VI. *On the Absorption-Spectra of Bromine and of Iodine Monochloride.*

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[Plate 4.]

The element bromine and the compound iodine monochloride possess nearly the same molecular weight. The colours of their vapours appear almost identical, and a rapid glance at the complicated absorption-spectra afforded by the two gases fails to detect any difference between them. It becomes, therefore, a matter of importance to ascertain whether the molecules of the two bodies, when gaseous, vibrate identically or similarly. We have accordingly undertaken a series of exact measurements of the absorption-spectra of these two gases, the results of which we have now the honour to communicate to the Royal Society.

The two spectra were compared simultaneously by means of one of Kirchhoff's model spectroscopes, 4 flint-glass prisms of 60° and 45° and a magnifying-power of 40 being employed. The position of the lines and of the well-defined edges of the bands in both spectra were read off by reflexion upon a fixed arbitrary scale; the positions of 27 air-lines lying between the extremes of the absorption-spectra were then determined upon the same scale, both the scale and prisms remaining untouched during the different series of observations. In order to determine the wave-lengths of each of the absorption-bands in the spectra of bromine and iodine monochloride, the wave-length of each of the 27 air-lines was ascertained by reference to the measurements of Thalén; in three cases, marked H, in the accompanying Table the numbers given by Huggins have been used.

Colour of ray.	Micrometer-scale reading.	Wave-length.	Colour of ray.	Micrometer-scale reading.	Wave-length.
Red	42·48	6602	Yellow ...	53·06	5666
	42·96	6562		54·81	5549
	43·61	6480		55·00	5541
Orange ...	46·81	6171		55·09	5534
	49·30	5949		55·17	5530
	49·47	5942		55·25	5524 H.
	49·54	5932		55·61	5495
	49·68	5929		55·86	5479
Yellow ...	51·68	5767		56·18	5462
	51·96	5745		56·29	5453
	52·48	5711		58·10	5350 H.
	52·83	5686	Green......	58·27	5339
	52·88	5680 H.		58·59	5320
	53·00	5675			

In order to reduce the micrometer-scale readings of the absorption-spectra to wave-lengths, a graphical method was adopted. In the first place, the wave-lengths of the 27 air-lines having been found as described, these numbers were taken as ordinates and plotted on curve-paper, the scale-readings of the air-lines being taken as abscissæ. The points thus obtained fell naturally into six groups or series, and a mean point for each group was then found by accurate measurement, and the curve drawn through the six mean points. In order to obtain the wave-lengths of the well-defined edge of the different bands of the absorption-spectra, it was merely necessary to ascertain from th curve the value of the ordinate corresponding to each scale-reading as abscissa. The positions of the six mean points, each corresponding to a group of air-lines needed for the construction of the curve, were ascertained by means of the arrangement seen in Plate 4. fig. 1. The wooden rod (A A) has a steel point (C C) fixed at one end, and a graduated paper scale at the other. At the end carrying the steel point is a strip of wood (T T P) placed at right angles to the rod, which it serves to support, so that the axis (C C) of the steel point is vertical, whilst the scale (S S) lies in a horizontal position, the end P sliding on the table when the rod is rotated round the point C C as centre. The curve-paper is now adjusted on the table, so that some one division on the scale describes a circle through one particular group of spots and also through two other groups, one on each side, which circle, if drawn, would pass not far from the mean points of the three groups.

In order now to find the exact position of the mean point of the middle group through which the curve is to pass, the distance from each point to the steel centre (C C) of the circle is first accurately read off on the divided scale. A point is then chosen and plotted near the middle of the group, as a mean of the several distances, such that the sum of the shortest distances of the several points of any one group to the curve drawn through this mean point is zero.

This process is repeated for each of the four groups in the middle, the centre of curvature for an end group being taken to be the same as that for the second group from that end. In one case an isolated point occurs, and this is taken as one group and the curve drawn through it.

The curve consists of arcs of circles which pass through the six mean points, with radii varying from $64\frac{1}{4}$ inches in length at the upper end to $61\frac{1}{2}$ inches at the lower end.

Absorption-Spectrum of Bromine.

