

Studies of the Band Spectrum of Halogen II. The Analysis of the Band Spectrum of Iodine, Bromine and Chlorine.

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ABSTRACT.

Iodine:— Series in diffuse Absorption Band Spectrum in the extreme red Part at ordinary Temperature. At a comparatively low vapour tension (its vapour pressure corresponding to 40°~110°C. and the thickness of the layer being about 5 cm.) a series of bands has been found in the extreme red part (700 $\mu\mu$ —800 $\mu\mu$). The edges of these bands are quite diffuse compared to those of well-known bands in the visible part, and vanish as its vapour pressure is raised up to a certain value. Mecke's formula for the band spectrum in the visible region is not applicable to these band series by a simple extension.

Series in Absorption Band Spectrum at high Temperature. When the vapour is heated up to about 1,100°C., a remarkable development of the absorption bands has been found. Some thirty additional edges of the absorption bands have been measured in wave-length to Mecke's observation. The majority of them were found to be expressed by his formula by a simple extension, i. e. giving higher values for n_1 and n_2 .

Bromine:— Series in Absorption Band Spectrum at ordinary Temperature. With various thicknesses of layers, ranging from 2 cm. to 6.5 m. at ordinary temperature (ca. 30°C.), about 180 heads of the absorption bands have been measured in the region from 513 $\mu\mu$ to 761 $\mu\mu$ and arranged them into 16 series. Empirical formulæ of the Deslandre type have been introduced.

Series in Absorption Band Spectrum at high Temperature. The vapour was sealed in a quartz tube at various vapour tensions and heated electrically up to about 1,100°C. and its absorption spectrum was examined. The action of high temperature upon the absorption increased in such a way that the thickness of the layer was increased. In addition to this, several stronger absorption bands appeared in the less refrangible part which were quite absent in the spectrum at ordinary temperature. These bands were found, however, practically represented as an extension of the VI series obtained in the spectrum at ordinary temperature.

Series in Emission Band Spectrum. With an ordinary vacuum tube, the emission band

spectrum was examined. About 20 strong heads of emission bands were measured in wave-length. These were compared with those obtained in the case of absorption and the lack of complementary relationship between the emission and absorption spectra has been verified. A series formula has been introduced to the band spectrum in emission.

Chlorine:— *Series in Absorption Band Spectrum at ordinary Temperature.* Using absorbing layers of various thicknesses (the largest of which being 12.6 m.), the writer has measured some seventy edges of absorption bands in the region from $480\mu\mu$ to $576\mu\mu$ and classified them into four series.

Series in Absorption Band Spectrum at high Temperature. With the thickness of layer ranging from 50 cm. to 2.5 m. of chlorine at one atmospheric pressure and a temperature of about 820°C ., new absorption bands have been found in the less refrangible part of the spectrum. Some edges of these bands were found to be represented by an extension of the IV series obtained in the absorption spectrum at ordinary temperature, and the rest of them have conformed to a new series. There are still observed abundant unclassified absorption bands developed almost in wavy forms. The absorption spectra taken in different conditions were compared with the emission band spectrum.

Some considerations upon the manifoldness of the band spectrum corresponding to the change of physical conditions have been offered and a probable vibrational isotope effect in the band spectrum has also been discussed.

The wave-length determination and the classification of the heads of the absorption bands of iodine vapour were first undertaken by Thalén. He observed 59 heads between $509\mu\mu$ and $683\mu\mu$, and classified them into 8 series. Morgan also measured 96 heads with an absorption layer of 20 cm. thick of iodine vapour at a temperature of 100°C .. Recently an accurate wave-length determination in the edges of the adsorption bands was made by Mecke¹ who found 115 heads of such absorption bands in the region from $490\mu\mu$ to $715\mu\mu$, and he classified these bands into 10 systems, and arranged them by a formula of the Deslandre's type. On the other hand, such an analysis in the absorption band spectra of bromine and chlorine has not yet, so far as the writer is aware, been undertaken. In the course of the former investigation, we have found a remarkable evolution of the absorption bands of iodine towards the less refractory part of the spectrum when the vapour is heated. The action of high temperature upon the absorption spectra of bromine and chlorine has next been studied and a similar result obtained. The writer has then examined the band spectrum of the halogen group under various physical conditions, and studied the analysis of the band spectrum obtained under the following respective conditions,

- i. e. (1) in the absorption at ordinary temperature,
- (2) in the absorption at high temperature and
- (3) in the emission in an ordinary vacuum tube,

and the results obtained so far will be given in the following pages.

¹ Ann. d. Phys., 71, 104 (1923).

The spectrographs chiefly used in this investigation were a Hilger replica grating spectrograph having a camera objective of a half meter focus and a 3 meter concave grating, one of Rowland's mounting; both dispersions on the photographic plate being 0.043 mm. and 0.17 mm. to the Ångström at the D-line in the first order spectrum respectively.

To obtain the edges of the absorption bands as distinct as possible, the Ilford process and panchromatic process plates were constantly used.

Iodine.

Details of the apparatus employed in this examination were given in the former communication¹ entitled "Studies of the Band Spectrum of Halogen I, The Absorption of Iodine Vapour" and here are omitted.

As stated in the previous communication, in iodine vapour at comparatively low vapour pressure a series of diffuse absorption bands was found in the extreme red. The photographs of these bands were taken with comparison of the Ni-arc and the wave-lengths were determined, and an experimental formula was given in the following expression,

$$\nu = 13455 - 84.8n - 0.28n^2$$

where $n = 0, 1, 2, \dots, 12$.

The agreement of both calculated and observed values may be seen in Table I.

Table I.—Iodine in Absorption at Low Temperature.

(at very low vapour pressure corresponding to 40°~100°C.)

$$\nu = 13455 - 84.8n - 0.28n^2$$

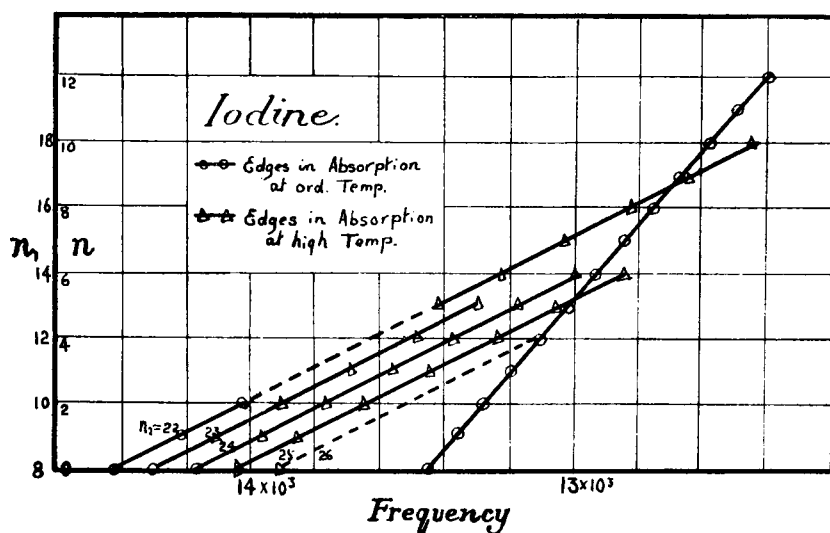
where $n = 0, 1, 2, \dots, 12$.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	7432.3	13455	13455	0	diffuse
1	7479.8	13369	13370	-1	"
2	7528.5	13283	13284	-1	"
3	7577.0	13198	13198	0	"
4	7672.5	13111	13111	0	"
5	7678.0	13024	13024	0	"
6	7729.5	12937	12936	1	"
7	7783	12849	12848	1	"
8	7839	12757	12759	-2	"
9	7892	12671	12669	2	"
10	7950	12579	12579	0	"
11	8009(?)	12488	12488	0	diffuse and faint
12	8063(?)	12402	12397	5	diffuse and faint

¹ These Memoirs, *suprà*, p. 315.

A graphical representation of these series was given in Fig. 1. In the diagram, a point surrounded by a small circle indicates the edge of the absorption band observed at low temperature.

Fig. 1. — Diagrammatic Representation of Series Relations for the Absorption Band Spectrum of Iodine in the extreme Red Part.



On the other hand, in heated iodine vapour, I have observed the absorption band also in the extreme red. This was examined under various conditions, changing the vapour pressure and the temperature of the bulb containing iodine. And in a certain favorable condition, some thirty additional heads were easily traced in the region from $715\mu\mu$ to $800\mu\mu$ on the photographic plate. The photographs of these bands were obtained also with the Ni-arc in comparison, and the wave-lengths were determined and the values thus obtained are given in the third column of Table II.

On the other hand, putting $n_1=10, 11, \dots, 18$ and $n_2=22, 23, \dots, 26$ in the Mecke formula

$$\nu = 18320.97 - 213.76n_1 + 0.596n_1^2 + 0.0021n_1^3 - 80.66n_2 - 1.013n_2^2 + 0.0033n_2^3$$

series of bands were obtained. They are given in the fifth column of the table. It is now found that the Mecke formula is generally applicable to the bands developed in the absorption spectra at high temperature.

Table II.— Iodine in Absorption at High Temperature (1100°C).

