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THE SPECTRA OF SOME HALOGEN COMPOUNDS AND PHENOMENA CONNECTED THEREWITH.*

CHARLES SHEARD and C. S. MORRIS.

A careful search of the literature on the spectra of compounds reveals but few papers of any importance. The first of these is by B. O. Peirce on the "Emission Spectra of Halogen Compounds of Mercury" in the *Annalen der Physik*, N. F. Vol. 6, 1879. His investigations were carried out using Geissler tubes excited by an induction coil; the tubes with the contained salt were heated by a Bunsen burner. With mercuric and mercurous chlorides he found a band lying between the yellow and the green mercury lines and observed that in the green region the continuous spectrum was filled with many fine, weak lines. The conclusion is drawn that the emission spectra of the two chlorides of mercury under heat are the same, due to the fact that the mercurous chloride dissociates into mercuric chloride and chlorine and the continuous spectrum is therefore due in both cases to the mercuric chloride. The iodide, bromide and chloride compounds of mercury gave continuous bands with their middle points at about 4430, 5000 and 5800 Angstroms respectively.

*Read before the American Physical Society, December, 1915.

In 1897 A. C. Jones published an article (*Ann. der Phy. N. E.* Vol. 62, page 31) in which he confirmed the results obtained by Peirce and extended the investigations on the bands into the ultraviolet region.

The latest research on the subject is by A. H. Chapman (*Physical Review, Second Series, Vol. IV, 1914*), who used mercuric iodide, ferric iodide and stannic iodide. In a generalized conclusion he says "that a wide emission band shading off towards the violet and the red is characteristic of the compounds investigated, and that when the absorption spectrum of the compound is available, there seems to be a definite relation existing between the absorption and emission bands. It would seem therefore that the vibrating system responsible for the emission is also effective in producing absorption in solution."

It is the purpose of the investigations here reported upon to extend our present knowledge of the emission spectra of compounds and to determine, if possible, something concerning the nature and structure of the vibrating system or systems responsible for the spectra. It was also hoped to make some comparisons between the emission and absorption spectra of the vapors with certain of the compounds used, but in this latter proposition little success has come. There have arisen, however, in connection with these latter investigations some very interesting phenomena which have either thrown some light on the main problem in hand or furnished a basis for some suggestions as to the nature of the thermions from heated salts.

APPARATUS.

The upper electrode of the apparatus used for examining emission spectra was a brass tube about seven-eighths inch in diameter and three inches long, the lower one being a brass tube about three-quarters inch in diameter and eight inches long, with one end tightly sealed with a brass plug. A water cooling jacket was constructed around the upper end of the lower electrode; this served as a screen to prevent direct contact of the gas flame with the rest of the apparatus and, operating as a cooler, preserved the waxed joints and corks. The two metal tubes were connected by a piece of heavy capillary tubing of about 1.3 mm. inside bore. Capillary tubes of

somewhat larger diameter were tried but discarded since the current density of the discharge was not sufficiently great to give an intense spectrum. Too small capillaries could not be used because they readily plugged up with vaporized salt. Rubber stoppers connected the capillary with the remaining parts of the tube.

The form of apparatus used in the attempts made to investigate the absorption spectra of the vapors is discussed later in this paper.

RESULTS.

A Geryck two-cylinder pump was connected to the spectrum tube and a low pressure, varying in different experiments from 1 cm. to 0.1 mm. mercury pressure, maintained. The discharge from the induction coil was then started and without heating the tube the spectrum was examined for lines due to the elements of the compound. In some instances there appeared nothing but the air spectrum,* but in a few cases, as zinc and mercuric iodide, some lines of the elements appeared, indicating that the compound dissociated a little at ordinary temperatures under low pressure. As soon, however, as a little heat was applied the air spectrum began to disappear and a spectrum peculiar to the compound appeared. This remained for some minutes, varying with the compound used, but in general, if further heating was discontinued the air spectrum gradually returned and replaced the spectrum of the compound; this process could be repeated until finally the lower half of the electrode would become red hot without any spectrum of the compound being in evidence. But if the heating of the tube was carried on rapidly the air spectrum was quickly replaced by lines characteristic of the elements of the compound, which in turn gave way to a continuous region or regions with a few lines peculiar to the members of the compound surviving. After heating for some time (usually fifteen to thirty minutes) the spectrum of the compound and its elements was rather quickly replaced by the air spectrum. These changes were so rapid, photographically considered, that few spectrograms have been obtained. The continuous regions

