Studies of the Band Spectrum of Halogen I. The Absorption of Iodine Vapour. (High Temperature and Foreign Gas Effects)

By

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Abstract.

High Temperature E_{rect} . In the heated iodine vapour a remarkable development of absorption bands has been found in the extreme red part. Series of investigations brought us to the conclusion that these bands might be attributed to a highly activated diatomic molecule, and with an increasing degree of activation its absorption would become developed towards the extreme red part.

Under a high dispersion, the absorption lines exist practically until complete dissociation of the diatomic molecules. This is inconsistent with Evans's conclusion, obtained with a spectrograph of small dispersion, that from 80 to 93 percent of the diatomic molecules are dissociated when the absorption spectrum disappears.

Foreign Gas Effect. There is no difference observable in the actions of chemically inert and chemically active gases or vapours upon the absorption spectrum of iodine vapour. The foreign gas effect is also identical with the effect of its own. They all act in a similar manner with the only difference that in the same conditions the chemically inert gas is less effective than the chemically active one, the effect of iodine vapour of its own being probably the least all. By the presence of the foreign gas, a great number of lines are selectively destroyed. On again increasing the pressure of the foreign gas up to the atmospheric pressure, the times become universally diffused and groups of lines come to unite into single broad lines or "blends."

The action of a foreign gas may be divided into two kinds, the one having a somewhat selectively destroying nature and the other a somewhat universally blurring one. At high temperatures the action of the first kind disappears and the selectively destroyed lines recover their intensities. The action of the second kind, on the other hand, is exaggerated by raising the temperature of the vapour.

As to the relations existing between the effects of high temperatures and the admixtures of foreign gases upon the individual absorption lines, they generally occur in contrary ways. Speaking generally, lines strengthened by raising the temperature are suppressed by the action of a foreign gas. The action of the high temperature and the presence of a foreign gas upon the absorption spectrum of iodine vapour have not yet been thoroughly studied. Konen investigated the absorption of iodine vapour at various temperatures ranging from room temperature up to 800°C, and found that at lower temperatures the absorption increased with the temperature but decreased at higher temperatures. A detailed study on the effect of the pressure upon the temperatures of the disappearance of the absorption bands was made by Evans.¹ The spectroscopes used by these investigators were not sufficient to resolve the individual absorption lines of iodine and their results were of rather macroscopic nature.

A study of the temperature effect upon the individual lines of absorption bands of iodine was first carried out by Wood and Kimura.² They found that the emission and absorption band spectra were not exact complements, but the former would be nearly complementary to the absorption spectrum at a high temperature.

In the present investigation, further study on the influence of high temperature and of the admixtures of foreign gases upon the absorption spectrum of iodine vapour was made with spectrographs of a higher and a lower dispersion, and the results obtained so far will be given in the following pages.

Experimental Arrangement.

A few years ago, the research was undertaken with a plane grating spectrograph of the Littrow type provided with an objective of 37 meter focus. But owing to the insufficient dispersive power, many of the lines could not be resolved, and so the investigation was postponed until we could use an achromatic objective of a longer focal length. A 5.5 meter focus objective was then purchased by Prof. M. Kimura with the fund given to him by the Department of Education and the following spectgraph was constructed. The instrument consists of a collimator of 3.7 meter focus, 15 cm. Michelson plane grating, and a telescope of 5.5 merer focus, the telescope and the collimator being placed at an angle of about 30°. The grating and the objectives of the collimator and of the telescope were doubly covered with a wooden and a thick cork box. The temperature within the enclosure was kept constant to within about 0.1° C. by a toluol The photographs were taken in the fourth order spectrum, thermostat. giving a scale of about 0.75 Ängstrom unit per millimeter. Enlarged

¹ Astrophys. J., 32, 1 (1910).

² Astrophys. J., 46, 181 (1917).

reproductions of the iodine absorption spectrum taken in the regions of $548\mu\mu$ and $603\mu\mu$ were given in Figures 1 and 2 in Plate I. The resolution of the absorption lines into individuals is fair, but there are, however, groups of lines not sufficiently resolved.