(at a pressure corresponding to about 140°C .)

$$\nu = 18320.97 - 213.76n_1 + 0.596n_1^2 + 0.0021n_1^3 - 80.66n_2 - 1.013n_2^2 + 0.0033n_2^3$$

where $n_1 = 8, 9, \dots, 18$ and $n_2 = 22, 23, \dots, 26$.

n_1	n_2	$\lambda(\text{Obs.})(\text{Vac.})$	$\nu(\text{Obs.})$	$\nu(\text{Cal.})$	Difference between $\nu(\text{Obs.})$ & $\nu(\text{Cal.})$	Remarks
8	25	7115.5	14053.7	14052.7	1.0	
10	22	7134.0	14017.4	14015.9	1.5	
9	24	7156.0	13974.3	13973.8	0.5	
8	26	7178.0	13931.5	13926.8	4.7	
10	23	7196.5	13895.6	13894.7	0.9	
9	25	7220.0	13850.4	13849.5	0.9	
10	24	7261.0	13772.2	13771.9	0.3	
11	23	7302.4	13694.2	13694.1	0.1	
10	25	7325.8	13650.4	13647.6	2.8	
11	24	7368.4	13571.4	13571.4	0.0	
		7388.8	13533.4			
12	23	7409.2	13496.7	13494.9	1.8	
11	25	7437.3	13445.8	13447.1	-1.3	
13	22	7456.0	13413.0	13418.3	-5.3	
12	24	7479.4	13370.0	13372.2	-2.2	
		7499.0	13335.1			
13	23	7521.0	13296.0	13297.0	-1.0	
12	25	7549.0	13245.6	13247.9	-2.3	
14	22	7566.0	13217.0	13221.7	-4.7	
13	24	7589.0	13177.0	13174.3	2.7	
12	26					faint
13	25	7663.4	13049.0	13049.9	-0.9	
15	22	7672.9	13032.9	13026.6	6.3	
14	24	7705.9	12977.0	12977.8	-0.8	
13	26					faint
14	25					faint
16	22	7790	12837	12832.8	4	
17	22	7912	12639	12640.4	1	
18	22	8026(?)	12460	12449.4	11	

These series of bands are also represented diagrammatically in Fig. 1 in comparison with those obtained at low temperature, and are marked by small triangles.

Bromine.

For an absorber, several tubes of various thicknesses of layers were prepared, the greatest thickness of layer being 6.5 meters at a pressure of about 26 cm. The bromine used in the present experiment was supplied

by the Merck Co. in Germany.

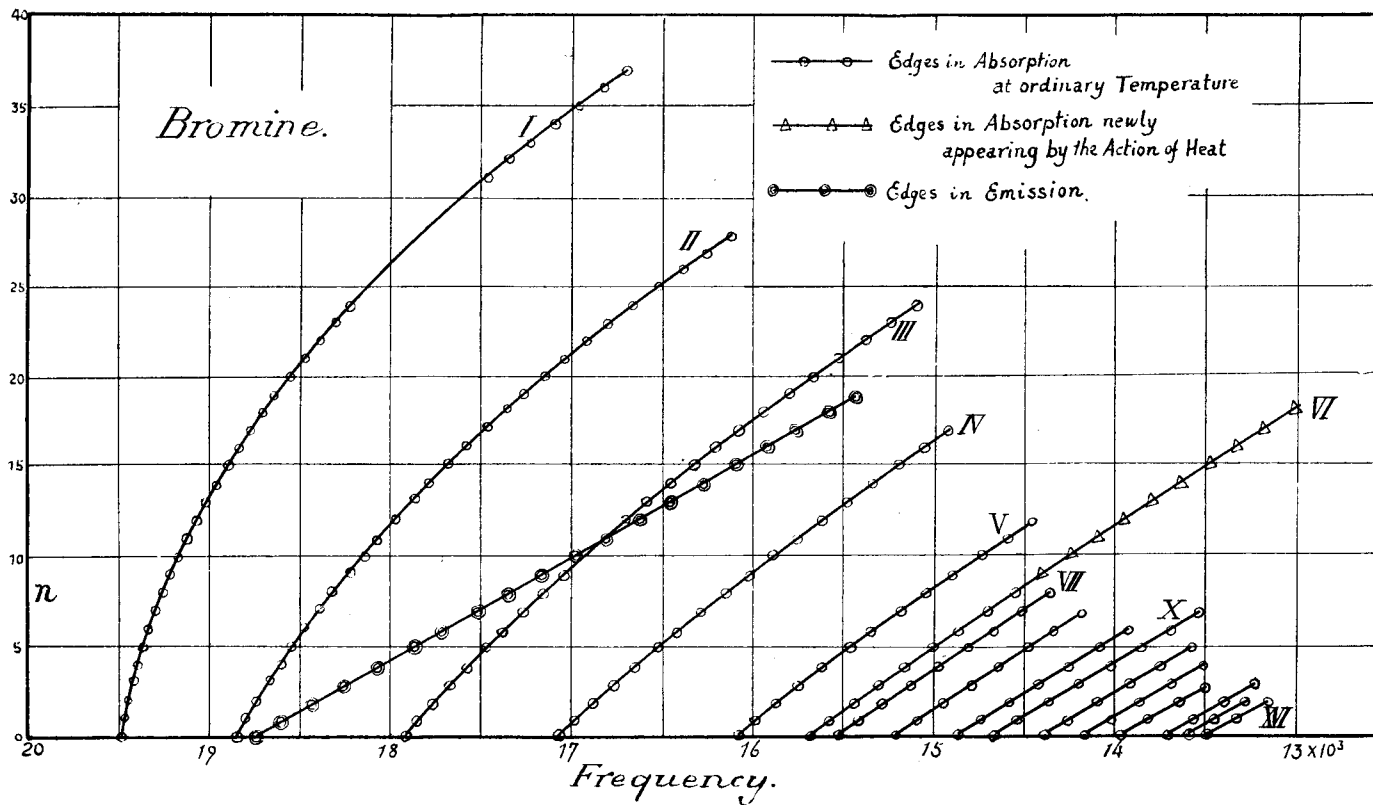
The apparatus employed in this experiment for the study of the effect of high temperature was the same as those used in the former investigation of the absorption of iodine at high temperature, and here details are also omitted.

The tube used in the study of the emission band spectrum was prepared with an ordinary tubing of a diameter of about 3.5 mm. and a length of 20 cm. and the large outer tinfoil electrodes. A quantity of well-dried copper bromide was introduced in a side tube attached to the main. This tube was connected to a pump, and during the process of exhaustion this was thoroughly heated with a Bunsen flame and then sealed off from the pump. A proper amount of bromine vapour was maintained by an occasional heating of the side tube containing copper bromide. The tube thus prepared gave a bright source when it was excited by an induction coil, and there was no need of making any troublesome connection with the pump during a long exposure. The channelled band spectrum emitted by such a tube was photographed with a three-prism spectrograph having a camera objective of 52 cm. focus.

At an ordinary temperature and with a moderate thickness of absorbing layer (10 cm.~20 cm.), the spectral range in absorption is very narrow and the heads of the absorption bands are very few in number. Using a very thick layer up to 6.5 m., however, the writer has found that the bands were developed remarkably towards the extreme red, and some 180 edges of absorption bands were easily measured on the photographic plate. As the thickness of layer was made to increase, the bands became remarkably developed towards the red and at the same time the channelled bands in the more refrangible part transformed into continuous one. For this reason, the entire channelled band spectrum could not be obtained on one plate and several plates for different thicknesses of layers had to be used to get the measurement of the wave-lengths of the edges of the absorption bands all over the spectral region.

With very thin layer at a pressure of about 26 cm., the absorption beyond the wave-length shorter side of 500μ is somewhat continuous, and just to the wave-length longer side of this continuous band, channelled ones which shaded towards the red appeared at about λ 5133. At first these bands are faint and gradually become sharper and more definite ranging at regularly increasing intervals and then gradually fading away. In all 38 heads of such bands were observed. The edges are fairly sharp to start with, but they gradually become somewhat diffused as they proceed towards the red. Another series appears at λ 5304 and a third at

Fig. 2. — Diagrammatic Representation of Series Relations for the Band Spectrum of Bromine.



λ 5574 and so on, and up to λ 7808 about 180 edges of absorption bands were found and classified into 16 series. The diagrammatical representation of these series is given in Fig. 2. In this diagram, points surrounded by small circles indicate the absorption edges observed at ordinary temperature and belonging to the series mentioned above.