This absorption-spectrum was first examined in 1833 by W. H. MILLER, but no accurate map has hitherto been published.

The bromine employed in our experiments was a portion of the sample used by one of us in the determination of the rate of thermal expansion of this liquid. It was obtained by distilling a large quantity of commercial bromine, after dehydration with oil of vitriol, and collecting separately the fraction boiling at about 60°, which amounted to about two thirds of the whole liquid operated upon. The sample was found to be free from iodine. In order to remove any chlorine which might be present, it was digested with powdered potassium bromide for several weeks, again distilled, and treated with phosphorus pentoxide. The pure bromine boiled constantly between 59°·6 and 59°·7 (corrected). Bar. (corrected and reduced) 765·2 millims.

The spectrum was obtained by allowing the rays from a lime-light to pass, before falling on the slit of the spectroscope, through bromine vapour contained in a long and strong narrow glass tube heated by means of a flame. The spectrum thus obtained is a channelled one, and consists of a large number of bands, 66 of which have been measured. Each band, like those of iodine*, is made up of a close association of fine lines, the whole stretching from wave-length 6801·5 in the red to wave-length 5244·1 in the green. Beyond these extremes the general absorption becomes too powerful to permit further bands to be seen. Each of these bands has a well-defined edge towards the blue end, and shades off gradually towards the less refrangible end of the spectrum, as shown in the drawing. The bands are by no means regularly dispersed throughout this length, but are more numerous, as well as more intense, in the yellow and green portions of the spectrum than in the red. The bands in the green form the best defined portion of the bromine spectrum, and the bands 5483·8 and 5460·1, although rather fainter than some others, are especially characteristic. The spectrum of the vapour of bromine at the ordinary temperature and that obtained when the vapour is heated differ from each other, inasmuch as the lines in the green beyond 5433·2 and in the red beyond 6101·4 are invisible in the cold, though visible in the heated vapour. A few lines, such as 5634·8 and 5580·6, in the green appear in the spectrum of the heated vapour, but not in that of the cold vapour; but, as a whole, the bands seen in the cold vapour are also seen in the heated vapour, and no change whatever in position is noticed. The least refrangible bands beyond 6526·9 are ill-defined; they appear directly upon heating, but fade quickly away as the vapour cools. The letter *f* placed after the wave-length denotes that the line is faint; *v.f* means very faint; and *s* denotes that the line is dark and well-defined.

* THALÉN, 'Le Spectre d'absorption de la vapeur d'Iode,' Upsal, 1869.

I. Absorption-Spectrum of Bromine.

Colour of rays.	Wave-lengths.	Remarks.
Red	6801·3	
	6777·2	
	6723·9	
	6649·1	
	6581·3	
	6526·9	
Orange	6468·9	...... s.
	6455·4	...... f.
	6413·0	...... s.
	6401·0	...... f.
	6372·6	...... f.
	6350·5	...... s.
	6336 7	...... f.
	6312·1	...... f.
	6292·8	...... s.
	6275·4	...... f.
	6263·9	...... f.
	6240·2	...... s.
	6223·3	...... f.
	6190·9	
	6169·7	
	6144·1	
	6119·0	
	6101·4	
	6072·2	...... s.
	6053·2	...... f.
	6027·3	
	6006·1	...... f.
	5987·5	...... s.
	5956·5	...... s.
	5945·1	...... f.
	5913·9	...... s.
	5905·9	...... f.
	5875·5	
	5870·7	...... v.f.
Yellow	5835·3	
	5797·7	
	5762·7	
	5727·5	
	5694·4	
	5660·4	
	5634·8	
	5624·4	
	5592·0	...... s.
	5580·6	...... f.
	5560·7	...... s.
	5556·8	...... f.
	5534·1	
	5510·3	
	5501·3	
	5483·8	
	5476·8	
	5460·1	
	5439·9	
	5418·2	
	5403·2	
	5380·3	
	5365·8	
	5347·5	
Green	5337·4	
	5306·8	
	5298·7	
	5292·2	
	5274·5	
	5258·8	
	5244·1	

Absorption-Spectrum of Iodine Monochloride.