One of the great difficulties met with in the present experiment was that, notwithstanding the steady constancy of the temperature within the grating chamber, the variation of room temperature especially in the winter season produced a displacement of the spectral lines. The change of the room temperature by 1°C. shifted the lines by about 0.04 mm. or about a 0.03 Ängstrom unit. In studying the effect of high temperature, owing to the small capacity of the room, the air of the room was soon warmed by the heat from an electric arc and an electric furnace. This gave us much trouble. The constancy of the room temperature was, however, practically attained at night by keeping the doors and windows wide open, and all the final plates relating to the temperature effect were obtained late at night.

The Ilford screened chromatic plate was used to photograph the absorption spectrum in the blue-green region and the Ilford special rapid, and also the rapid process panchromatic plates, in the region from orange to extreme red.

For the study of the iodine absorption at high temperature, two quartz tubes having a length of 17.5 cm. and of 20 cm. were chiefly used, each tube being constructed from two quartz test tubes. Beside these, two quartz bulbs of 5 cm. diameter were also used. For heating the quartz tube, an electric furnace having a heating tube 30 cm. long and 3 cm. internal diameter, and for the bulbs the flame of two Meker burners were The temperature inside the furnace close to the quartz vessel was used. measured by a Pt-Rh thermocouple, the junction being placed inside a The thermocouple was tested by the melting points of quartz tube. copper, aluminium and zinc, and it was found that the readings did not differ more than 10° C., consequently the temperature recorded by this instrument was considered to be practically correct. The uniformity of the temperature all over the whole length of the quartz tube was tested, and this proved to be practically good.

The vapour pressure of iodine in the quartz tube was determined from the data obtained by Steizner and Niederschulte.¹ The degree of the dissociation of the iodine vapour at any temperature and pressure was calculated from the equation given by Planck.²

I Verh. Phys. Gez., 7, 159 (1905).

² Treatise on Thermodynamics, p. 220.

A few iodine crystals were introduced into the main tube AB (in Fig.



I) and the side tube D
Was connected to a Geade pump. The tube
AB was well evacuated
and sealed at the neck
between C and D. Next,

the iodine was made to condense within the side tube C by cooling it and the whole tube was then immersed in a hot water bath at a certain temperature to fill the tube AB at a required pressure of iodine. The water of the bath was then allowed to cool down to the room temperature. Thereupon all the iodine exerting the pressure corresponding to this temperature was made to condense inside the wall of the main tube AB. Next, the tube AB was taken out of the bath and the side tube C containing superfluous iodine sealed off. Thus the required tube was obtained. Though the repeated manipulations for various vapour pressures gave considerable trouble, we could by this method overcome the difficulty of keeping the vapour density constant for a long time of exposure. Besides this, the vapour pressure of iodine was deduced from the temperature of the side tube, the coldest parts of the apparatus.

As the light source, the crater of the positive pole of a heavy current carbon arc was constantly used.

High Temperature Effect,

The absorption spectrum of the iodine vapour at various pressures was first studied with the spectrograph having a Hilger replica grating; the dispersion on a photographic plate being 0.043 mm. per Angstrom at the D-line in the first order spectrum.

At a certain very low pressure, the absorption first appeared in the blue-green region. The bulb used in this experiment was of quartz of 5 cm. diameter. The vapour pressure was calculated from the temperature of the side tube attached to it. As the vapour density was raised to the one corresponding to 40° C., the visible absorption* became strengthened, and another system of absorption bands appeared in the extreme red ($7000 \sim 8000$ A). The latter bands were quite diffused and they continued their appearance up to the vapour pressure corresponding to a temperature of about 110 C. As the vapour pressure was further raised, the absorption

^{*} We here mean, by the term "visible absorption," the well-recognized channelled absorption band spectrum in the region from the blue-green to the red.

in this region became somewhat total, while the absorption at the more refrangible part became more definite and developed towards the red (up to about 7000 Ű). The quartz bulb was then taken out from the bath and thoroughly heated in a coal gas flame to a temperature of about 800° C., the vapour tension being kept at a constant value corresponding to about 140° C. It was found that absorption bands now developed toward the extreme red. This may be seen from Figs. 3 and 4, Plate I. Thus iodine at constant vapour pressure shows stronger absorption bands in the extreme red when it is heated.