For the wave-lengths of these band series the following empirical formulæ of an usual Deslandre type have been calculated :-

for the 1st series $\nu_1 = 19490.2 - 13.96n - 1.513n^2 - 0.0038n^3$

where $n = 0, 1, 2, \dots, 36, 37,$

for the 2nd series $\nu_2 = 18849.8 - 52.15n - 1.633n^2 + 0.0010n^3$

where $n = 0, 1, 2, \dots, 27, 28,$

for the 3rd series $\nu_3 = 17934.0 - 83.60n - 1.550n^2 + 0.0030n^3$

where $n = 0, 1, 2, \dots, 23, 24,$

for the 4th series $\nu_4 = 17096.6 - 107.12n - 1.314n^2 + 0.0051n^3$

where $n = 0, 1, 2, \dots, 16, 17,$

for the 5th series $\nu_5 = 16100.9 - 124.19n - 1.259n^2 + 0.0170n^3$

where $n = 0, 1, 2, \dots, 11, 12,$

for the 6th series $\nu_6 = 15702.0 - 135.16n - 1.113n^2 + 0.021n^3$

where $n = 0, 1, 2, \dots, 7, 8,$

for the 7th series $\nu_7 = 15553.0 - 149.0n$

where $n = 0, 1, 2, \dots, 8,$

for the 8th series $\nu_8 = 15220.8 - 155.4n$

where $n = 0, 1, 2, \dots, 8,$

for the 9th series $\nu_9 = 14879.0 - 159.2n$

where $n = 0, 1, 2, \dots, 6,$

for the 10th series $\nu_{10} = 14657.8 - 163.1n$

where $n = 0, 1, 2, \dots, 7,$

for the 11th series $\nu_{11} = 14424.5 - 165.9n$

where $n = 0, 1, 2, 3, 4, 5,$

for the 12th series $\nu_{12} = 14172.9 - 167.4n$

where $n = 0, 1, 2, 3, 4,$

for the 13th series $\nu_{13} = 13982.7 - 171.0n$

where $n = 0, 1, 2, 3, 4,$

for the 14th series $\nu_{14} = 13722.2 - 173.8n$

where $n = 0, 1, 2, 3,$

for the 15th series $\nu_{15} = 13610.8 - 176.4n$

where $n = 0, 1, 2, 3,$ and

for the 16th series $\nu_{16} = 13494.5 - 177.0n$

where $n = 0, 1, 2.$

Data for the consideration of regularity in the edges of the bands are

given in the following tables which show the difference between observed and calculated wave-numbers in the fifth column.

Table III.- Bromine in Absorption, Series I.

(p; 26 cm.; d: 2-5 cm.)

$$\nu_1 = 19490.2 - 13.96n - 1.513n^2 - 0.0038n^3$$

where n=0, 1, 2,, 36, 37.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	5130.4	19491.7	19490.2	1.5	
1	5134.4	19476.5	19474.7	1.8	
2	5140.1	19454.9	19456.2	-1.3	
3	5145.2	19435.6	19435.6	0.0	
4	5152.5	19408.1	19409.9	-1.8	
5	5159.8	19380.7	19382.1	-1.4	
6	5168.0	19349.9	19351.1	-1.2	
7	5177.0	19316.2	19317.0	-0.8	
8	5187.0	19279.0	19279.7	-0.7	
9	5197.8	19238.9	19239.2	-0.3	
10	5209.5	19195.7	19195.5	0.2	
11	5222.2	19149.0	19148.5	0.5	
12	5235.9	19098.9	19098.2	0.7	
13	5250.5	19045.8	19044.7	1.1	
14	5266.2	18989.0	18987.8	1.2	
15	5283.0	18928.6	18927.5	1.1	
16	5300.8	18865.1	18863.9	1.2	
17	5319.8	18797.7	18796.9	0.8	
18	5339.9	18726.9	18726.5	0.4	
19	5361.1	18652.9	18652.7	0.2	
20	5383.6	18574.9	18575.4	-0.5	
21	5407.2	18493.9	18494.6	-0.7	
22	5432.1	18409.1	18410.3	-1.2	
23	5458.2	18321.1	18322.5	-1.4	
24	—		18231.2		faint (?)
25	—		18136.2		"
26	—		18037.6		"
27	—		17935.5		"
28	—		17829.7		"
29	—		17720.2		"
30	—		17607.1		"
31	—		17490.2		"

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
32	5761(?)	17358	17369.6	-12	broad and diffuse
33	5800(?)	17241	17245.3	-4	"
34	5845(?)	17109	17117.2	-8	"
35	5888	16984	16985.2	-1	"
36	5935	16849	16849.5	-1	"
37	5984	16711	16709.9	1	"

Table IV.—Bromine in Absorption, Series II.

(p: 26 cm.; d: 5-8 cm.)

$$\nu_2 = 18849.8 - 52.15n - 1.633n^2 + 0.0010n^3$$

where $n=0, 1, 2, \dots, 27, 28$.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	5305.5	18848.4	18849.8	1.4	
1	5319.3	18799.5	18796.0	3.5	
2	5335.6	18742.0	18739.0	3.0	
3	5351.5	18686.4	18688.7	-2.3	
4	5372.0	18615.0	18615.1	-0.1	
5	5391.0	18549.4	18548.3	1.1	
6	5411.0	18480.9	18478.3	2.6	
7	5433.2	18405.4	18405.1	0.3	
8	5455.1	18331.5	18328.6	2.9	
9	5478.2	18254.2	18248.9	5.3	
10	5504.8	18162.7	18166.0	-3.3	
11	5530.7	18080.6	18079.9	0.7	
12	5558.6	17990.1	17990.6	-0.5	
13	5586.2	17901.3	17898.1	3.2	
14	5618.2	17799.3	17802.4	-3.1	
15	5649.6	17700.4	17703.9	-3.5	
16	5682.6	17597.6	17601.4	-3.8	
17	5713.6	17502.1	17496.2	5.9	
18	5751.7	17386.2	17387.8	-1.6	
19	5788.0	17277.1	17276.2	0.9	
20	5827.5	17160.0	17161.6	-1.6	
21	5867.3	17043.6	17043.8	-0.2	
22	5908.6	16924.5	16922.8	1.7	
23	5951.7	16801.9	16798.7	3.2	
24	5999.3	16668.6	16671.4	-2.8	

n	$\lambda(\text{Obs.})(\text{Vac.})$	$\nu(\text{Obs.})$	$\nu(\text{Cal.})$	Difference between $\nu(\text{Obs.})$ & $\nu(\text{Cal.})$	Remarks
25	6045.0	16542.6	16541.0	1.6	
26	6096.0	16404.2	16407.6	-3.4	
27	6147.7	16266.2	16271.0	-4.8	
28	6199.9	16129.3	16131.3	-2.0	

Table V.- Bromine in Absorption. Series III.

(p : 26 cm.; d : 10 cm.)

$$\nu_s = 17934.0 - 83.60n - 1.550n^2 + 0.0030n^3$$

where $n=0, 1, 2, \dots, 23, 24.$

n	$\lambda(\text{Obs.})(\text{Vac.})$	$\nu(\text{Obs.})$	$\nu(\text{Cal.})$	Difference between $\nu(\text{Obs.})$ & $\nu(\text{Cal.})$	Remarks
0	5575.8	17934.6	17934.0	0.6	
1	5602.2	17850.1	17849.8	0.3	
2	5628.6	17766.4	17761.6	4.8	
3	5659.1	17670.7	17670.3	0.4	
4	5688.8	17578.4	17576.0	2.4	
5	5721.1	17479.2	17478.6	0.6	
6	5755.3	17375.3	17378.3	-3.0	
7	5788.8	17274.7	17274.9	-0.2	
8	5825.0	17167.4	17168.5	-1.1	
9	5862.1	17058.7	17059.2	-0.5	
10	5901.6	16944.6	16947.0	-2.4	
11	5941.6	16830.5	16831.8	-1.3	
12	5982.6	16715.1	16713.8	1.3	
13	6026.0	16594.8	16592.8	2.0	
14	6070.5	16473.1	16469.0	4.1	
15	6119.5	16340.2	16342.3	-2.1	
16	6167.7	16213.5	16212.9	0.6	
17	6218.6	16080.8	16080.5	0.3	
18	6271.9	15944.0	15945.5	-1.5	
19	6326.3	15807.0	15807.6	-0.6	
20	6384.0	15664.2	15667.0	-2.8	
21	6442.0	15523.1	15523.6	-0.5	
22	6502.0	15379.9	15377.5	2.4	
23	6565.8	15230.4	15228.7	1.7	
24	6632	15078	15077.3	1	

Table VI.-Bromine in Absorption. Series IV.

(p: 26 cm.; d: 10 cm.)

$$\nu_1 = 17096.6 - 107.12n - 1.341n^2 + 0.0051n^3$$

where n=0, 1, 2,, 17.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	5848.2	17099.3	17096.6	2.7	
1	5886.4	16988.3	16988.1	0.2	
2	5925.6	16875.8	16877.4	-1.6	
3	5966.0	16761.7	16763.3	-1.6	
4	6007.2	16646.7	16647.0	-0.3	
5	6050.6	16527.3	16528.1	-0.8	
6	6095.6	16405.3	16406.7	-1.4	
7	6141.0	16284.0	16282.8	1.2	
8	6189.0	16157.7	16156.4	1.3	
9	6240.7	16023.8	16023.9	-0.1	
10	6289.4	15899.8	15896.4	3.4	
11	6343.3	15764.7	15762.8	1.9	
12	6398.5	15628.7	15626.9	1.8	
13	6454.0	15494.3	15494.6	-0.3	
14	6516.0	15346.8	15348.1	-1.3	
15	6576.6	15205.4	15205.3	0.1	
16	6640.9	15058.2	15060.3	-2.1	
17	6705.8	14912.5	14913.1	-0.6	

Table VII. - Bromine in Absorption. Series V.

(p: 26 cm.; d: 50 cm.)

$$\nu_5 = 16100.9 - 124.19n - 1.259n^2 + 0.0170n^3$$

where n=0, 1, 2,, 12.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6210.7	16101.1	16100.9	0.2	
1	6258.8	15977.5	15975.5	2.0	
2	6312.0	15842.8	15847.6	-4.8	
3	6362.9	15716.1	15717.6	-1.5	
4	6416.4	15585.1	15584.9	0.2	
5	6471.2	15453.1	15450.6	2.5	
6	6530.4	15313.0	15314.1	-1.1	
7	6589.8	15175.0	15175.7	-0.7	
8	6651.0	15035.3	15035.5	-0.2	

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
9	6715.0	14892.0	14893.6	-1.6	
10	6778.8	14751.9	14750.1	1.8	
11	6846.7	14605.6	14605.1	0.5	
12	6915(?)	14461	14458.7	2	diffuse and faint

Table VIII.- Bromine in Absorption. Series VI.

