

XXXIV. *On the Photographic Transparency of various Bodies, and on the Photographic Effects of Metallic and other Spectra obtained by means of the Electric Spark.*
 By W. A. MILLER, M.D., LL.D., Treas. & V.P.R.S., Professor of Chemistry in King's College, London.

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1. At the Meeting of the British Association held in Manchester last autumn, I exhibited some photographs of spectra from the electric spark obtained between wires of different metals by means of an induction-coil. Upon this occasion a hollow prism filled with bisulphide of carbon was employed, because, owing to its great dispersive power, it furnished spectra in which the lines under examination were more widely separated and exhibited with greater distinctness than by any other medium in ordinary use.

Plate XXXIX. fig. 30 exhibits a copy of the photograph of the solar spectrum obtained by means of a hollow glass prism filled with bisulphide of carbon, contrasted with the spectrum obtained through the same prism simultaneously from the spark between copper terminals of the secondary coil in the induction apparatus. In this, and in all the subsequent figures, the less refrangible end of the spectrum is upon the left-hand side of the Plate.

The great prolongation of the more refrangible portion of the spectrum beyond the part visible to the unaided eye, led me to believe that the bisulphide was a material which exerted but little absorbent action upon the chemical rays. Subsequent experiments have, however, convinced me that this opinion was erroneous, and have rendered it necessary to modify considerably the conclusions deduced from those experiments.

2. At the time that that paper was written, I believed that the photographic effects produced by the electric spectra of all the metals furnished results in a great degree similar to each other, if not actually identical. This, it will be seen from subsequent statements, is correct so far as the fact of the similarity in this portion of the spectra is concerned, but is erroneous as regards the general conclusion deduced from it. During the past winter I have renewed these experiments, substituting a quartz-train for glass and bisulphide of carbon, and have chiefly used a fine quartz prism, kindly lent to me by my friend Mr. GASSIOT. The refracting-angle of this prism is about 60° ; its faces are about 2 inches long and $1\frac{5}{8}$ inch broad, and are so cut as to furnish a singly refracted beam for the medium rays, by transmitting it along the axis of the crystal. It is well known, from the experiments of Prof. STOKES* and M. E. BECQUEREL, that quartz is remarkable for its transparency to both fluorescent and phosphorogenic rays of high refrangibility.

* Phil. Trans. 1852, p. 540.

It was soon evident that the absorbent action of the bisulphide was far greater than I had imagined, and that in reality the spectrum which it transmitted was composed of rays which did not extend beyond one-tenth or one-twelfth of the entire length of the spectrum obtained by the use of a quartz-train*.

3. The dispersive power of rock-crystal is, however, comparatively low, and the difficulty of obtaining with it a spectrum free from the effects of double refraction through its entire length is great; so that it appeared to be worth while, as a preliminary inquiry, to ascertain whether any singly refracting medium could be procured, better adapted to researches of this nature by sufficient permeability to the chemical rays, and by tolerably high dispersive power. Although no material on the whole preferable to quartz has been found, the investigation gave results of considerable interest.

4. Before proceeding to detail these results, it will, however, be convenient, as several distinct subjects will be discussed in this paper, to state the order in which I propose to arrange my remarks, and the heads to which they will be referred.

I shall commence with

(1) *The absorption of chemical rays by transmission through different media.*

a. By transmission through solids.

b. By transmission through liquids.

c. By transmission through gases and vapours.

(2) *The absorption of the chemical rays by reflexion from polished surfaces.*

(3) *The photographic effects of the electric spectra of different metals taken in air,* including

a. Pure metals.

b. Alloys.

(4) *Photographic effects of electric spectra of different metals produced by transmitting the sparks through gases other than atmospheric air.*

5. The general results of my experiments upon the absorption of the chemical rays are the following:—

(1) Colourless bodies which possess equal powers of transmitting the luminous rays vary greatly in permeability to the chemical rays.

(2) *Diactinic* solids (that is to say, solids which are permeable to the chemical rays) preserve their diactinic power both when liquefied and when converted into vapour.

(3) Colourless solids which are transparent to light, but which exert a considerable

* The absorptive power of the bisulphide for the chemical rays was, however, noticed by M. E. BECQUEREL as far back as 1843, as I find by again referring to his paper, *Annales de Chimie*, sér. 3. vol. ix. p. 301. In this paper M. BECQUEREL describes the absorbent action of various solids and liquids upon the chemical rays, but, from having used solar light, he failed to remark the great difference between the absorptive powers of quartz and glass. Although he used prisms of rock-salt, rock-crystal, and alum, his results do not indicate the real difference in their absorptive power; and as in all his experiments on liquids he employed a vessel with flint-glass sides to hold them, his conclusions are vitiated by the same error which affected my own earlier inquiries on the subject.

