculations, due largely to the apparently contradictory results reported by many experimenters. There were many groups between those who believed that *all* matter is in a state of transformation and those who held that there was no conclusive evidence of the transformation of *any* chemical element into another element. The former were eager to accept the statement that, by the time changes observed in their spectra, certain gases in vacuum tubes had been shown to be undergoing transformation. Some of the latter denied the reality of any such changes. Others resorted to divers methods in attempting to account for the source of the matter responsible for the new spectral lines which had been observed.

Perhaps the most common "explanation" by those who objected to the idea that matter can be transformed was that the new lines were due to gas occluded on the walls of the tube or the surface of the metal electrodes, and gradually liberated in the partial vacuum. Others thought the gas might have been contained *within* the material of the tube walls or electrodes, and slowly liberated. Some advanced the idea that the gas might have diffused through the tube walls, through the electrodes, or between the two where the electrodes were sealed in. One went so far as to suggest that an electric discharge through a tube might carry gas into it, like a current through an electrolyte. The wildest speculation was that electricity itself is the "stuff" from which all matter is made, and that some had been trapped in the tubes and matter created.

The writer hoped to eliminate some of the above "explanations" by using electrodeless tubes of two different materials. There was no electric discharge *through* the tube, there were no seals for leakage, and there were no metal electrodes to liberate absorbed or adsorbed gases. The objections above named were thus reduced to two, the question of the porosity of the tube walls, and the gas absorbed or adsorbed by those walls. The weight of these two objections should be increased or lessened somewhat by the use of both quartz and glass tubes, as both materials would not be expected to have the *same* porosity, absorption or adsorption, and the same reaction to X-rays and ultra-violet light.

All the tubes used in this study were of the dumb bell type, 12 cm. long, with cylindrical bulbs 2 cm. in diameter and 4 cm. long, connected by a capillary 4 cm. long. There were two quartz tubes and two glass tubes of each of the gases—argon, bromine, chlorine, carbon dioxide, helium, hydrogen, iodine, nitrogen, oxygen, sulphur dioxide, watery

"Proc. Ind. Acad. Sci., vol. 34, 1924 (1925)."

vapor and xenon, and two quartz tubes of carbon monoxide, krypton and neon.

Another series of tubes of the same shape and size as the gas tubes above named was made by washing out the tubes with nitrogen and then including in each of the cylindrical bulbs in a rarefied nitrogen atmosphere from one to ten grams of some "chemically pure" metal, the amount depending on the density of the element and its cost per gram. There were two quartz and two glass tubes for each of the elements mercury, thorium and uranium. There were two glass tubes for each of the elements—aluminum, antimony, arsenic, barium, bismuth, carlmium, copper, magnesium, manganese, selenium, sulphur and tin. All the tubes, both quartz and glass, were filled, pumped and sealed by the late Sir William Ramsey.

The spectrograms were made with a large Hilger quartz spectrograph using 8x10 inch dry plates. Light from the capillary of the dumb bell vacuum tubes was focussed directly on the slit of the spectrograph by means of two quartz lenses, one of them a cylindrical lens. A strip of tin foil wrapped about each of the large cylindrical ends of the tubes formed a sort of condenser, which was connected in parallel with a glass plate condenser of about 200 cm. capacity, both condensers being in parallel with a 0.5 cm. spark gap between small brass spheres. This system was connected through a short series spark gap in each line, to a 20,000 volt transformer operated by a 60 cycle, 110 volt current. When the potential of the transformer rose to the point that a spark jumped the two series gaps the condensing system was charged. This in turn discharged through the shorter gap in parallel with it, the oscillations being more or less independent of the transformer cir-Thus the vacuum tubes were operated entirely by induction, and cuit. as a consequence much longer exposures were necessary than would have been required with electrode tubes. The adjustable wedge in front of the slit of the spectrograph was set to give a slit length of 0.6 cm., and the plate exposed 40 minutes. Without disturbing any of the adjustments the slit was then lengthened to 1.4 cm. and the plate exposed 15 minutes. Finally the slit was lengthened to 2.5 cm. and the plate exposed five minutes. Consequently each line in the spectrogram had three different times of exposure, the two ends an exposure of five minutes, the center of 60 minutes, and the portion between of 20 minutes. These times of exposure were varied somewhat with different tubes in order to bring out as clearly as possible both the strong and weak lines in a given spectrogram. As the tubes aged it was necessary to increase the times of exposure-in some cases to as much as five hours. The final spectrogram of one of the mercury tubes could not be taken until the tube had been heated to restore its luminosity.