This compound was prepared by heating a mixture of iodine and finely powdered potassium chlorate. After repeated distillation from potassium chlorate it boiled constantly between 99°·7 and 100°·7. Corrected and reduced barometer 744·3 millims.

The spectrum of iodine monochloride is likewise a channelled one, generally resembling that of bromine, but differing essentially from it as well in the position of the bands as in their distribution. For the purpose of mapping its absorption-spectrum the chloride was placed in a cylindrical glass tube, 14 centims. in length, having flattened ends, the rays from the lime-light passing through the length of the tube, which was then heated with a lamp.

The spectra of the moderately heated and strongly heated vapour exhibit differences similar to those seen in the case of bromine. Thus at the higher temperature a great increase in the number of bands in the green is observed, none of the bands from 5679·5 to the end (5276·1) being visible at the lower temperature. No change in the position of the bands or lines common to the vapour at both temperatures is, however, observed on heating or cooling, so that in other respects, and as regards by far the majority of the lines or bands, no alteration is produced by heat.

II. Absorption-Spectrum of Iodine Monochloride.

Colour.	Wave-length.	Remarks.
Red	6475·1	
Orange ...	6442·9	
	6421·3	
	6383·7	
	6372·6	
	6324·9	
	6318·0	
	6266·8	
	6216·9	
	6181·5	
	6167·9	
	6155·0	
	6122·6	
	6112·8	
	6079·2	
	6071·3	
	6040·9	
	6033·2	
	6021·3	...... *f.*
	6005·2	...... *s.*
	5995·9	...... *f.*
	5974·1	...... *f.*
	5957·3	...... *s.*
	5944·3	...... *f.*
	5918·7	
	5905·1	
	5886·7	
	5877·8	
	5861·4	
Yellow ...	5852·3	
	5843·7	
	5820·5	...... *s.*
	5815·9	...... *f.*
Yellow ...	5788·8	...... *s.*
	5782·0	...... *f.*
	5751·0	
	5744·4	...... *v.f.*
	5719·6	...... *s.*
	5713·0	...... *f.*
	5685·8	
	5679·5	
	5658·3	
	5650·0	
	5632·1	
	5628·6	
	5618·4	
	5600·7	
	5590·0	
	5572·0	
	5561·3	
	5552·9	
	5535·4	
	5523·6	
	5508·4	
	5501·3	
	5482·5	
	5459·5	
	5435·1	
	5412·1	
	5394·3	
	5368·1	
	5349·8	
	5330·0	
Green......	5315·5	
	5295·0	
	5276·1	

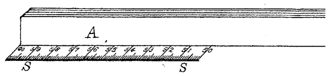
A careful comparison of the absorption-spectra of bromine and iodine monochloride shows that although a large number of bands are nearly coincident, the spectra, as a whole, are not identical either when the vapours are examined at low or at high temperatures, or when the length of the columns of absorbing gas is varied. Out of the 66 lines mapped in each of the two spectra only two, viz. 6475·1 and 6372·6, appear to be truly coincident. The differences between the two spectra are seen, first, in the red portion, inasmuch as six bands are observed in the bromine beyond the last, 6475·1, in the iodine monochloride; and, secondly, in the green portions, where the chloride spectrum exhibits a larger number of closely set or double lines than are seen in the corresponding portions of the spectrum of bromine.

The curve and the map, on half the scale of ANGSTRÖM'S "spectre normal," have been very carefully drawn by Mr. WILLIAM DODGSON, to whom we beg to tender our thanks.

[NOTE.—Since the above paper was read, Professor STOKES has suggested to us that the wave-lengths might have been more easily determined by means of a curve in which the coordinates were the deviation, less a constant, and the squared reciprocals of the wave-length, less a constant, a curve which would come out almost a straight line. We communicated this suggestion to Mr. A. M. WORTHINGTON, who has worked it out, and who endorses Prof. STOKES'S recommendation.]

Roscoe & Thorpe.

Absorption Spe



Br.