(p: 26 cm.; d: 1.2m. at 30°C. and 17.5cm. at 1100°C.)

$$\nu_0 = 15702.0 - 135.16n - 1.113n^2 + 0.021n^3$$

where n=0, 1, 2,, 18.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6368.2	15703.0	15702.0	1.0	
1	6424.8	15564.7	15565.7	-1.0	
2	6480.2	15431.6	15427.4	4.2	
3	6542.0	15285.9	15287.1	-1.2	
4	6602.0	15146.9	15144.9	2.0	
5	6668.0	14997.0	15001.0	-4.0	
6	6731.2	14856.2	14850.4	5.8	
7	6797.0	14712.4	14708.5	3.9	
8	6868.5	14559.2	14560.2	-1.0	newly developed by the action of heat.
9	6941.7	14405.7	14410.7	-5.0	"
10	7012.9	14259.4	14260.1	-0.7	"
11	7087.4	14109.5	14108.5	1.0	"
	(7093.0)	(14098.4)			"
	{ 7164.4	13957.9	13956.1	1.8	"
12	{ (7169.3)	(13948.4)			"
	{ (7173.0)	(13941.2)			"
	{ (7178.2)	(13931.1)			" (?)
	{ (7241.3)	(13809.7)			"
13	{ 7247.4	13798.1	13803.0	-5.0	"
	{ (7253.4)	(13786.6)			"
14	{ 7326	13650	13649.2	1	"
	{ (7403.0)	(13508.0)			"
15	{ 7410.8	13493.8	13495.0	-1.2	"
	{ (7418.5)	(13479.8)			"
	{ (7426.5)	(13465.3)			"
16	7495.6	13341.2	13340.5	0.7	"
17	7586	13182	13185.8	-4	"
18	(?)		13034.0		diffuse and faint

Table IX. - Bromine in Absorption, Series VII.

(p: 26cm.; d: 1.2m.)

$$\nu_7 = 15553.0 - 149.0n$$

where n=0, 1, 2,, 8.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6429.0	15554.5	15553.0	1.5	
1	6492.3	15402.9	15404.0	-1.1	
2	6557.8	15249.0	15255.0	-6.0	
3	6618.5	15109.2	15106.0	3.2	
4	6684.0	14961.1	14957.0	4.1	
5	6752.8	14808.7	14808.0	0.7	
6	6821	14661	14659.0	2	
7	6891.6	14510.4	14510.0	0.4	
8	6964	14361	14361.0	0	trace

Table X. - Bromine in Absorption, Series VIII.

(p: 26cm.; d: 1.2m.)

$$\nu_8 = 15220.8 - 155.4n$$

where n=0, 1, 2,, 8.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6569.9	15220.9	15220.8	0.1	
1	6628.8	15085.7	15085.4	0.3	
2	6701.0	14923.2	14930.0	-6.8	
3	6765.6	14780.7	14774.6	6.1	
4	6838.4	14623.3	14619.2	4.1	
5	6916.8	14457.6	14463.8	-6.2	
6	6987.0	14312.3	14308.4	3.9	
7	7065.4	14153.5	14153.0	0.5	
8					fainter trace

Table XI. - Bromine in Absorption, Series IX.

(p: 26cm.; d: 1.2m.)

$$\nu_9 = 14879.0 - 159.2n$$

where n=0, 1, 2,, 6.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6719.8	14881.4	14879.0	2.4	
1	6794.3	14718.2	14719.8	-1.6	
2	6867.4	14561.6	14561.6	0.0	
3	6946.1	14396.6	14401.4	5.2	
4	7020.4	14244.2	14242.2	2.0	
5	7101.0	14082.5	14083.0	-0.5	
6	7181	13926	13923.8	2	

Table XII.- Bromine in Absorption. Series X.

(p : 26cm.; d : 2.1m.)

$$\nu_{10} = 14657.8 - 163.11n$$

where $n = 0, 1, 2, \dots, 7$.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6821.9	14658.7	14657.8	0.9	
1	6900.9	14490.9	14494.7	-3.8	
2	6978.4	14329.9	14331.6	-1.7	
3	7056.1	14172.1	14168.5	3.6	
4	7140.2	14005.2	14005.4	-0.2	
5	7222.0	13846.6	13842.3	4.3	
6	7311.1	13677.8	13679.2	-1.4	
7	7399.5	13514.4	13516.1	-1.7	

Table XIII.- Bromine in Absorption. Series XI.

(p : 26cm.; d : 2.1m.)

$$\nu_{11} = 14424.5 - 165.9n$$

where $n = 0, 1, 2, 3, 4, 5$.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	6932.6	14424.6	14424.5	0.1	
1	7014.4	14256.4	14258.6	-2.2	
2	7097.0	14090.5	14092.7	-2.2	
3	7178.0	13931.5	13926.8	4.7	
4	7267.2	13760.5	13760.9	-0.4	
5	7351(?)	13604	13595.0	-9	

Table XIV.—Bromine in Absorption. Series XII.

(p : 26cm.; d : 3.25m.)

$$\nu_{12} = 14172.9 - 167.4n$$

where n=0, 1, 2, 3, 4.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	7056.9	14170.5	14172.9	-2.4	
1	7140.0	14005.6	14004.5	1.1	
2	7226.0	13838.9	13837.1	1.8	
3	7315.5	13669.6	13669.7	0.1	
4	7407.0	13500.7	13502.3	-1.6	

Table XV.—Bromine in Absorption. Series XIII.

(p : 26cm.; d : 3.25m.)

$$\nu_{13} = 13982.7 - 171.0n$$

where n=0, 1, 2, 3, 4.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	7152.0	13984.1	13982.7	1.4	
1	7240.8	13810.6	13811.7	-1.1	
2	7330.6	13641.4	13640.7	0.7	
3	7424.7	13468.6	13469.7	-1.1	
4	(?)				faint

Table XVI.—Bromine in Absorption. Series XIV.

(p : 26cm.; d : 3.25m.)

$$\nu_{14} = 13722.2 - 173.8n$$

where n=0, 1, 2, 3.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	7287.5	13722.1	13722.2	-0.1	
1	7381.0	13548.3	13548.4	-0.1	
2	7476.8	13374.7	13374.6	0.1	
3	(?)				

Table XVII.-Bromine in Absorption. Series XV.

(p: 26cm.; d: 6.5m.)

$$\nu_{15} = 13610.8 - 176.4n$$

where $n = 0, 1, 2, 3$.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	7347.0	13611.0	13610.8	0.2	diffuse
1	7443.8	13434.0	13434.4	-0.4	
2	7542.6	13258.0	13257.9	0.1	
3	(?)				

Table XVIII.-Bromine in Absorption. Series XVI.

(p: 26cm.; d: 6.5m.)

$$\nu_{16} = 13494.5 - 177.0n$$

where $n = 0, 1, 2$.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	7410.5	13494.4	13494.5	-0.1	diffuse "
1	7509	13317	13317.5	-1	
2	7610	13141	13140.5	0	

In the above tables, the large deviations in the wave-number units between the observed and the calculated are probably due partly to observational errors, since the edges of the bands are generally diffuse and indistinct, and partly to indicate the imperfection of our formulæ.

Roscoe and Thorpe¹ have already found that the absorption band of bromine vapour was developed towards the red by the action of heat. According to Evans,² the high temperature spectrum is very different from the low temperature spectrum. A further study on the action of high temperature upon the absorption spectrum has been also carried out in the present study. By the action of heat, the absorption increases as if its vapour pressure or thickness of layer were increased, and bands are developed towards the red. In addition to this, a new band system appears up to the extreme red. The latter bands were compared with those at ordinary temperature in the same spectral region. We obtained these spectra under different conditions on one plate. Each spectrum designated by "a" is the absorption spectrum at ordinary temperature

¹ Kayser, *Handbuch der Spektroskopie*, **3**, 320.

² *Astrophys. J.*, **32**, 291 (1910).

(30°C.), thickness of layer being 6.5m., and that designated by "b" at about 1,100°C., its vapour pressure corresponding to the temperature of 30°C., and thickness of layer 17.5 cm. in the latter case. The former were taken with the small dispersion grating spectrograph in the first order spectrum and the latter with the concave grating spectrograph of 3 meter focus in the second order spectrum. This is also represented diagrammatically in Fig. 2. The difference in the distribution of bands between the two is remarkable. As indicated in that diagram, however, and also in the table (Table VIII) these systems of bands developed at a high temperature are expressed practically by an extension of the 6th band series. The agreement between the observed and calculated values is fairly good as given in that table. There are, however, several absorption bands not classified, and these bands will be discussed later in this paper.

Quite recently Prof. M. Kimura¹ studied the emission band spectrum of bromine in relation to its absorption band spectrum and arrived at the conclusion, inconsistent with the results obtained by Eder and Valenta and Hasselberg,² that the absorption spectrum did not correspond to the emission band spectrum even in general appearance. In the present investigation, it was also observed that the distribution of bands in emission was quite different from that of absorption. These are to be seen in the diagram already given (Fig. 2) and also in Fig. 5, Plate IV. The edges of the bands in emission are practically expressed, in wave-number units, by the following formula,

$$\nu = 18767.1 - 175.9n$$

where $n = 0, 1, 2, \dots, 19.$

The observed and the calculated values are given in the following Table XIX. The lack of good agreement between the observed and the calculated may be due to the extraordinary diffuseness of the absorption edges as well as to the imperfection of this formula.