*A careful study was made of the spectrum given by the empty tube both when cold and when heated. Under both conditions a large number of bands, diffuse toward the violet, were found in the region 4861 to 4142 t. m. and are due to nitrogen. Some lines and narrow bands were measured in the red-yellow region, but thus far it has been impossible to identify them.

or bands found in the spectra of the compounds studied are indicated in the following data. The pressure in nearly every case was about 2 mm. of mercury, but it was discovered that a considerable range of pressure (from 0.5 to 10 mms. mercury) had little effect upon the results.

I. Iodides.

Calcium Iodide.

BANDS	REMARKS
6075-5845 (?)	Seemingly continuous but uncertain.
5615-5528	Fairly sharp on red side, diffuse at blue.
5180-5100	" " " " " " "
4830-4787	" " " " " " "
4507-4465	" " " " " " "
4438-4375 (?)	Apparently continuous, but uncertain.

Mercuric Iodide.

BANDS	REMARKS
6072-5845	Sharp towards red, diffuse towards violet.
5605-5535	" " " " " " "
5195-5132	" " " " " " "
4828-4788	" " " " " " "
4506-4470	More or less diffuse at both ends.
4450-4375	" " " " " " "

A few prominent lines were measured and identified as follows: 6563 and 4861 due to hydrogen and 5790, 5769, 5461, 4916 and 4358 due to mercury. These lines were present at all stages of operation of the tube. A considerable number of iodine lines made their appearance on first heating the tube.

Zinc Iodide.

Upon the first heating of the zinc iodide the following simple line spectrum of zinc and iodine was obtained; 5781, 5766 and 5448 of iodine, 5182 and 4912 of zinc and in addition 6563 of hydrogen and 4358 of mercury.

With rather low heat the following bands were obtained: 5610-5535; 5195-5116 and 4829-4780. All of these were fairly sharp towards the red and diffuse toward the violet end. A number of sharp lines were also present at this stage of the experiment and a majority of these were measured; 6363, 5894, 4810, 4722, 4680 due to zinc; 6131, 6076, 5961, 5739, 5696, 5628, 5165, 4667, 4645, 4635 due to iodine and the following lines which have thus far not been identified—6235, 6203, 6027, 5937, 5839, 5816, 5119.

Cadmium Iodide.

Heat was applied slowly; numerous spectral lines appeared together with what we concluded to be the same three bands as found in zinc iodide, but as heat was applied the compound quickly ceased to function—due doubtless to rapid vaporization—and the air spectrum returned so quickly with each increase of temperature up to the highest degree attainable that no measurements could be made.

II. Chlorides.

Fused Stannic Chloride.

Low heat gave a continuous region from 5800 to 4400 diffuse at both ends. The following lines were noted when the salt was first heated: 6453, 5799, 5631, 5588, 5563, 5333 and 4525, due to tin and 5460 due to chlorine.

It was found on the initial heating that the tin lines appeared very prominent when the pressure was of the order of a centimeter of mercury, but that these lines disappeared in general and the continuous spectrum named above appeared as the pressure was reduced. With further experimentation this pressure effect disappeared for reasons which will be suggested in the concluding portions of this paper.

Ferric Chloride.

The continuous region, 5900-4800 Angstroms, was not sharply defined at either limit.

It was difficult to get a discharge to pass through the tube containing the ferric chloride when it was heated. The capillary filled readily with a brownish liquid which overflowed the ends of the rubber cork stoppers and operated to form a conducting layer along the surface.

After the disappearance of the air spectrum the characteristic yellow and green lines of mercury and the red and blue lines of hydrogen appeared.* With further heating a continuous region, indeterminate at both ends, occurred from approximately 4800 to 5900. There was no evidence of any iron lines at any period of the experimentation.

*Mercury vapor and hydrogen were present as "impurities" in all these experiments, the mercury coming from the McLeod gauge used to measure pressures.

Manganous Chloride.

Low heat gave a continuous region from 5900 to 4450, diffuse at both ends.

The prominent lines were identified as manganese 6017, 4822, 4783 and 4754, in addition to three or four lines belonging to hydrogen and mercury. The spectral examination showed the presence of the base of the compound only; no lines due to chlorine were detected.