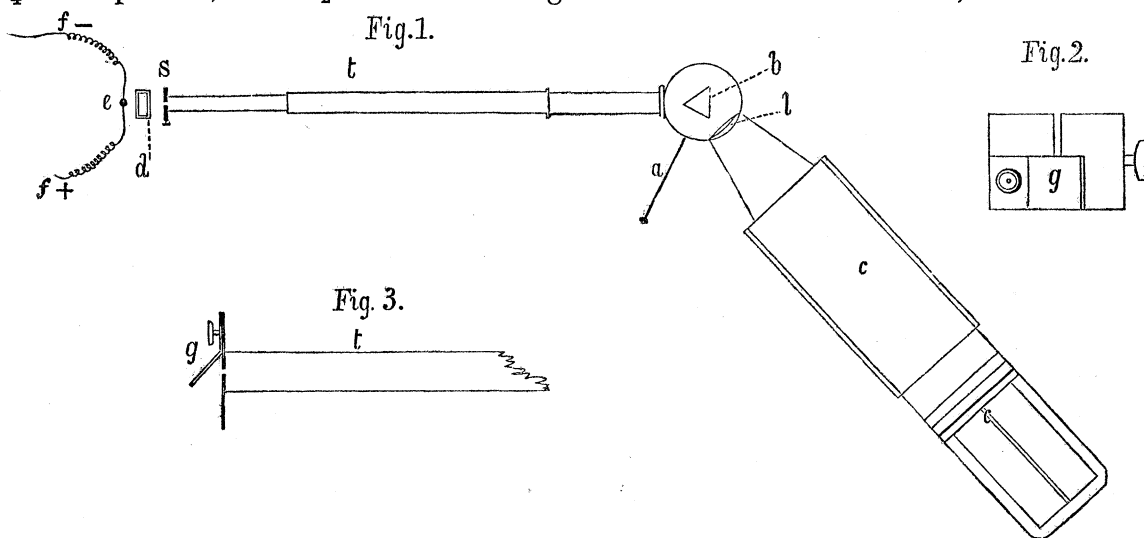
absorptive effect upon the chemical rays, preserve their absorptive power with greater or less intensity both in the liquid and the gaseous state (21).

Whether the compound be dissolved in water or be liquefied by heat, these conclusions are equally true as regards liquids. Water is perfectly permeable to the chemical rays; and this circumstance, conjoined with the fact that in no instance does the process of solution seem to interfere with the special action of the substance dissolved upon the incident rays, renders it practicable to submit to trial a great number of bodies which it would otherwise be impossible to subject to experiments of this nature, owing to the extreme difficulty of obtaining them in crystals of sufficient size and limpidity.

§ 1. ABSORPTION OF THE CHEMICAL RAYS.

a. *By transmission through Solids.*

6. The general arrangement of the apparatus employed in this inquiry is represented in fig. 1, in which the observer is supposed to be looking down upon the instrument. *c, c* is a camera which allows of a considerable range of adjustment, and is attached to a cylindrical box, within which is a prism *b*, of rock-crystal. At *l* is a quartz lens of $1\frac{1}{4}$ -inch aperture, and $17\frac{1}{2}$ inches focal length. At one end of the tube *t*, which can be



lengthened or shortened by a sliding joint, is a slit *s*, provided with a screw for regulating the width of the opening. This slit is arranged parallel to the axis of the prism, and in these experiments was adjusted to a distance of 37 inches from the lens *l*. The prism is placed at about its angle of minimum deviation for the mean ray, and, for facility of manipulation, can be turned round upon its own axis by means of the lever *a*. The angle formed between the camera and the tube *t* also admits of variation as circumstances may require. At *d* is placed the substance the transparency of which is to be tested; and at *e* are the metallic electrodes, which are connected with secondary wires *ff* of a 10-inch induction-coil, not shown in the figure. The wires of the coil terminate in electrodes composed of fine silver. The coil was excited by means of a battery consisting of five

elements of GROVE'S construction, a condenser being included in the primary circuit, whilst a small Leyden jar, exposing about 75 square inches of metallic coating upon each of its surfaces, was introduced into the secondary circuit. In this way a torrent of sparks could be maintained between the electrodes at e without any sensible variation of power, for ten minutes at a time, or longer if necessary. In these experiments, an exposure of the sensitive plate for five minutes in the camera was requisite.

At a suitable distance behind the lens (about 26 inches*), a collodion plate coated with iodide, or occasionally with a mixture of iodide and bromide of silver, was supported in the camera, for the purpose of receiving the image of the spectrum †. The plate was excited by the use of a bath of nitrate of silver containing 30 grains of the nitrate to an ounce of water. The image was developed in the usual way by means of pyrogallic acid, in the proportion of one grain to the ounce of water, and fixed with cyanide of potassium.