¹ These Memoirs, **4**, 128 (1920.)

² Kayser, Handbuch der Spektroskopie, **5**, 188.

Table XIX.-Bromine in Emission.
(Vacuum tube.)

$$\nu = 18767.1 - 175.9n$$

where $n=0, 1, 2, \dots, 19.$

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	5330	18762	18767.1	-5	
1	5379	18591	18591.2	0	
2	5428	18423	18415.3	8	
3	5480.5	18246	18239.4	7	
4	5535.5	18065	18063.5	9	
5	5589	17892	17887.6	4	
6	5644	17718	17711.7	6	
7	5701	17541	17535.8	5	
8	5760	17361	17359.9	1	
9	5820.5	17181	17184.0	-3	
10	5881.5	17002	17008.1	-6	
11	5943	16827	16832.2	-5	
12	6005.5	16651	16656.3	-5	
13	6069	16477	16480.4	-3	
14	6135	16300	16304.5	-5	
15	6198	16134	16128.6	5	
16	6271.5	15945	15952.7	-8	
17	6338.5	15777	15776.8	0	
18	6412.5	15595	15600.9	6	
19	6479.5	15433	15425.0	8	

Chlorine.

Laird¹ succeeded in obtaining the decided absorption bands of chlorine with a column of 1.37 meters long and a great number of absorption lines in the spectral region between 545 $\mu\mu$ and 480 $\mu\mu$ has been measured. In our present experiment, however, very few of the edges of absorption bands with this order of length of absorption column appeared. But as increasing the length of column of chlorine promised to intensify and develop the edges of the absorption bands more and more towards the red, tubes of various thicknesses of layers, the longest of which being 12.6 meters long, and at one atmospheric pressure were used.

The tubes being exhausted, chlorine was let in until the total pressure, as measured by a manometer attached, was one atmospheric pressure.

¹ Astrophys. J., 14, 85 (1901).

The chlorine was used in the present experiment was prepared from concentric hydrochloric acid and potassium permanganate and this was dried in the usual way.

When we examine the photographs of the absorption band spectrum of chlorine taken through a column of 1.5m. thick at the temperature of 5°C., a system of bands is observed to start at about 480 μ . At first, these bands are faint, but with growing term they become gradually intense and wide in separation, and then finally become diffuse and faint. The whole group of bands conform to a series (Series I). Another series of bands starts at 494 μ , and so on. In all, seventy edges of such bands were measured and classified into four series. A diagrammatical representation of these series is given in Fig. 3, and the following empirical formula has been calculated :

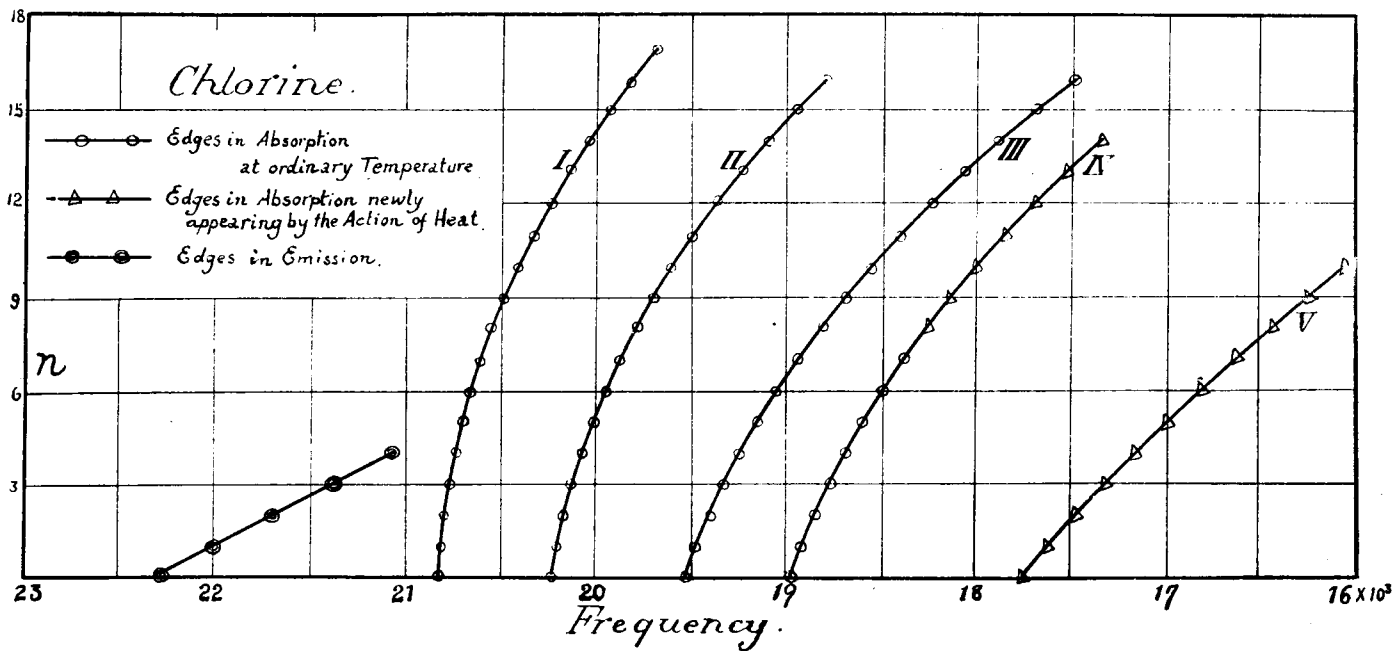
$$\nu_{1,2,3,4} = (20836.5 - 550.1n_0) - 7.13n - 2.650n^2 - 0.05577n^3,$$

where $n_0 = 0, 1, 2, 3,$ and $n = 0, 1, 2, \dots, 21.$

In the study of the absorption at high temperatures, the quartz tubes of 17.5 cm. long used with the iodine and bromine were, in the present case, not long enough. A combustion tube (from Jena) of 2.5m. long, both ends being blown into bulbs was then substituted and this was filled with chlorine at one atmospheric pressure. Nichel-chrome wire was wound round the tube covered previously with asbestos papers and the whole was heated electrically up to about 820°C. The colour of chlorine gas at ordinary temperature is a pale greenish yellow, but it becomes brownish at high temperature (820°C.) almost exactly resembling that of bromine vapour at ordinary temperature.

The absorption spectrum was next studied with the spectrographs mentioned above. The mode of evolution of the absorption bands was similar to that of bromine. Enlarged reproductions of a portion of these spectra are given in Figs. 1 and 2, Plate V. The former was taken with the small dispersion spectroscope and the latter with the concave grating one of the second order spectrum. A minute study upon the absorption spectrum of heated chlorine soon revealed to us that, besides general strengthening of the intensity of the absorption bands, the band series termed Series IV developed remarkably and also a new series (Series V) appeared which was utterly absent in the low temperature spectrum even with the largest thickness of layer (12.6m.) of this gas. In the high temperature spectrum, there were still more numerous absorption bands to be observed in the less refractory part, but these were somewhat wavy in form, and the wave-length measurement of these bands was impossible. The fifth series is practically represented by a following formula,

Fig. 3.- Diagrammatic Representation of Series Relations for the Band Spectrum of Chlorine.



Studies of the Band Spectrum of Halogen II.

The value of n indicated in this diagram is for the series I and V. For the series II, III and IV, on the other hand, the values of n at the origin are 3, 7 and 7 respectively.

$$\nu_3 = 17765.2 - 116.8n - 9.61n^2 - 0.438n^3$$

where $n=0, 1, 2, \dots, 10$.

We give for these five series the following tables showing the observed values compared with the calculated.

Table XX.- Chlorine in Absorption. Series I.

(p: 1 atm.; d: 2.5m.)

$$\nu_1 = (20836.5 - 550.1n_0) - 7.13n - 2.650n^2 - 0.05577n^3$$

where $n_0=0$; $n=0, 1, 2, 3, \dots, 17$.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	4799.3	20836.4	20836.5	-0.1	
1	4801.3	20827.7	20826.7	1.0	
2	4805.8	20808.2	20811.2	-3.0	
3	4809.3	20793.0	20789.8	3.2	
4	4817.5	20757.7	20762.0	-4.3	
5	4824.5	20727.5	20727.6	-0.1	
6	4835.1	20682.1	20686.3	-4.2	
7	4846.5	20633.5	20637.6	-4.1	
8	4858.7	20581.6	20581.3	0.3	
9	4873.4	20519.6	20517.5	2.1	
10	4891.4	20444.1	20444.4	-0.3	
11	4910.6	2036.41	20363.2	0.9	
12	4931.5	20277.8	20273.0	4.8	
13	4956.0	20177.6	20173.4	4.2	
14	4982.4	20070.7	20064.2	6.5	
15	5013.0	19948.1	19955.1	-7.1	
16	5048.3	19808.7	19815.4	-6.7	
17	5083.0	19673.4	19675.2	-1.8	

Table XXI.- Chlorine in Absorption. Series II.