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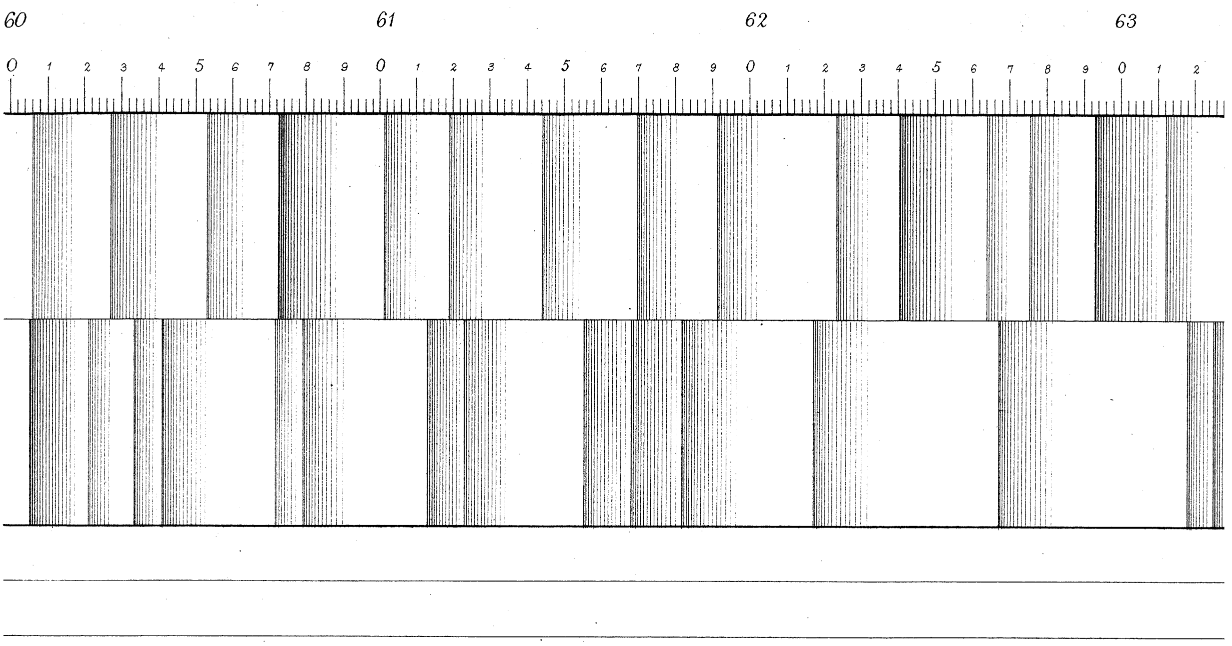