As the present paper will chiefly deal with the effects of high temperature and the admixture of foreign gas upon the individual absorption lines of the band spectrum of iodine vapour, as to the precise determination in wave-length and the classification of heads of the absorption bands will be given in a separate paper.

As stated above, the action of high temperature upon the individual absorption lines was first examined by Wood and Kimura. The present writer also studied the effect of high temperature upon the individual absorption lines. The spectrograph used in this experiment was the large grating instrument described above and the photograph was taken in the fourth order spectrum. Some enlarged reproductions are given in Figs. 5, 6, 7 and 8, Plate I. The effect came out to be quite complicated. The upper spectra in each spectrogram are of iodine vapour at ordinary temperature and the lower those at high temperature (about 1,000°C). The difference is, however, remarkable. If we compare these two spectra taken under different conditions, we notice that some lines are much stronger in the lower spectrum than in the upper. Besides this, new lines appear in the spectrum of the heated iodine vapour. In the spectrograms of heated iodine vapour such lines are indicated by the arrows, while those quenched in the heated vapour are shown by the arrows in those of ordinary iodine vapour. A closer examination of these spectra shows that in the heated vapour many of the absorption lines suffer shifting, narrowing, broadening and blending. It seems also that the absorption lines generally increase in the heated vapour.

Evans¹ has investigated the critical temperature at which the absorption spectrum of iodine vapour disappears, and showed that from 80 to 93 percent of the diatomic molecules are dissociated when the absorption spectrum disappears. The instrument used by him was not able to resolve the lines of the absorption spectrum, and it is desirable that his conclusion

I Loc. cit.

should be tested with a more powerful apparatus. With our spectrograph the absorption lines did not disappear and there remained still diffuse but definite lines at such a temperature that the absorption lines apparently disappeared when they were observed with the smaller spectrograph. These were shown in Fig. 9, Plate II. On these reproductions a portion of the spectrum (D-line region) was given, fainter traces of the absorption lines seen on the original negative being, however, entirely invisible especially in Figs. 9b and 9c. The result of the observation is given in Table II.

Table	II.		
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Vapour	pressure :	(45° C.)
Thickness	of layer:	17.5 cm.

Temperature	Dissociation	Observations			
of Furnace	of Furnace Degree		under high Dispersion		
60° C.	2 × 10 ⁻⁷ %	sharp & distinct	sharp & distinct		
220	2.3×10-1	sharp & distinct	sharp & distinct		
420	25.7	somewhat indistinct	sharp & distinct		
700	49-8	faint & indistinct	somewhat indistinct		
760	72.8	faint	somewhat indistinct		
820	84-3	Trace	somewhat blurred		
850	88.7	barest Trace	faint but definite		
920	94•7	no	faint but definite		
1,000	97.5	no	fainter Trace		
1,020	97.9	по	barest Trace		
1,100° C.	99 . 98 %	no	no		

As may be seen in the above table, it is probable that the molecule show absorption until its degree of dissociation is practically complete.

Next, the mode of disappearance of the absorption lines produced by a rise of temperature has been studied. A greater majority of the absorption lines are unaffected and the remaining lines are gradually affected with increasing temperature from about 150° C. to $1,000^{\circ}$ C., producing no sudden change. Besides these a great number of fainter lines at ordinary temperature are strengthened and also new lines appear while a few lines perfectly disappear. In addition, as previously stated, the displacement, broadening, narrowing and fusing of the absorption lines are brought about in a quite complicated way. On further raising the temperature the lines become blurred and then finally disappear.