(p: 1 atm.; d: 4.0m.)

$$\nu_2 = (20836.9 - 550.1n_0) - 7.13n - 2.650n^2 - 0.05577n^3$$

where $n_0=1$; $n=3, 4, 5, \dots, 19$.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
3	4940.6	20240.5	20239.7	0.8	
4	4948.0	20210.2	20211.9	-1.7	
5	4955.9	20178.0	20177.5	0.5	
6	4966.8	20133.7	20136.2	-2.5	
7	4979.4	20082.7	20087.5	-4.8	

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
8	4993.6	20025.6	20031.2	-5.6	
9	5009.6	19961.6	19966.9	-5.3	
10	5027.3	19891.4	19894.3	-2.9	
11	5048.3	19808.7	19813.1	-4.4	
12	5072.4	19714.5	19722.9	-8.4	
13	5097.5	19617.5	19623.3	-5.8	
14	5126.4	19506.9	19514.1	-7.2	
15	5157.6	19388.9	19395.0	-6.1	
16	5192.2	19259.7	19265.4	-5.7	
17	5230.0	19120.5	19124.5	-4.0	
18	5271.5	18969.9	18974.2	-4.3	
19	5316.6	18809.0	18811.8	-2.8	

Table XXII.-Chlorine in Absorption. Series III.

(p : 1 atm.; d : 8.2m.)

$$\nu_3 = (20836.5 - 550.1n_0) - 7.13n - 2.65n^2 - 0.05577n^3$$

where $n_0 = 2$; $n = 7, 8, \dots, 23$.

n	$\lambda(\text{Obs.})(\text{Vac.})$	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
7	5118.6	19536.6	19537.4	-0.8	
8	5133.9	19481.4	19481.1	0.3	
9	5149.0	19421.3	19416.8	4.5	
10	5170.6	19340.1	19344.2	-3.9	
11	5191.4	19262.5	19263.0	-0.5	
12	5216.0	19171.8	19172.8	-1.0	
13	5242.9	19073.4	19073.2	0.2	
14	5272.4	18966.7	18964.0	2.7	
15	5306.7	18844.1	18844.9	-0.8	
16	5344.7	18710.1	18715.3	-5.2	
17	5382.5	18578.7	18575.2	3.5	
18	5429.5	18417.9	18424.1	-6.2	
19	5475.9	18261.8	18261.7	0.1	
20	5528.3	18088.8	18087.5	1.3	
21	5588.5	17893.9	17895.4	-1.5	
22	5649.1	17701.9	17703.0	-1.1	
23	5715.8	17495.4	17491.9	3.5	

Table XXIII.—Chlorine in Absorption. Series IV.
 (p: 1 atm.; d: 12.6m. at 5°C. and 2.5m. at ca. 820°C.)
 $\nu_4 = (20836.5 - 550.1n_0) - 7.13n^1 - 2.650n^2 - 0.05577n^3$
 where $n_0 = 3$, and $n = 7, 8, \dots, 20, 21$.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
7	5264.9	18993.7	18987.3	6.4	
8	5280.8	18936.5	18931.0	5.5	
9	5298.1	18874.7	18866.7	8.0	
10	5319.5	18798.8	18794.1	4.7	
11	5343.4	18714.7	18712.9	1.8	
12	5368.5	18627.2	18622.7	-5.5	
13	5398.7	18523.0	18523.1	-0.1	
14	5430.5	18414.5	18413.9	0.6	
15	5465.7	18295.9	18294.8	1.1	{ quite faint at ordi- nary temp. and stro- ngly developed by the action of heat
16	5504.5	18167.0	18165.2	1.8	"
17	5548.0	18024.5	18025.1	-0.6	"
18	5597.0	17866.7	17874.0	2.7	"
19	5647.5	17707.0	17711.6	-4.6	"
20	5702.4	17536.5	17537.4	1.1	"
21	5763.0	17352.1	17351.3	0.8	"

Table XXIV.—Chlorine in Absorption. Series V.

(p: 1 atm.; d: 2.5m. at ca. 820°C.)
 $\nu_5 = 17765.2 - 116.8n - 9.61n^2 + 0.438n^3$
 where $n = 0, 1, 2, \dots, 10$.

n	λ (Obs.)(Vac.)	ν (Obs.)	ν (Cal.)	Difference between ν (Obs.) & ν (Cal.)	Remarks
0	5629.0	17765.1	17765.2	-0.1	absent at ordinary temperature
1	5669.7	17637.6	17639.2	-1.6	"
2	5715.6	17496.0	17495.3	0.7	"
3	5767.5	17338.5	17340.1	-1.6	"
4	5825.2	17166.8	17172.2	-5.4	"
5	5883.6	16994.1	16995.7	-1.6	"
6	5947.7	16813.1	16813.0	0.2	"
7	6012.7	16631.5	16626.9	4.6	"
8	6082.5	16440.6	16440.1	0.5	"
9	6152	16255	16254.9	0	"
10	6221	16075	16074.2	1	"

The emission band spectrum of this element is not yet thoroughly studied, its series relations being quite unknown.

According to Kimura and Fukuda,¹ chlorine, when excited electrically, emits light strongly in the band spectrum in the region where the gas absorbs light most strongly. In the emission band spectrum obtained by these investigators, a series of remarkable intensity is easily recognized. The wave-lengths of the edges of this series were roughly measured and tabulated as follows :

Table XXV.- Chlorine in Emission.
(Vacuum Tube)

λ (Obs.) (Vac.)	ν (Obs.)
4748	21062
4680	21368
4612	21683
4546	21997
4482	22311

A diagrammatical representation of these bands have been already shown in Fig. 3 in comparison with those of the absorption. As may be readily seen from that figure, the difference in the distribution of the edges is remarkable.

Next, the absorption spectra under different conditions have been photographed on one plate. The difference

between these spectra is also remarkable as is to be seen in the reproductions given in Figs. 3 and 4, Plate V. The former was taken with the replica grating spectrograph and the latter with the concave grating one. In each spectrogram, the upper ones are the absorption spectra obtained with an absorbing layer of 12.6m. thick at ordinary temperature, and the lower ones with a layer of 2.5m. at the high temperature of ca. 820°C. There are, as may be seen in Fig. 4, Plate V, many lines which do not coincide with each other.

Laird² has measured a great number of absorption lines at ordinary temperature in the region from 545 $\mu\mu$ to 480 $\mu\mu$. In our present investigation we have observed a remarkable development of absorption bands toward the red and absorption lines could be measured beyond 670 $\mu\mu$. The photographs of these absorption band spectra were taken with the concave grating spectrograph of the 2nd order spectrum with the comparison of Fe-arc and their enlarged reproductions are given on Plate VI.

¹ These Memoirs, 4, 155 (1920).

² *Loc. cit.*

Concluding Remarks.

The study of the band spectrum of a substance in the state of gas and in various physical conditions enables us to widen our knowledge of the movement and the structure of the molecule.

Now, the quantum theory of the band spectrum shows us the general mechanism of all absorption and emission phenomena. A molecule in the normal state possesses a certain value of internal energy. Under the influence of different agents, such as radiation, thermal motion, electric discharge, or chemical action, the molecule is activated. It is quite natural to consider that the emission or absorption spectrum changes with the degree of activation of the molecule. The centers of the absorption of the band spectrum observed with a thinner layer and at lower temperature may be the molecules of the less activated from the normal state than those with a layer at higher temperature or with a thicker layer at ordinary temperature.

In the channelled band spectrum of the halogen group, we have, in the present study, analysed the edges of the bands into series of the Deslandre type. To each classified series molecules of different degrees of activation may respectively correspond. It is also readily conceivable that the relative abundance of the molecules of different degrees of excitation can be roughly calculated from the thickness of layer necessary to render visible the absorption of each band series in equal intensity. In the case of the absorption spectrum of bromine vapour, for instance, at ordinary temperature (30°C.), a layer of 3 cm. thick is sufficient to render the first band series visible at a certain intensity, while for Series XVI the layer must be as large as 650 cm. long to obtain its absorption at the same intensity. Therefore the relative abundance of the absorbing centers of the 1st and the 16th series may be in the ratio of about 220 : 1.

Now, the quantum theory of the band spectrum predicts that the interval between the consecutive bands of each series are approximately proportional to the molecular vibrational frequencies. The frequency, on the other hand, should be increased with the degree of activation by external agencies (the effects of mutual collision and the thermal motion of molecules might be prevailing ones), and therefore, in the absorption spectrum, the magnitude of the intervals should be greater in the series of a higher order than in that of a lower one. This is readily seen to be the case from Figs. 4 and 5 given in the next page.

Fig. 4.