III. Bromides.*Calcium Bromide.*

Low heat gave a continuous region, 5500 to 4850, shading off at each end.

After the discharge had passed for a little time, but before heating the apparatus, the lines present were measured and identified as those of hydrogen and mercury. This indicates that practically none, if any, of the calcium bromide vaporized and dissociated under low pressure at room temperature.

Mercurous Bromide.

Strong heating gave a continuous region from 5072 to 4912.

Zinc Bromide.

With excessive heating there was obtained a continuous region from 5550 to 5055, neither limit being sharply defined. With the bottom of the lower electrode red hot there was a small, but very intense continuous band, about 100 Angstroms wide, with its center at about 5055, together with a region, much less luminous, which appeared to be continuous from 5550 to 5150.

ABSORPTION SPECTRA OF THE VAPORS.

Chapman (Phys. Rev. 2nd Series, Vol. IV, p. 28, 1914) came to the conclusion that the vibrating system giving the emission spectra of the compounds was also potent in producing absorption in solutions. It is reasonable to suppose that the vibrating system might also persist and preserve its identity in the vaporous state and that the absorption spectrum of the compound should be the complement of the emission spectrum. Several attempts were made to see if such were the case. A tube was constructed, 22 inches in length, with an inside diameter of $1\frac{1}{2}$ inches. The ends were provided with jackets for water cooling. Plano-convex lenses of about 20 cms.

focal length were waxed on to the ends to assist in focusing the light, passing as a parallel beam of light through the tube, upon the slit of the spectrometer. The source of illumination was a Nernst glower. The tube was heated by a long gas burner set between the water cooled jackets. Two chief difficulties arose in the use of the apparatus; one was the condensation of the vapor on the cold glass ends, the other was leakage at high temperatures. Various schemes for improvement were tried, but the time allotted to this portion of the work was too meager to obtain satisfactory results except possibly in one case.

Several trials were made with stannic chloride, a substance which vaporizes readily at a low temperature. Heat was applied rapidly and subsequently a volume of vapor was produced which appeared to cut off all the light coming through the spectroscopy, except a broad band in the red end. By making comparison with the emission spectrum for this compound, it seems probable that the absorption and emission spectra are complementary.

The emission spectra, being produced under electrical excitation, are due to ionization set up by some external agency. Since there is no such external source of ionization in the experiments just described, it might be concluded that there would be no ions present and hence, if certain lines of reasoning relative to the production of absorption spectra were followed out, no absorption spectra could be expected. An examination of the inside of the tube, after using mercuric iodide or stannic chloride for example, showed a bright metallic mirror at the water-cooled ends. This proved that dissociation must have occurred and therefore presumably some ionization; a considerable number of experiments by various investigators (Richardson, Willows, Beattie, Schmidt, Sheard et al.) have shown the existence of negative ions of iodine and bromine when their salts have been heated under potential.*

*It is of interest in this connection to cite the experiments of Lenard (*Annalen der Physik*, 17, page 197, 1905) made with beads of the fused salts of the alkali metals supported upon platinum wires in the Bunsen flame. The emitted light was found to be strongly colored, the color depending upon the metal. An examination of the absorption spectra of the fused salts showed that the color of the transmitted light was complementary to that of the emitted light, as should follow from Kirchhoff's law. The salts were colorless, however, when cold, showing that some sort of dissociation resulted from the high temperatures, metallic ions being set free which had the property of absorbing and emitting radiations of the same frequency. In the case of most of the salts examined the color was found to depend upon the metal, i. e., upon the cations; the borates and silicates were marked exceptions, however, the color being due to the anions, the nature of the metal being immaterial.

DEPOSITION OF METALLIC MIRRORS.

When a discharge tube was opened after a spectral examination of a salt it was found that there was a thin metallic deposit covering the inside of the lower electrode in the portion near the water cooled end. It cannot be stated that these were present in the case of every substance investigated; but in the case of mercuric iodide, cadmium iodide, zinc bromide and tin chloride metallic mirrors, almost as brilliant as if polished, were noticed. This shows that considerable dissociation and reduction of the compound occurred under heat and the electrical excitation.