The iodine vapour plays its absorption at best at a certain temperature. This was first noticed by Konen. He determined the temperature to be about 500°C. In the present experiment, an examination of this dictum was also undertaken. A bulb containing iodine was examined in absorption in various spectral regions, and at various temperatures. And the relation of the degree of dissociation and the time of exposure to secure negative plates of a certain degree of blackness was studied. A diagram showing this relation is given below. The curve I in full line is the one showing



the dissociation degree of the vapour corresponding to the temperature of 75° C. Curves II and III drawn as broken lines, on the other hand, are the time curves for the $589\mu\mu$ and $500\mu\mu$ regions respectively to obtain a certain blackness of the negative plates. One set of photographs (corresponding to curve II) was given Fig. 10, Plate II. The latter two curves will give, in a rough measure, the change of absorption in intensity with the temperature of the vapour.

Foreign Gas Effect.

In this section, we shall describe the effects of the admixture of external gases or vapours upon the absorption spectrum of iodine vapour. As the external gases, hydrogen, oxygen, nitrogen, carbon dioxide, air, carbon bisulphide vapour, alcohol vapour, etc., were used.

In the case of hydrogen, oxygen, and carbon dioxide, each gas was in-

troduced into the evacuated iodine bulb E (in Fig. 3) from the cylinder A



containing the gas at a high pressure through a regulator B, drying chamber C, and a manometer D, and at the desired pressure the bulb was sealed.

Two similar bulbs containing an equal amount of iodine, one of which was thoroughly evacuated while the other contained air at various pressures, were heated in a water bath to the same temperature, some iodine remaining in a solid state, and their absorption spectra were photographed with the instrument of the smaller dispersion. It was found that in the visible part the absorption increased with the rise of the air pressure, while the diffuse absorption band in the extreme red, well developed at very much lower vapour pressure, remained almost unaffected by the admixture of air up to the atmospheric pressure. Next, to a bulb provided with a fine capillary about 2 cm. long, a very small quantity of iodine was introduced and this was well evacuated and then sealed. The bulb was then thoroughly heated in a water bath until all the iodine crystals had evaporated, and its absorption was photographed. The air was then introduced to the bulb practically without altering its volume, by cutting off the tip of the capillary, and this was again heated up to that temperature and its absorption spectrum was compared with the former. There was no difference noticeable between the two.

Next, the influence of the presence of the vapours of alcohol and carbon bisulphide at high pressure in iodine was studied. Two tubes of similar size (about 8 cc. capacity) were prepared, and an equal amount of iodine and equal volume of these substances were separately introduced into the tubes. Such tube was placed in a brass tube provided with two vertical slits made on the opposite end of a diameter and this was heated in a coal gas flame, the temperature of the tube being measured by a thermometer inserted in the lower part of the brass tube (Fig. 4). The colour of the vapour and its absorption spectrum were observed with a



small direct vision spectroscope with a wavelength scale while heating until the apparatus exploded. The pressure of the vapour was deduced from the temperature at the time of explosion of the apparatus. The pressure of alcohol and carbon bisulphide vapours was found to be about 200 atmospheres. Up to this pressure, there was no difference noticeable in the absorption spectrum of both vapour mixtures with our spectroscope.

Next, to tweleve bulbs of one litre capacity, hydrogen and oxygen were separately introduced at pressures of 2, 5, 10, 18, 36 and 76 cm. of mercury respectively. Each bulb was heated in the flame of a coal gas burner to 70° C., and its absorption spectrum was photographed with the instrument of high disper-

It was found that, in all cases, the effect of the hydrogen admixture sion. upon the absorption spectrum of iodine vapour was greater than that of oxygen at the same pressure. The action of hydrogen at a pressure of 5 cm. seemed to be practically the same as that of oxygen at a pressure of 18 cm. Enlarged reproductions showing the effects of both gases at 18 cm. are given in Figs. 14c and 14d, Plate III. As may be seen in the photographs, the degree of blurring of the lines in the lower spectrum is slightly greater than in the upper one. In Figs. 14a and 14b, spectra of pure iodine at ordinary and at high temperature are given for the sake of comparison. The change produced in the absorption spectrum by the admixture of carbon bisulphide vapour and of ethyl ether vapour at a pressure of 18 cm. with iodine were also examined, and it was found that the vapours produced practically the same effect. This effect was somewhat smaller than that of hydorgen and slightly greater than those of oxygen, nitrogen, carbon dioxide and air at the same pressure.