1. Quartz Tubes Exposed to Ultra-Violet Light.—After taking the spectrograms of the 36 quartz tubes, two of each of the elements previously enumerated, one of each pair of tubes was marked A and the other B. The A tubes were laid away in a light tight cabinet to be used only as a check against possible time changes in case any change was found in the spectrograms of any of the B tubes, after exposure to

ultra-violet light. The B tubes were arranged in two closely packed rows at distances ranging from 15 cm. to 25 cm. from a 400 watt mercury arc in quartz.

The neck (capillary) of each tube was thoroughly shielded from the rays from the arc, to guard against any effect the radiation might have on its transparency. After exposing the 18 B quartz tubes 14 hours per day for 20 days, a total of 280 hours, spectrograms were made of each of them and compared with the spectrograms of the same tubes taken before exposure to ultra-violet radiation.

Altogether six spectrograms were taken of each of the 36 quartz tubes-18 A tubes and 18 B tubes. The six spectrograms were taken after exposure of the B tubes to ultra-violet light for periods of 0 hours, 280 hours, 1,000 hours, 2,000 hours, 4,000 hours and 8,000 hours. A study was made of the spectrograms of the A tubes to determine whether or not there were any time changes. The B tube spectrograms were studied to determine whether or not they showed any changes not shown on the A tube spectrograms which might be attributed to the action of ultra-violet light. The study was interrupted by the war, but was resumed four years ago. I have carried the study as far as it seems practicable with the spectrograms on hand. These were made on a large Hilger quartz spectrograph and the wave length scale was photographed on every plate. However, this scale does not permit of a sufficiently accurate estimation of wave lengths to enable a positive identification of some of the lines appearing on the plates. Before this can be done it will be necessary to take another series of spectrograms with an iron or other comparison spectrum on every plate. Inasmuch as the press of other duties will prevent my continuing this study in the near future I am publishing a brief statement of my results to date.

2. Glass Tubes Exposed to X-Rays.—The procedure for testing the effect of X-rays on matter contained in a vacuum tube differed from that already described for determining the effect of ultra-violet light only in that the quartz arc lamp was replaced by an X-ray tube and glass tubes were used instead of the more expensive quartz tubes required for the ultra-violet light experiment. Various types of X-ray tubes were used at different times—all operated by an eight-inch heavy discharge induction coil. The intensity of the X-rays differed considerably from time to time, and no attempt was made to keep the intensity constant or to measure it. On the average, however, the rays were somewhat harder than are used for fluoroscopic work and of an intensity that would have given a good radiograph of the hand in two seconds if the hand had been held at the same distance from the X-ray tube that the spectral tubes were placed.

There were 27 pairs of glass tubes, two for each of the elements previously named. The procedure was practically the same as was followed with the quartz tubes. After taking spectrograms of all the tubes, one of each pair was labeled A and laid away as a check. The others were marked B, and were exposed to X-rays for 10 hours, and their spectrograms again taken. Succeeding series of spectrograms were taken after exposures of 20 hours, 50 hours and 150 hours. Only the cylindrical ends of the tubes were exposed to the X-rays, the necks (capillaries) being screened behind strips of sheet lead 0.6 cm. thick. All the X-ray exposures were made soon after starting the experiment, before the modern powerful X-ray apparatus was available.

Results

1. Quartz Tubes Exposed to Ultra-Violet Light. Bromine, Xenon. —These gases showed no change in their spectra except the gradual decrease in spectral intensity which spark tubes usually exhibit with use.

Argon.—The argon spectrum at first contained numerous mercury lines. These lines soon disappeared from the A plates, later from the B plates. There was no apparent change in the argon spectrum.

Sulphur-Dioxide.—The spectrograms from the sulphur dioxide tubes showed very numerous lines of other substances, water vapor lines being very prominent. There were also a few weak mercury lines and cyanogen heads, and a very strong carbon line at 2478. There was as much variation in line intensity amongst the plates from one tube, as from the two tubes—A and B. It appeared, however, that the watery vapor and mercury lines tended to decrease in intensity and the carbon and cyanogen lines to increase. H_{α} 6563 appeared on plates near the end of the series.

Helium.—A few mercury lines and several weak nitrogen bands which appeared in the first of the series, gradually disappeared, leaving a helium spectrum of increased brilliancy on the later plates. The increase in intensity was particularly noticeable in line He 3820. This is in accord with the well known fact that the vacuum tube spectrum of helium in the presence of impurities increases in brilliancy with a decrease in pressure in the tube. Such a decrease in pressure doubtless resulted from continued sparking of the tubes.