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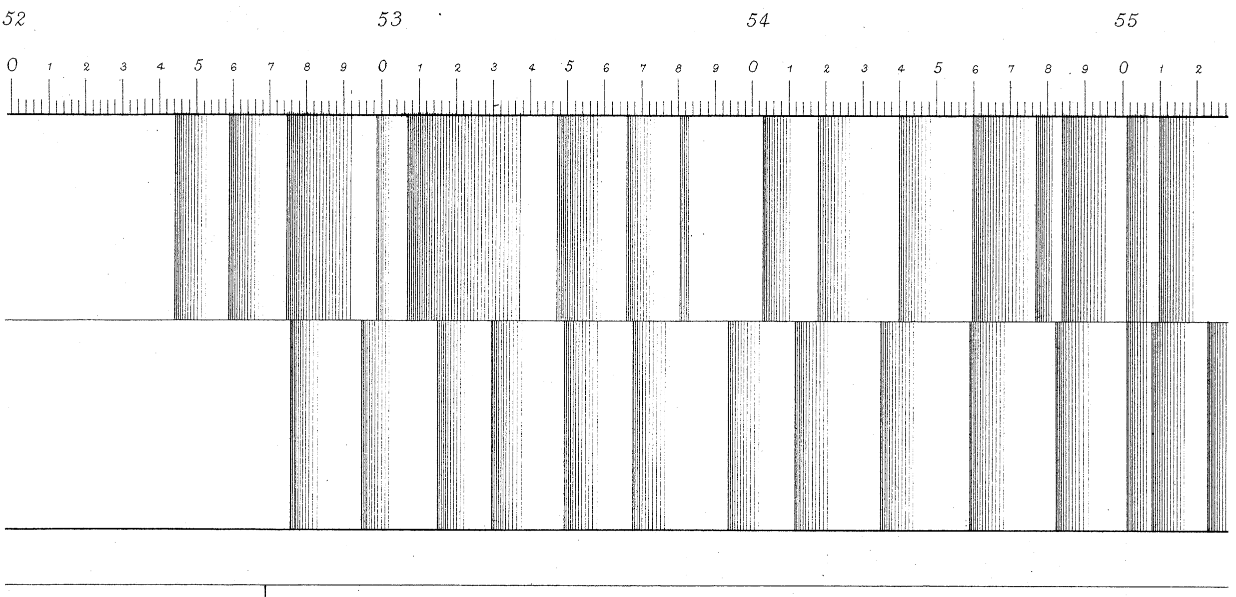
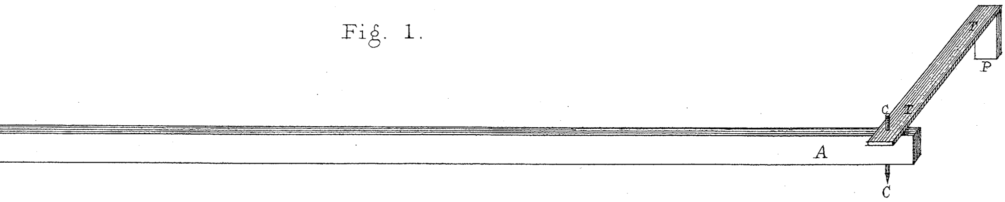
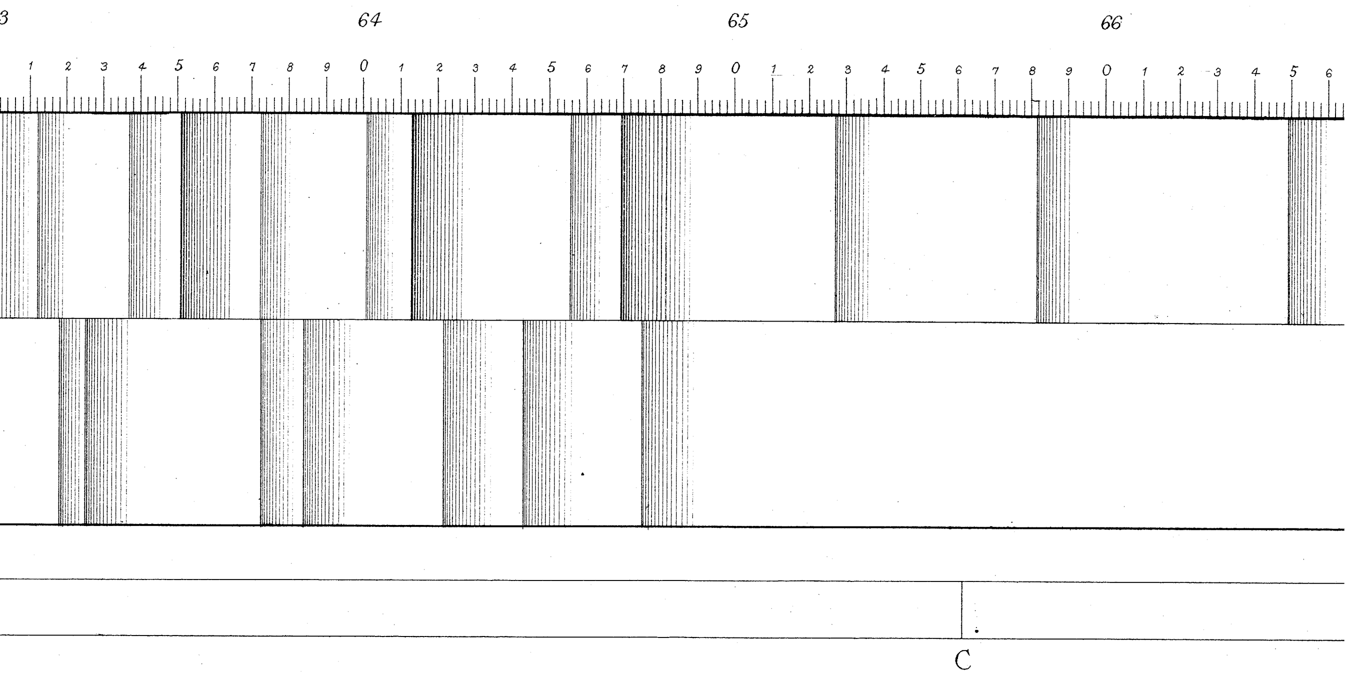
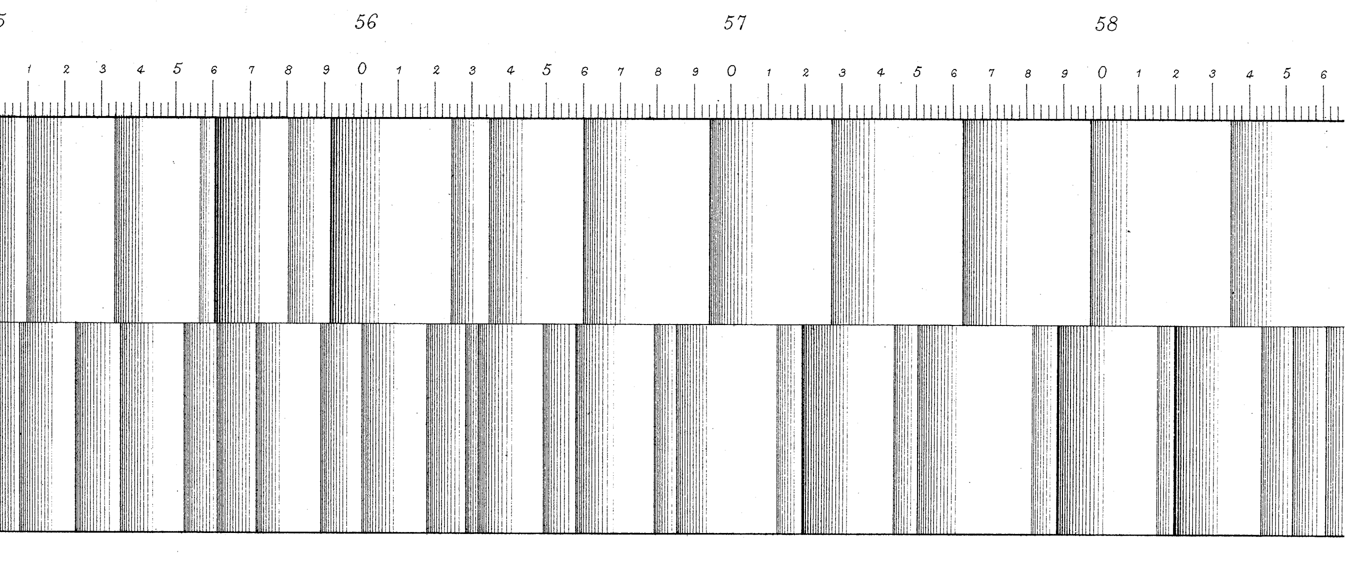