7. The spectra of electric sparks so obtained were remarkable for their great length; indeed they extended beyond the termination of the visible rays for a space equal to five or six times the length of the luminous portion.

For the convenience of comparing the results of the various experiments together, I have adopted an arbitrary fixed scale, the fiducial point of which is the line H in the solar spectrum. Calling this 100, the more refrangible rays are numbered onwards, and the less refrangible rays backwards from it, the line B in the solar spectrum being at 84: the length of the spectrum from silver points extends from 96·5 upon this scale to 170·5. The solar spectrum for the purpose of this comparison was projected upon the collodion plate by means of a small mirror of polished steel (*g*, fig. 2) placed so as to form an angle of 45° with the surface of the plate carrying the slit, and to cover a portion of the vertical slit, as shown by an end view of the tube at *g*, fig. 3, whilst the direct image from the silver points fell simultaneously, parallel to that of the solar spectrum, upon the collodion plate in the camera.

8. The following Table contains a list of the various substances subjected to experiment. All these bodies allowed the less refrangible rays to pass, but cut off the rays of medium and extreme refrangibility wherever absorption occurred at all.

* This distance was found by experiment to give nearly a flat field, with the image of the slit formed by all the different rays in focus simultaneously. My friend and colleague, Professor J. C. MAXWELL, kindly calculated for me the relative positions of lens and prism necessary to ensure an approximatively flat field for the visible rays.

If the lens be placed between the slit and the prism, a very great difference occurs between the points of convergence of the most refrangible and the least refrangible rays, amounting with the lens and prism which I used to nearly 14 inches. When the lens is before the prism, both coincide in augmenting the convergence of the more refrangible rays; whereas when the lens is placed behind the prism, as shown in the figure, the convergence occasioned by the lens is neutralized by the prism, which now acts in the opposite direction upon the diverging rays as they fall upon it from the slit.

† My friend Mr. PRIZEX, who assisted me in these experiments, prepared the collodion for me, following nearly the directions given by HARDWICH in his 'Manual of Photographic Chemistry,' 6th edition, p. 262. It was iodized with a mixture of equal parts of iodides of potassium and cadmium, and was perfectly uniform in its action, even for weeks after it had been iodized, if kept in the dark.

TABLE I.—Diactinic Power of Solids.

Name of substance.	Thickness, in inches.	Termination of spectrum.	Relative lengths of spectra.	Remarks.
Ice	about 0·5	170·5	74·0	Faint bluish tinge. With quartz-train. Faint image of spectrum.
Diamond* (<i>l</i>)	0·032	155·5	59·0	
Diamond (<i>m</i>)	0·017	159·5	62·0	
Diamond (<i>A</i>)	0·182	115·5	19·0	
Sapphire (24)	0·13	116·0	19·5	
Sapphire (<i>B</i>)	0·093	112·0	15·5	
Sapphire (<i>n</i>)	0·12	111·0	14·5	
Quartz	0·16	170·5	74·0	
White Topaz	0·19	162·0	65·5	
Mica	0·007	114·5	18·0	
Oil of Vitriol	0·75	160·5	64·0	Pale green. Faint pink. Full blue.
Sulphate of Lime (solid)	about 0·3	155·5	59·0	
Sulphate of Baryta (solid)	about 0·4	154·5	58·0	
Sulphate of Magnesia (solid)	0·34	158·0	61·5	
Sulphate of Potash	Sat. soln. 0·75 in.	159·5	63·0	
Sulphate of Soda	"	159·5	63·0	
Sulphate of Ammonia	"	145·5?	49·0?	
Sulphate of Zinc	"	152·5	56·0	
Alum	"	159·5	63·0	
Sulphate of Iron	"	105·0	8·5	
Sulphate of Manganese	"	144·5	48·0	
Sulphate of Copper	"	112·5	16·0	
Sulphite of Soda	"	127·5	31·0	
Hyposulphite of Soda	"	108·5	12·0	
Fluor-spar	0·17	170·5	74·0	
Fluoride of Sodium	Sat. soln. 0·75 in.	159·5	63·0	
Fluoride of Ammonium	"	166·5	70·0	
Hydrochloric Acid, sp. gr. 1·1	0·75 in.	152·5	56·0	Faint rose-colour. Spectrum cut off abruptly. Spectrum cut off abruptly.
Rock-salt (solid)	0·75	159·5	63·0	
Chloride of Potassium	Sat. soln. 0·75 in.	159·5	63·0	
Chloride of Ammonium	"	155·0	58·5	
Chloride of Barium	"	153·0	56·5	
Chloride of Strontium	"	152·0	55·5	
Chloride of Calcium	"	147·0	50·5	
Chloride of Zinc	"	145·5	49·0	
Chloride of Manganese	"	104·5	8·0	
Chloride of Tin (SnCl)	"	108·5	12·0	
Chloride of Tin (SnCl ₂)	Strong solution.	114·5	18·0	