The pressure in the bulb was next raised with iodine vapour itself and the pressure effect was compared with the effect of foreign gas at the same pressure. The bulbs used in the study of foreign gas effect are not applicable in this case, as they are too thick to transmit the light. Consequently the one shown in the annexed figure (Fig. 5) was devised. Such bulbs having various thicknesses, each being within one millimeter, were pumped out and sealed with extreme care. One was selected from among these bulbs, which on heating up to the temperature giving the same vapour



pressure with the total pressure of the foreign gas mixture gave the same intensity of absorption with the foreign gas mixture in the region examined when it was observed with the small dispersion spectrograph. This region of both absorption spectra was then analysed with the high dispersive one. It was now found that the effect of iodine vapour itself appeared in the same sense as that of the foreign gas. The effect of iodine vapour itself was, however, smaller than any other foreign gas effect at the same pressure, and the degree of blurring in the former was less than in the latter.

Now, it is probable that the effects of foreign gases and vapours upon the absorption spectrum of iodine vapour will increase in the following order.

/ Iodine \	Oxygen Nitrogen	Carbon bisulphide v	vapour		
vapour	Carbon dioxide Air ,	Ethyl ether vapour	and t	hen I	Hydrogen.
itself /	,	Alcohol vapour			

The effect of iodine vapour itself seems to be the least of all the external gases or vapours. But owing to the extreme thinness of the absorbing layer in this case, it is impossible to draw a direct conclusion from the above result only, and further investigation is necessary to settle this matter.

Now, a minute study of the effect of external gas upon the individual lines of the iodine absorption will be described below.

A foreign gas was admitted into a bulb containing iodine step by step, and the changes occurring in the absorption spectrum of iodine were examined. At first, some of the absorption lines of the iodine vapour were selectively destroyed leaving the greater part of the absorption lines unchanged. There were, however, lines (though very few in number) greatly enhanced, and also those which had newly appeared. The pressure was raised by a further admixture of the foreign gas, the effect came out gradually universal and all the lines came apparently to unite in somewhat diffuse, broad single lines or "blends" up to the atmospheric pressure. These are shown in Figs. 12b, 12d and 12e, and also in Figs. 13b, 13c and 13d, Plate III.

As to the regularity of the effect of foreign gas, a few remarks may be permitted. In the blue-green region the heads of the absorption bands are very close together and the lines belonging probably to the different partial bands seem to be quite intermingled. The regularity governing the absorption lines in this region was hard to trace. In the less refrangible part, however, there is a fairly large spacing between the consecutive heads of the partial bands, and the main constituents of one partial band could easily be picked out in this region. The main constituents of a partial band were relatively unaffected by the external gas and also by the high temperature. The minor constituents, on the other hand, were greatly affected by the actions of both. A greater part of the lines of the minor constituents were selectively destroyed by the foreign gas effect, while these were, in general, strengthened by the heating effect. An enlarged reproduction indicating both effects it shown in Fig. 11, Plate II. The difference between the two spectra is remarkable.

Next, the action of high temperature upon the absorption spectrum of the iodine vapour mixed with a foreign gas has been studied. On heating the mixture of iodine vapour and the external gas, the lines selectively destroyed recurred and recovered their intensities. These are shown in Fig. 12, Plate III and also in the annexed rough sketch. (Fig. 6). Among the lines termed minor constituents there are groups of lines, each being separated about 1.7 Å and constituted of apparently four lines in a similar form. The actions of foreign gas and high temperature upon these lines are quite interesting. On letting a foreign gas, the two outer components of each group are selectively destroyed, leaving the central two components having about on A separation and equal intensities. The mixture was then heated, and the vanished outer components reappeared. Though the absorption lines of this spectrum thus obtained are diffuse and blurred, the distribution in the absorption lines and in intensity are nearly equal to those in the pure iodine vapour at ordinary temperature.