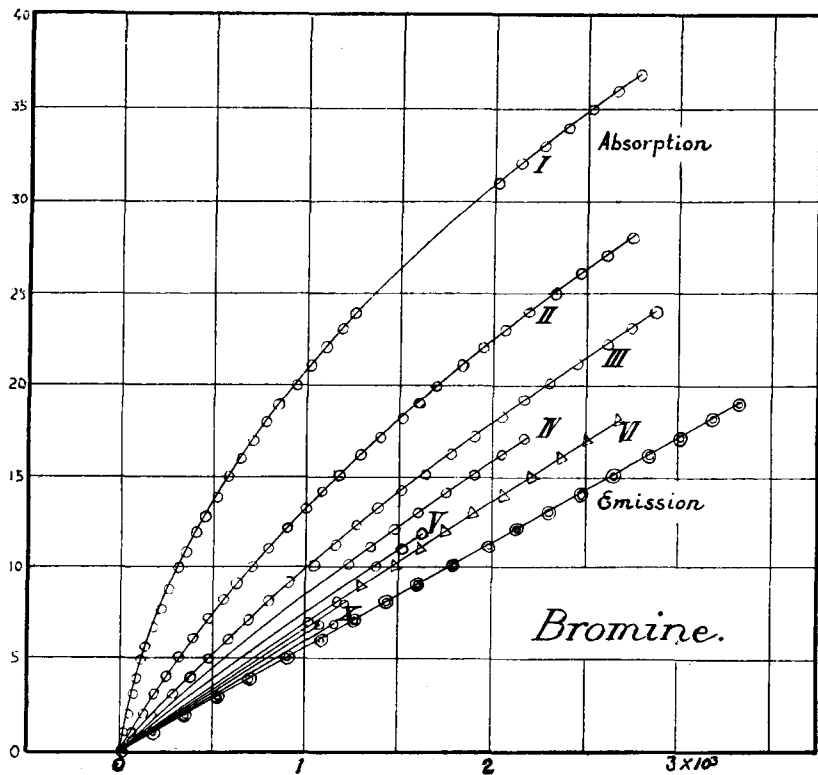
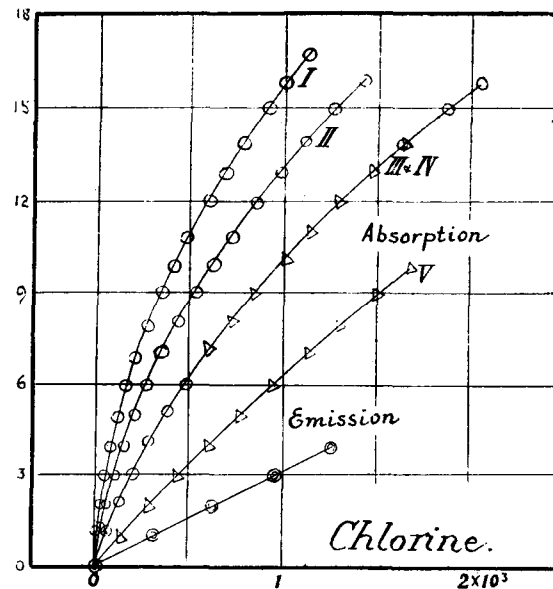


Fig. 5.



Figs. 4 & 5. - Diagrammatic Representations of the Changes in Intervals between the consecutive Members (or of the Inclinations) of the successive Series in the Band Spectra of Bromine and Chlorine.

In these figures, the frequencies of the initial edges of each series are placed at zero frequencies and consequently all the series start from a single point. The inclination of the 1st series is the least of all the series, and this increases on proceeding from the 2nd to the 3rd series, and from the 3rd to the 4th series, and so forth. The separations of the consecutive bands in emission, on the other hand, are generally the largest.¹ This is quite in harmony with our above consideration; the degree of activation of molecules in emission should be the greatest.

In the diagrams already given in Figs. 2 and 3, it may readily be seen that the emission and absorption bands differ in position and the former shifts towards the more refrangible part from the latter, the amount of displacement being larger in the case of chlorine than in bromine. This shows that the energy contribution from the electron transition in emission is much greater than in absorption. In the case of iodine, however, this contribution in both cases might be the same and the emission spectrum is nearly exactly complementary to each other.

It is highly probable that, in the cases of bromine and chlorine, on account of the stronger electron affinity of these elements than that of iodine, the electron makes a large inward jump at the moment of the combination of atoms into molecules. Hence the emission band spectra of these elements will displace towards the more refrangible part of the spectrum from those of the absorption. And these amounts of displacement might have probably an intimate relation with the electron affinity of these elements. But a further investigation of the series analysis is called for to decide this problem with certainty.

It is concluded in our experiments that the amount of gas necessary to render visible the absorption band spectrum of the elements of the halogen group decreases with increasing atomic weight. In the case of iodine vapour, for instance, with an absorption layer of 3 cm. thick and a pressure of a few millimeters, a heavy absorption can be produced, while in the case of chlorine even with a layer of 12.6 m. thick and even at one atmospheric pressure it gives a rather weaker absorption. This fact shows to us that the iodine molecule is more sensitive to radiation than bromine and chlorine, and that the latter are too strong in electron affinity to cause the outward electron jump by the action of external

¹ In the case of bromine, the separations of the consecutive bands of the 15th and the 16th series in absorption are slightly greater than those in emission. The possible reason for this is that the wave-lengths of the band edges do not, in general, indicate those of "zero-lines", and the separations of the consecutive bands do not give those of "zero-lines" strictly.

agencies, and by an expenditure of radiation energies and consequently, the phenomenon of fluorescence is not to be observed in ordinary conditions.

Again, the quantum theory of the band spectrum indicates that there should be quite appreciable differences between the spectra of isotope molecules, the largest portion of them being due to the change of the molecular vibrational frequencies. The expected isotope effect has been already discussed in connection with one of the infra-red absorption bands of hydrogen chloride by Loomis¹ and Kratzer,² and recently in connection with the visible bands of various compounds such as BO, SiN, CuCl, CuBr, and CuI by Mulliken.³

Now, Aston's positive ray analysis has shown that chlorine consists of a mixture of isotopes of atomic weights 35 and 37, bromine has isotopes of atomic weights 79 and 81, while iodine is "pure" with a single atomic weight 127. These experimental data readily are reconciled with our results that, in the cases of bromine and chlorine, the edges of the absorption bands are very diffuse and indistinct compared with those of iodine.

In the absorption band spectrum of the heated bromine vapour we have also observed a series of bands accompanied by satellite ones, the separations of these satellites in each partial band being nearly equal and increasing with the growing term. This is shown in Fig. 3a, on Plate IV. The absorption edges marked by the lines are those of which the separation due to the expected isotope effect is distinct. There are, however, several bands whose components are not determined, owing to the extreme diffuseness of these bands. Simple calculations for the expected vibrational isotope effect show that the order of magnitude of separation nearly coincides with the observational values.

According to the atomic weight of bromine 79.916, the relative abundance of isotopes 79 and 81 is in the ratio of 54.2 : 45.8. The absorption centre of the band spectrum is without doubt diatomic, and with two kinds of isotopes three kinds of molecules should be expected. If a simple probability law holds in combination of isotopes into molecules, the relative abundance in the isotope molecules of $\text{Br}^{79}-\text{Br}^{79}$, $\text{Br}^{79}-\text{Br}^{81}$ and $\text{Br}^{81}-\text{Br}^{81}$

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- 1 Nature, **105**, 547 (1920).
Astrophys. J., **52**, 248 (1920).
 - 2 Zeit. f. Phys., **3**, 460 (1920).
 - 3 Nature, **165**, 58 (1923).
Phys. Rev., **25**, 119 (1925).
Phys. Rev., **25**, 259 (1925).

should be in the ratio of 29 : 50 : 21. This is quite, though in a qualitative measure, consistent with our results obtained from our photographs that the central component in each band is the strongest of all other components. But, owing to the impossibility of precise measurements of the separations as well as of the relative intensities of the component bands, it is, at present, impossible to decide this question with certainty.

In the case of chlorine, on the other hand, there are abundant absorption bands, newly evolved in the absorption spectrum of heated chlorine towards the red in an almost wavy form. This is probably due to the vibrational isotope effect of molecules $\text{Cl}^{35}-\text{Cl}^{35}$, $\text{Cl}^{35}-\text{Cl}^{37}$ and $\text{Cl}^{37}-\text{Cl}^{37}$, but in our present experiment, the conclusion is also reserved and further study upon this point is necessary.

In conclusion, the writer wishes to express his hearty thanks to Prof. M. Kimura for the interest he has taken in this work and also for his invaluable advice.

Bromine

PL. IV.

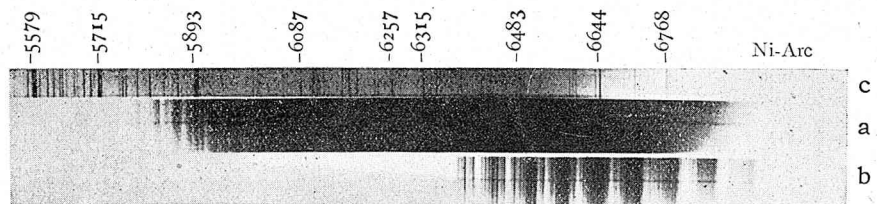


Fig. 1. a: Absorption at ord. Temp., d: 17.5 cm. P: ca. 26 cm.
 b: " at high Temp. (1000°C.), d: 17.5 cm. P: 26 cm.
 c: Nickel Arc Comparison.

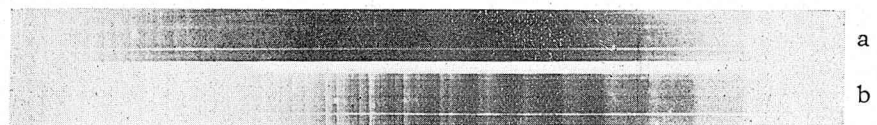


Fig. 2. a: Absorption at ord. Temp. d: 17.5 cm. P: ca. 8 cm.
 b: " at high Temp. (1000°C.).