Hydrogen.—Mercury lines appeared in both A and B spectra, being much stronger in A. Succeeding plates showed no change in the spectra except a gradual decrease of intensity of all lines. The line H^{δ} 4102 appeared on the first plate of the A series, but not on any other plate of either series.

Carbon Dioxide.—A few mercury and carbon bands, numerous carbon dioxide bands, and some carbon lines appeared on early plates. Later plates showed a gradual change of these bands into line spectra, with considerable change in the relative intensity of some of the lines. CO_2 4131 was much stronger on the later plates. C 3580, strong on A plates, was absent from B plates. Line Hg 3544 was present on both but was much stronger and sharper on A plates. Hg 2536 completely disappeared on the last of the B series.

Carbon Monoxide.—Numerous mercury lines appeared on early plates from both A and B tubes, being particularly strong on the A plates. Many of these completely disappeared from later plates of both series. The strong line Hg 2536, one of the most persistent in most spectrograms, was not found on the later plates from the carbon monoxide tubes. The same may be said of Hg 3023.

Lines C 3167 and N 3371 appeared on B plates only and with increasing sharpness and decreasing width. Of the four lines of the cyanogen group iv., the two inner lines were greatly weakened on B plates and all four sharpened on A plates.

Neon.—Both the A and B neon tubes, supposed to have been filled with pure neon, gave spectra with numerous mercury lines and nitrogen bands. In fact, only a few neon lines appeared except in the red. However, the mercury and nitrogen spectra were profoundly affected by the neon. Certain mercury lines appeared on the plate that did not appear on the plates from mercury tubes except under prolonged exposure, and some mercury lines that appeared very strong on the mercury plates were weak or absent entirely from the neon plates. The head lines of the nitrogen bands were much weaker than on the spectra from nitrogen plates, but the weaker members of the bands were more intense on the neon plates. In other words, the lines in the nitrogen bands on the plates made from the neon tubes were of much more nearly uniform intensity than on the plates made from the nitrogen tubes. Some unidentified lines appear on some of the plates. Many lines with feathery edges toward the violet appear as sharp lines on the later plates.

Krypton.—Only two changes were observed in the krypton spectrum. Later B plates showed some variation in the intensities of the lines as compared with earlier plates in the series, particularly in the region near 4400. Further, near 4500, three lines appeared on later plates where there were but two on earlier plates.

Chlorine.—Most of the lines on the chlorine plates were nitrogen lines, the nitrogen heads being sharper on the chlorine plates and not fading away so rapidly toward the violet as in the plates from nitrogen tubes. The violet edges of the lines were not so feathery. However, the chief difference is in the fact that the chlorine plate showed four lines between 3847 and 3881 while the nitrogen lines to the red end were very much weaker than in the nitrogen plate on which there were four lines between 3870 and 3942. The first group of four showed an exact correspondence with some of the mercury plates, and the last four with some of the nitrogen plates. Both groups appeared on the later nitrogen plates from glass tubes.

Iodine.—The iodine lines agreed in position but differed enormously in relative intensity from the figures given in spectrum tables. B plates showed a progressive increase in sharpness and number of the individual lines and a decrease in the density of the band areas.

Nitrogen.—The first nitrogen plates showed mercury lines from both A and B tubes, the line Hg 2536 being particularly strong. This line, together with 3032, soon disappeared from the B plates but maintained its strength on the A plates. New lines at 2528 and at 2605 appeared on the later B plates. Plates of the B series showed the nitrogen lines stronger on B than on A in the violet end of the spectrum.

Oxygen.—Besides a few oxygen lines, both the A and B plates showed a number of mercury lines, some common to both series and some on each series not found at all on plates of the other series. The mercury lines gradually disappeared from both series, the rate being greatest in the case of the B plates.

Watery Vapor.—Plates from quartz tubes showed no marked change in the spectrograms of either the A or B series. Many of the stronger lines and bands were clearly due to nitrogen and mercury, the latter in some instances being stronger than on the plates from mercury tubes. But few watery vapor lines were identified.