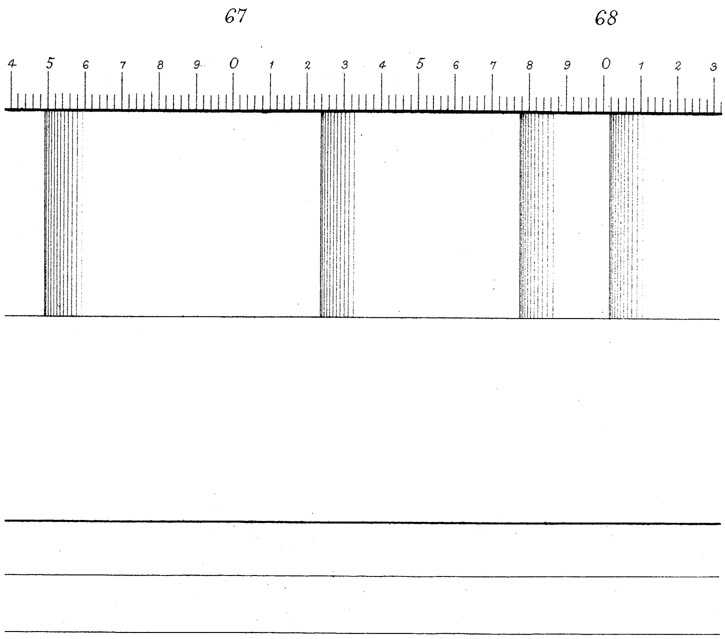
Spectra of Bromine and Iodine Mono-chloride.