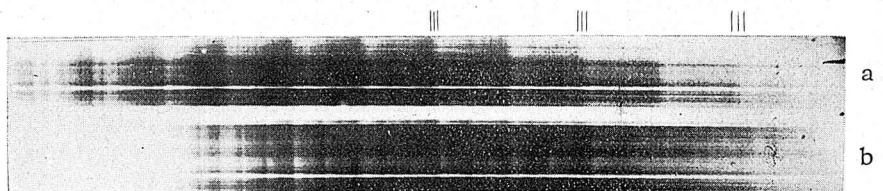


Fig. 3. a: Absorption at high Temp. (1100°C.), d: 17.5 cm. P: 26 cm.,
 b: Absorption at ord. Temp. (30°C.), d: 650 cm. P: 26 cm.

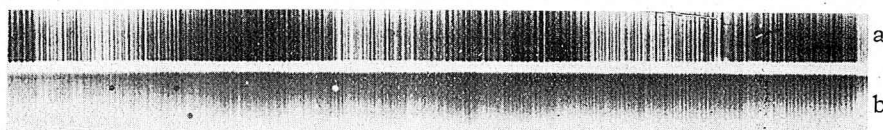


Fig. 4. Ditto. (A portion of spectra given in Fig. 3.) 10-foot, Concave Grating, 2nd order.

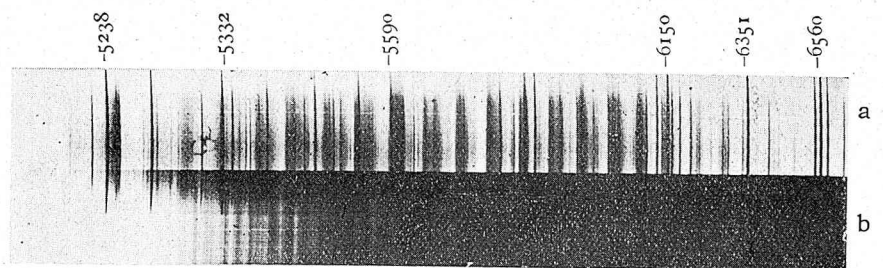


Fig. 5. a: Emission (Vacuum Tube). b: Absorption at ord. Temp.

Chlorine

PL. V.

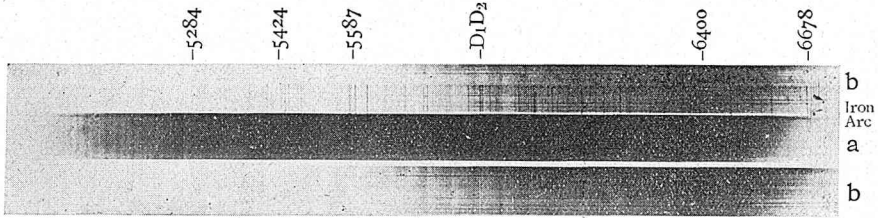


Fig. 1. a: Absorption at ord. Temp. d: 2.5 m. P: 1 atm.
 b: Absorption at high Temp. (820°C). d: 2.5 m. P: 1 atm.



Fig. 2. a: Absorption at ord. Temp., d: 2.5 m. P: 1 atm. 10-foot Concave Grating,
 b: " at high Temp. D-line Region. 2nd Order.

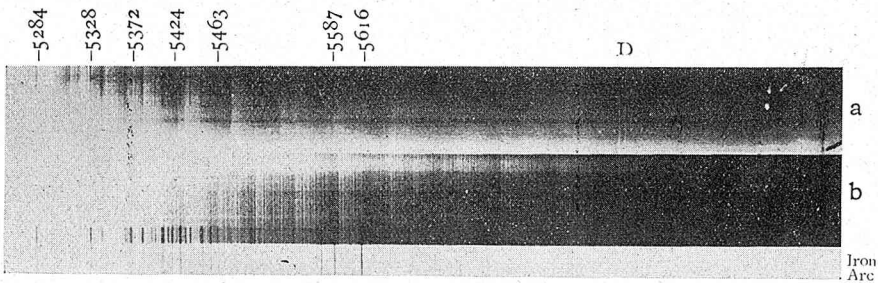


Fig. 3. a: Absorption at ord. Temp., d: 12.6 m. P: 1 atm.
 b: " at high Temp. (820°C). d: 2.5 m. P: 1 atm.

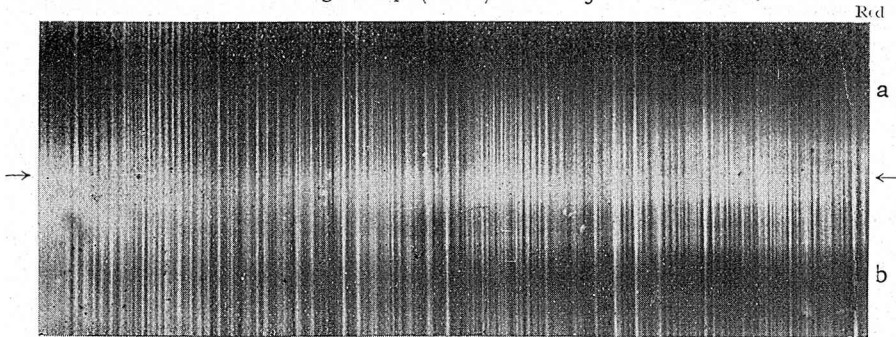


Fig. 4. a: Absorption at ord. Temp. d: 12.6m, P: 1 atm. 10-foot Concave Gra-
 b: " at high Temp. (820°C). d: 2.5m, P: 1 atm. ting, 2nd Order.

Chlorine

Pl. VI.

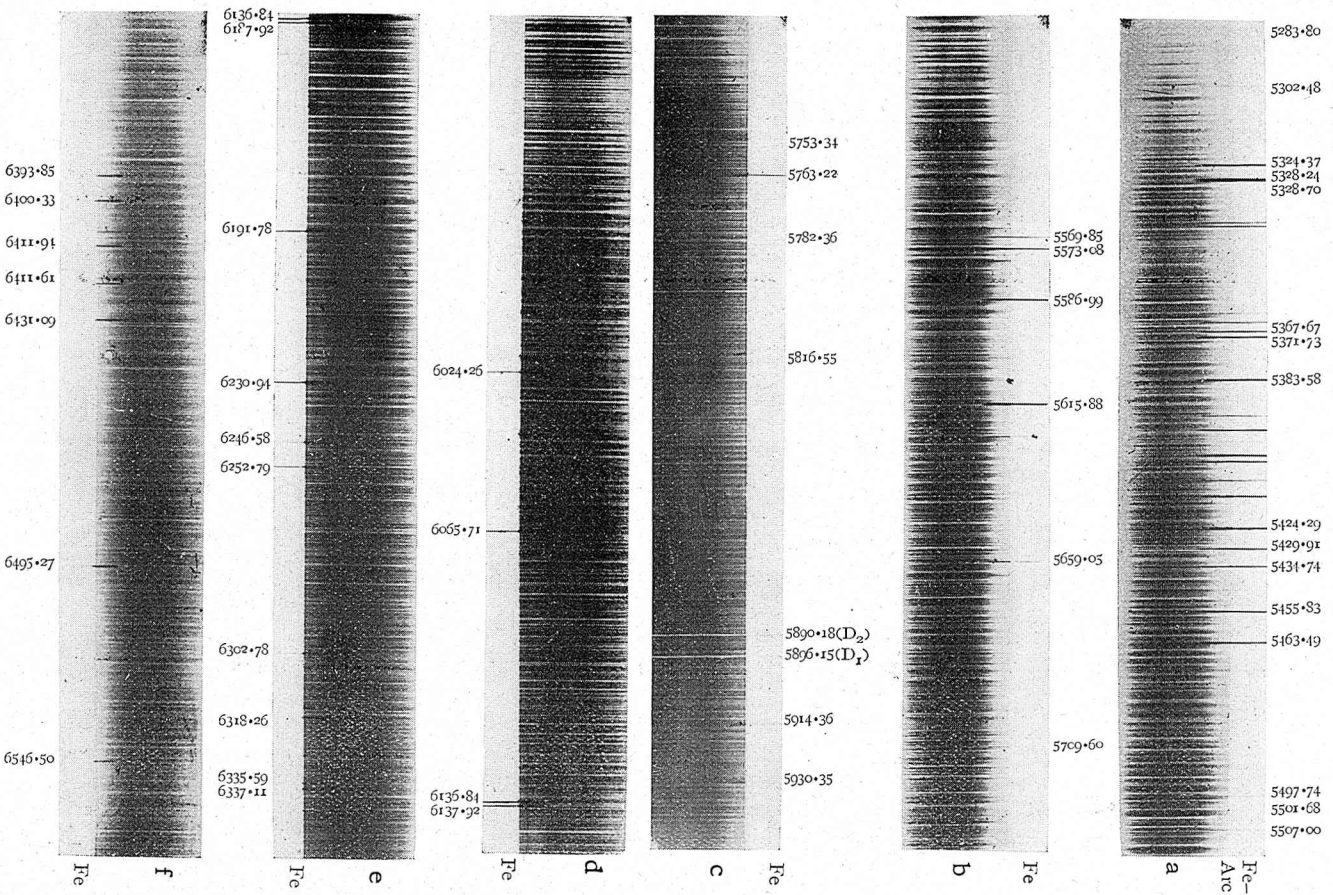


Fig. 5. Absorption Spectrum at high Temp. (820°C.) 10-foot Concave Grating, 2nd order.
 a, b and c: 80 cm. layer; d, e and f: 250 cm. at 1 atmosphere.