Now, from the results obtained so far in our experiments the action of the foreign gas molecule, which is the same as the simple pressure effect of iodine of its own, would modify the absorption spectrum of iodine vapour in two ways. The one is of a selectively destroying nature and



it disappears almost entirely on heating, and the other is of a universally burring nature and it increases with the rise of temperature.

Concluding Remarks.

As stated above in the previous sections, on heating the bulb containing iodine vapour, a remarkable development of the absorption bands was observed in the extreme red part.

The influence of high temperature upon the absorption spectrum for various substances has been carried out by different investigators. It has been generally accepted that the absorption is displaced toward the red side by a rise of temperature.

An important study on the influence of temperature on the absorption spectra of melted salts has been carried out by Retschinsky.¹ He examined the absorption spectra of 30 salts at temperatures varying from 15° to 1, 087° C., and it was found that the limit of absorption of the melted salts with the rise of temperature shifts towards the red. He attributed these facts to the change in the molecular aggregations.

In the case of iodine vapour we have a wellknown parallel relation of the dissociation process. According to Steubing,² on the other hand, the

I Ann. d. Phys., 27, 100 (1908).

² Zeit. f. Phys., 1, 426 (1920), Ann. d. Phys., 64, 673 (1921).

emission band spectrum and also the fluorescent band spectrum of iodine vapour produced by white light are not to be ascribed to an ionized atom nor molecule but to a neutral molecule in an intermediate state between the ionized and the completely neutral conditions, and it may be a matter of course with the case of absorption.

In the present experiment, we have obtained the following results: The higher the vapour density, the more the number of heads of the absorption bands increases when the bulb containing iodine vapour is heated; and two differenct absorption apparatuses, the one with a thicker layer at very low vapour tension, and the other with a very thin layer (about 1/3 mm. thick) and at relatively high vapour pressure (corresponding to about 140° C.), which are adjusted to absorb the blue-green at the same intensity, play absorption of different intensities in the red part, the former being weaker than the latter; and also the absorption center displaces towards the less refrangible part with increasing of temperature. From these results, it is thought quite appropriate to conclude that the bands in the extreme red evolved by the action of heat are to be attributed to the partial dissociated or activated molecule.

As for the effect of the foreign gas, both chemically inert and chemically active gases or vapours act upon the absorption spectrum of the iodine vapour in a similar manner to iodine vapour itself. Only from this point, the effect of foreign gas may be considered to be a simple pressure or mechanical effect. But taking the fact into consideration that by the action of heat upon the mixture, the effect of the foreign gas disappears to some degree, we are clearly dealing with something more complicated than the simple pressure effect. Now, the effect of foreign gas might be divided into two kinds; the one a selectively destroying, and the other a universally blurring action. The former might be considered to be a suppressing action on the molecular rotation as a whole, and the latter a disturbing one on the rotational quantum.

The common lines which are less sensitive to the action of high temperature and the effect of the presence of the foreign gas are, in general, regularly spaced, to which we have given the term "main constituents" of the fluted band, and these lines might probably correspond to the lower rotational quantum number. The groups of lines termed "minor constituents," on the other hand, might be the components of a partial band at the tail part situated just ahead and corresponding to the higher rotational quantum number. The components of a partial band might probably become sensitive to the two actions more and more with the growing quantum number.

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Anyhow, speaking generally, it seems to be certain that the action of high temperature and the effect of the presence of foreign gas upon the absorption spectrum of iodine vapour occur in opposite way. It is concluded that the former causes an evolution of new quantum states in the molecular rotation as well as in the molecular vibration, or in a simple word "activation," and the latter causes suppression and disturbance of these motions.

In conclusion, the writer is anxious to express his great indebtedness and warm thanks to Prof. M. Kimura, who suggested the investigation, and under whose constant direction and advice it was carried out.



 D_2

a

b

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d

e

g

h

Fig.

9.



by Heat Action. Vap. Press : (45°C.) Thickness of Layer: 17.5 cm. Magnification : 3 2.7 Å per Centimeter.



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