Quartz Tubes Containing Metals in a Rarefied Nitrogen Atmosphere. *—Mercury.*—In addition to the mercury spectrum, the earlier plates of both the A and B series showed several hydrogen lines and traces of several of the cyanogen bands, the stronger ones heading at 3883. Later plates in the series showed a fading out of both the cyanogen and hydrogen lines in addition to many of the weaker lines of the mercury The mercury spectrum of the B tube near the close of the spectrum. series became so weak that it was concluded to heat the tube in a Bunsen burner to restore its luminosity. The tube was not heated to a very high temperature—probably to about 400° C. The spectrum of this reheated tube was very different from its spectrum before heating. The cyanogen band heading at 3883 now came out very strong, as did also some of the hydrogen lines-particularly the line He 6563, which did not appear at all on most of the early plates. On the plate from the reheated tube it was very strong. All the lines in the spectrum of the reheated tube were very much sharper than before heating. Extending from about 3095 to 3165 there was a series of fine lines closely packed, apparently almost equally spaced and of equal intensity, each edge of the band being terminated by a line of greater intensity than the others. The mercury lines 3126 and 3132 were very strong and sharp almost at the center of this band. There was no appearance of this band on any of the earlier plates of either series. The most conspicuous feature of the mercury plate from the reheated tube is the appearance of a strong and sharp pair of lines at about 3360 and 3370—the longer component of the pair appears on earlier mercury plates, the CO_2 plates, nitrogen, krypton and chlorine plates, which show some nitrogen lines. Both lines of the pair appear on hydrogen plates, being much stronger on the B series. The pair appears on xenon plates with the shorter component much stronger than the other. The pair does not appear on plates from other elements. It would appear that the longer component might be N 3371 and the shorter Cy 3361. Spectrum tables give both these lines as being hazy toward the violet, but such is not the case here. The carbon plates show a pair of lines at about this position but with a separation of only .6, while here it is 1.1.

Nitrogen-Thorium and Nitrogen-Uranium.—Spectra from the nitrogen-thorium and nitrogen-uranium tubes show nothing but the nitrogen spectrum, along with a few mercury lines. The mercury lines grew weaker and many disappeared in the later plates of the series.

2. Glass Tubes Exposed to X-Rays.—*Bromine.*—The bromine spectrograms from the A and B glass tubes were alike but they were unlike

those from the bromine quartz tubes in that the relative intensities of the spectral lines were very different. No spectral changes except a gradual decrease in intensity.

Xenon.-Same as for quartz tubes.

Argon.—No change except in the relative intensities of some of the lines.

Sulphur Dioxide.—Spectrograms from glass tubes containing this gas showed even greater anomalies than were shown by the quartz tube spectrograms. In addition to the lines present in the latter, the former contained some nitrogen lines. The variation in line intensities was more pronounced.

Helium.—Early plates showed several mercury and hydrogen and many nitrogen lines, chiefly in the nitrogen bands. As in the case of the quartz tubes, these lines faded out and the helium spectrum increased in brilliancy as the series progressed. The hydrogen lines persisted longer than did the mercury or nitrogen lines.

Hydrogen.—The glass tubes showed more mercury lines than did the quartz hydrogen tubes. Succeeding plates showed little variation in the intensity of the lines due to these impurities, except in the case of line Hg 3984, which did not appear on the last plates of the B series.

Carbon Dioxide.—Mercury and carbon bands were stronger in the spectra from glass tubes than from those of quartz, and did not fade out or change over to line spectra as rapidly as in the case of the quartz tubes.

Chlorine.—The plates showed similar changes to those observed in the case of chlorine in quartz, except that the changes were not so pronounced.

Iodine.—Same result as for quartz tubes.

Oxygen.—The glass tubes exposed to X-rays gave the same result as quartz tubes exposed to ultra-violet light.

Watery Vapor.—There was a marked difference between the spectra of the A series and B series, lines of the former being quite strong, of the latter very weak. There was considerable difference, too, between the watery vapor spectrograms of the glass and quartz tubes, more differences than correspondences.

Glass Tubes Containing Metals in a Rarefied Nitrogen Atmosphere.

Nitrogen-Mercury.—Both mercury and nitrogen spectra strong. A and B spectra practically identical with little change in either except a gradual diminution of intensity of all lines.

Nitrogen-Thorium and Nitrogen-Uranium.—Glass tubes containing these elements gave practically the same spectra as did the quartz tubes, minus, of course, the extreme violet end of the spectrum. Many of the lines, particularly from the nitrogen-thorium tube, appeared to match those obtained from the watery vapor tube.

Nitrogen-Aluminum, Nitrogen-Arsenic and Nitrogen-Copper.—There was not a trace of a mercury line on any of the plates. All the lines were nitrogen lines and like those of the B series for nitrogen in quartz tubes, except that both ends of the spectrograms were very weak on all plates.

Nitrogen-Antimony.—The lines of the nitrogen band near 3900 are more pronounced on B plates than on A plates.

Nitrogen-Barium.—Early plates had some lines of nitrogen, mercury, hydrogen and watery vapor. Later plates showed a suppression of all the lines except those of hydrogen. Even the nitrogen lines had completely disappeared from the later plates. Strangely enough, barium line 4283 appears in both series of plates, being stronger in the A plates.