These mirrors, as stated in a preceding paragraph, were also obtained with two compounds which were heated in the apparatus used for investigating absorption spectra. The mirrors obtained from stannic chloride were almost as bright as is the surface of clean mercury. In these experiments no external agent was used except the heat. It is therefore apparent that under heat alone some metallic compounds (at least halogens) are dissociated, the metal being set free. There can have been no reducing agent present, such as would have been the case had the salts been introduced into the flame, unless the residual gas present in the tube could have acted as such agent. This seems improbable in view of the low pressures used.

Some interesting results on "Flame Reactions" have been published recently by Bancroft and Weiser (*Journal of Physical Chemistry*, Vol. XVIII, 1914) in which they have obtained metallic deposits on cold porcelain introduced into a Bunsen flame which was fed with chlorides and nitrates of copper, cadmium, tin, mercury and silver. These experimenters concluded that "the reducing action of the flame gases is not essential, though at times it may increase the decomposition." With this conclusion the writers of this paper are in accord and feel that the results detailed above establish the legitimacy of this conclusion since the question of flame gases does not enter.

POSSIBLE NATURE OF THE SYSTEMS PRODUCING THE BAND SPECTRA OF THE COMPOUNDS.

In order to present the experimental facts in concise form and to provide a ready reference table in connection with the ensuing discussion the following brief resume of the data obtained on the emission spectra of the compounds is introduced.

Continuous Spectral Regions or Bands.*Iodides.*

CALCIUM	MERCURIC	ZINC
6075-5845 (?)	6072-5845	
5615-5528	5605-5535	5610-5535
5180-5100	5195-5132	5195-5116
4830-4787	4828-4788	4829-4780
4507-4465	4506-4470	
4438-4360 (?)	4450-4375	

Chlorides

Stannic	5800-4400
Ferric	5900-4800
Manganous	5900-4450

Bromides

Calcium	5500-4850
Mercurous	5075-4912
Zinc	5550-5150

A survey of these results shows that the banded or continuous regions are in general nearly identical amongst the members of any particular group of halogens. In the case of the chlorides and bromides the continuous regions were diffuse or shaded off at each end. In the case of the iodides, however, all the bands except those at 4500-4470 and 4450-4370 were fairly sharp at the longer wave length ends.

It appears that there is some common vibrating or emitting system which is operative in each of these halogen classes. The only common element present, so far as known, in the iodides examined is iodine, and so on for the chlorides and bromides. It seems reasonable to attribute the general similarity of spectra in each of the halogen groups to the halogen members acting directly or in combination as hereinafter suggested. The compounds on initial heating showed, in general, some lines characteristic of the base and of the radical. There is, therefore, some dissociation of the original compounds and production of ions, both positive and negative, some of which to say the least are elemental constituents of the compound designated.

The residues from the various salts were different in color and structure from the compound introduced. For example, the residue from stannic chloride (original salt white in color) came out violet, manganous chloride (original salt slightly pinkish) came out lavender in color. These color effects indicate chemical changes. Examinations of several residues, using the polarizing microscope, were very kindly made by Mr. J. B. Dickson, then of the Department of Chemistry of

the Ohio State University. The following notes are taken from his report:

- Hg Br.* Metallic mercury unmistakably present. Tiny globules of mercury found under 'scope on surface of lumps of Hg Br.
Cd I₂. Showed presence of metallic cadmium by reflected light.
Zn Br₂. Could get no evidence of presence of free zinc.
Fe₂ Cl₆. Under magnifier, presence of numerous green spots showing existence of FeCl₂, or Fe₂Cl₄, (the latter formula being now considered preferable by chemists).
Ca Br₂. All tests showed presence of metallic calcium.
Hg I₂. In this case there was considerable reduction to Hg I.