Fig. 1.





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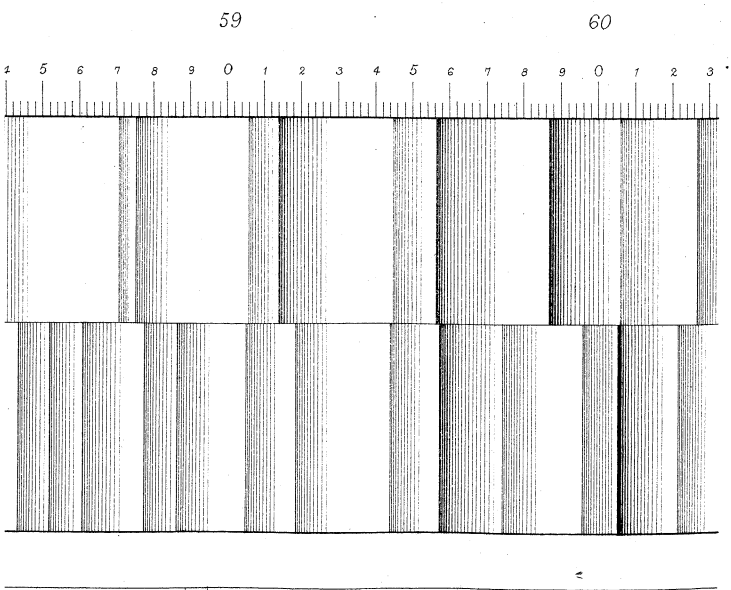
68
4 5 6 7 8 9 0 1 2 3 4 5 6 7 8 9 0 1 2 3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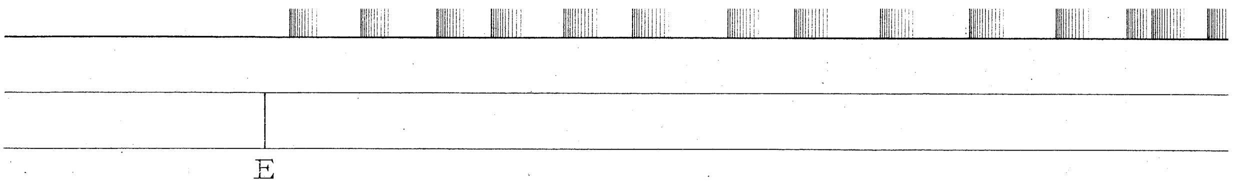
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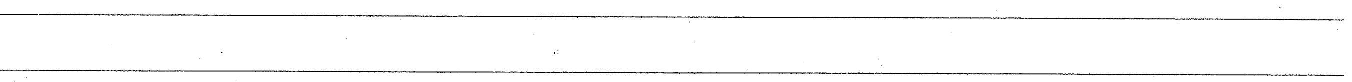

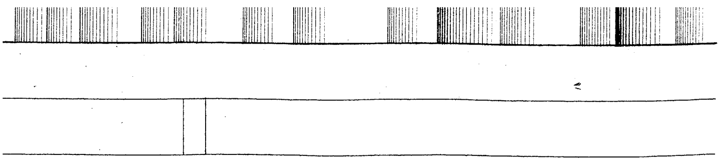
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W. West & C° lith.

Absorption Spectra of Bromine and Iodine Mono-chloride.

Fig. 1.