Nitrogen-Bizmuth, Nitrogen-Magnesium and Nitrogen-Selenium.— Spectrum entirely due to nitrogen. No change except a gradual change in intensity.

Nitrogen-Cadmium.—The early plates exhibit fairly strong nitrogen and mercury lines, and a few very weak hydrogen lines. The plates from both series of tubes show a decrease in the intensity of the nitrogen lines. The last series of the plates show no nitrogen or mercury lines whatever, the spectrum being entirely due to hydrogen. Similar change to that shown on nitrogen-barium plates.

Nitrogen-Manganese.—A weak nitrogen spectrum with hydrogen line 6563. The pair at 3360 and 3370, mentioned under quartz-mercury, are the most prominent of any of the lines on the plate. No time change apparent.

Nitrogen-Sulphur.—The lines on the A and B series agree in position but differ in intensity. The sulphur line 4525 appears strong on plates of the A series, with less intensity on the plates of the B series. Nitrogen lines, however, are more intense on the latter. No time change was observed.

Nitrogen-Tin.—The vacuum in these tubes appeared to be very high, and good spectra were not obtained. The plates showed several hydrogen and a few nitrogen lines. No time change was observed.

It is impossible to summarize the results of this investigation. The foregoing are only a few of thousands of notes jotted down as the study was going on. All together, more than five hundred spectrograms were studied, and on many of them the wave length and intensity of every line were measured. Nevertheless, there are on some of the plates numerous lines of somewhat uncertain origin, and some others whose wave length and intensity do not even approximately match with lines for *any* element whatever. The uncertainty is further emphasized by the fact that the author has not found any agreement whatever between the wave lengths and intensities of many, too often most, of the lines attributed by different observers to the same substance. Notwithstanding the enormous amount of work already done in mapping spectra, it appears that an even greater amount remains to be done before complete, dependable spectral tables are available. Nevertheless, it would seem that this investigation warrants the following conclusions:

1. The most skilled chemist can not, in most cases, insure the absolute purity of the gas in a spectral tube and can not in some cases produce two spectral tubes that will yield identical spectra. 2. Spectra obtained from electrode and electrodeless tubes supposed to contain the same gas differ considerably, particularly in the relative intensities of their lines and the intensities of the lines due to impurities.

3. The spectra of electrodeless tubes vary with the potential, capacity and inductance of the electrical circuit, just as in the case of eletrode tubes, though to a smaller degree.

4. Electrodeless tubes exhausted with a mercury pump show mercury lines unless the mercury vapor is absorbed before or after entering the tube. Such metals as aluminum, arsenic, copper and tin, introduced into a vacuum tube, gradually absorb the mercury vapor and thus free the spectrum of mercury lines.

5. The gradual increase in the vacuum of spectral tubes in use, and consequently the usual gradual decrease in spectral brilliancy, is just as marked in the case of electrodeless tubes as with electrode tubes containing the same gas.

6. The rate at which the gases disappear in quartz and glass vacuum tubes in use is about the same, but exposure to ultra-violet light and X-rays changes the rate somewhat, increasing the rate in some gases much more than in others.

7. Heating a mercury-quartz tube whose vacuum has become too high, profoundly changes the tube's spectrum.

8. The amount of gas liberated from granulated metal contained in rarefied nitrogen gas within a glass tube is very small, not detectable in most cases, even though the metal be exposed to X-rays for 150 hours.

9. There is nothing in this investigation with electrodeless tubes that supports the objections urged against previous investigations with electrode tubes that the spectral changes observed were due to leakage about the electrodes, disintegration of the electrodes, electricity "trapped in the tube" or to the electric transport of matter. Some of the spectral changes observed with electrodeless tubes are fully as marked as with electrode tubes.

10. Bands in the early spectrograms of carbon dioxide, nitrogen and to a lesser degree of iodine, mercury and a few others, gradually gave place in later spectrograms to lines of these elements. The spectral lines became increasingly sharper and of more nearly uniform intensity.

The writer wishes to acknowledge with sincere thanks the aid received in this research from the Elizabeth Thompson Science Fund and from Colonel George Fabyan, founder of the Riverbank Laboratories at Geneva, Illinois. The Trustees of the Elizabeth Thompson Science Fund made the grant which enabled me to purchase the vacuum tubes used in this investigation. Colonel Fabyan provided the funds with which I secured an expert assistant who worked four months with me, studying spectrograms.

Waterman Institute for Research, Indiana University.

13 - 30567