The writers are disposed therefore to believe that there is dissociation and ionization of some portions of the original compound into its basic and radical components, but that there is also, under the proper conditions, a dissociation of the vaporized salt into a positively charged sub-compound and negatively charged radical. To illustrate, let us take mercuric iodide (Hg I₂). This in part dissociates into Hg₊₊ or 2 Hg₊ and I₋ or 2 I₋, or positive ions of mercury carrying a single or double charge and negative ions of iodide carrying a single or double charge. In addition there is, as evidenced by the analysis of the residue after heating, a considerable dissociation into Hg I₊ or positively charged mercurous iodide and I₋ or negatively charged ions of iodine. It is probable that the banded or continuous spectra arise from the recombination of the oppositely charged mercurous iodide and iodine which are formed from the vaporized, non-dissociated salt present in the capillary portion of the discharge tube, although it is not likely that there is a permanent recombination of mercuric chloride formed. We can say that we have the emission spectrum of the original compound if we admit such a process. That some such process is operative is made plausible by the fact that the banded regions in the case of the iodides have their heads at or near a prominent iodine line. In the case of the chlorides we find extended continuous regions which include the spectrum from the blue to the orange-yellow region. There is no evidence of lines or bands in the red end of the spectrum. The spectrum of chlorine exhibits a richness of lines in the region 5000-4100 Angstroms and a dearth of anything in the red region except the line 6095. The same explanation made for the iodides seems satisfactory here. If stannic chloride dissociates in part into ions of tin and chlorine and in part into positively charged molecules of stannous

chloride and negatively charged ions of chlorine we should expect the experimental results detailed above. Furthermore, none of these banded regions appeared to be associated in any manner with the element making up the base of the salt. This is clearly proven, we believe, by the fact that the banded regions were practically identical in any halogen group irrespective of the base present. Possibly the best illustration is afforded by mercuric iodide in which the lines characteristic of mercury coexisted with the broad bands and were prominent and sharp with no tendency towards broadening or diffuseness.

These experiments also throw light upon the investigations of Professor O. W. Richardson on the specific charge of the ions. In investigating zinc iodide he found that the negative ions were iodine and the positive ions, during the initial stages of heating, correspond most closely to ions of zinc carrying a double charge. We found the spectrum of zinc and iodine present in the early stages of heating, but also found that the zinc lines soon disappeared. In the case of manganous chloride, Richardson found initial values which would correspond to manganese, but with further heating a value of "m" equal to 90 indicating possibly the existence of positively charged $Mn Cl$. The results of the experiments made by the writers support such conclusions as these. In the case of ferric chloride no spectral evidence of the presence of iron was found at any period of the experimentation, but after sufficient heating a continuous spectrum within the limits of 5900 and 4800 Angstroms was developed. This may indicate, if we follow out the line of argument given in the preceding paragraph, a dissociation into negative ions of chlorine, (Cl_-) or $(2Cl_-)$ and positively charged sub-compounds of iron and chlorine ($Fe Cl_{++}$). If such a positively charged molecular structure existed it would have a value of "m" equal to 45, which would be in accord with Richardson's experimental values of 40.2, 39.3 and 39.8. It is to be stated in this connection, however, that the analysis of the residue from $Fe Cl_3$ did not show the existence of such a compound as $Fe Cl$, but did show the sub-compound $Fe Cl_2$. The chemistry of compounds at high temperatures is still somewhat of an unopened book; without doubt there are formed and exist at such temperatures molecular structures or sub-compounds or recombinations of the elements of the original substance of which we know little. The postulation of the

formation of such ionized structures seems to us to be as likely a basis of explanation of some of the values of the specific charge of the ions obtained as the present partially accepted theories of gas ions or ions characteristic of the elements present when salts are heated under potential. The latter premise is apparently correct in many instances, but the assumption of an impurity, such as sodium, when the value of "m" lies near 23, or of potassium when the value of "m" lies near 39, seems a trifle far fetched in some instances.

CONCLUSIONS.

1. The halogen compounds investigated exhibit broad bands or continuous spectra which are probably due to the formation of positively charged sub-compounds and subsequent recombination with the negatively charged ions characteristic of the radical of the salt.

2. The bands and continuous spectra obtained are in general agreement as to number, position and character for the compounds of any specified haloid investigated. Continuous spectra are exhibited by the chlorides and bromides and several bands by the iodides.

3. The radical and not the basic element of the compound investigated appears to be the essential controlling factor.

4. There is present in the initial stages of heating of several of the compounds a dissociation into positive and negative ions spectrally determined to be the two components of the original compound.

5. There is found in the discharge tube in nearly every case a metallic deposit or mirror of the base of the salt investigated. These deposits were also found when no external ionizing agent other than heat was employed. These experiments settle in the negative the question as to whether or not the reducing action of the flame gases of a Bunsen burner is necessary for the deposition of the metallic constituent of a salt.

6. The evidence points to the conclusion that there is an absorption spectrum of the vapor of the compound which corresponds to its emission spectrum.