* I am indebted to my friend Professor W. H. MILLER, of Cambridge, for the opportunity of examining the diamonds and sapphires alluded to above. *l* was a slice of diamond bounded by cleavage-planes, from the Warburton Collection. *m* a somewhat thicker slice from the same collection. *A* a large octahedral diamond from the Humian Collection: all these were colourless. The sapphire 24 was a large six-sided prism from the Brooke Collection; that marked B was a smaller prism of a faint bluish tinge from Professor MILLER's own collection. *n* is a colourless crystal of sapphire from the Warburton Collection. I made an application to the Trustees of the British Museum for permission to use some of the limpid specimens in their collection, but was informed that even for such a purpose the Act of Parliament forbids them to allow any mineral to pass off their premises. Mr. Maskelyne was kind enough to lend me a fine colourless topaz from his own collection.—[Feb. 1863.]

TABLE I. (*continued*).

Name of substance.	Thickness, in inches.	Termination of spectrum.	Relative lengths of spectra.	Remarks.
Chloride of Arsenic (AsCl_3)...	Liquid.	101.5	5.0	Spectrum cut off abruptly.
Corrosive Sublimate	Sat. soln. 0.75 in.	128.5	32.0	Spectrum cut off abruptly.
Bromide of Sodium	"	144.5	48.0	
Bromide of Potassium	"	144.5	48.0	
Iodide of Sodium	"	114.5	18.0	Spectra terminate abruptly.
Iodide of Potassium	"	114.5	18.0	
Cyanide of Potassium	"	105.5?	9.0?	Prepared by LIEBIG's process.
Cyanide of Mercury	"	145.5	49.0	
Sulphocyanide of Potassium...	"	112.5?	16.0?	Slightly yellowish.
Hydrate of Soda	"	131.5	35.0	From sulphate by precipitation with baryta.
Hydrate of Potash.....	"	129.5	33.0	
Hydrate of Ammonia	Sp. gr. 0.945	170.5	74.0	Rather feeble spectrum.
Hydrate of Baryta	Sat. soln. 0.75 in.	158.0	61.5	
Hydrate of Strontia	"	150.0	53.5	CRUM's solution. [lution.
Hydrate of Alumina	Strength of solution	146.0	49.5	
Hydrate of Silica	not determined.	152.0	55.5	Dialysed from hydrochloric so-
Carbonate of Soda	Sat. soln. 0.75 in.	146.0	49.5	From ignited bicarbonate.
Carbonate of Potash	"	146.0	49.5	
Iceland Spar	0.35	160.0	63.5	
Bicarbonate of Soda	Sat. soln. 0.75 in.	145.0	48.5	
Bicarbonate of Potash	"	142.0	45.5	
Sesquicarbonate of Ammonia .	"	152.0	55.5	
Boracic Acid	"	143.0	46.5	Faint beyond 109.
Borax	"	158.5	62.0	
Phosphoric Acid	"	117.5?	21.0	Equal weights of same salt; one dried at 300° F., the other ignited.
Phosphate of Soda (HO , } 2NaO, PO_5)	{ Solution of 60 grains of dried salt in 1 oz. of water. }	156.5	60.0	
Pyrophosphate of Soda, } 2NaO, PO_5		156.5	60.0	
Triarsenate of Soda (3NaO , } As O_5)	Sat. soln. 0.75 in.	127.5	31.0	
Arsenic Acid	"	119.5	23.0	
Chlorate of Potash.....	"	145.5	49.0	
Nitric Acid	Sp. gr. 1.3	106.5	10.0	Colourless.
Nitrate of Soda	Sat. soln. 0.75 in.	112.5	16.0	All the spectra of the nitrates are cut off sharply.
Nitrate of Potash	"	112.5	16.0	
Nitrate of Ammonia	"	112.5	16.0	
Nitrate of Lime.....	"	112.5	16.0	
Nitrate of Magnesia	"	112.5	16.0	
Nitrate of Baryta	"	111.5	15.0	
Nitrate of Strontia.....	"	111.5	15.0	
Nitrate of Nickel	"	absorbed	0.0	Intense green solution.
Nitrate of Lead	"	111.5	15.0	
Subnitrate of Mercury	"	111.5	15.0	
Nitrate of Silver	"	106.0	9.5	

TABLE I. (*continued*).

Name of substance.	Thickness, in inches.	Termination of spectrum.	Relative lengths of spectra.	Remarks.
Acetic Acid	Glacial, liquefied	112.5	16.0	Spectrum ends abruptly.
Acetate of Soda.....	Sat. soln. 0.75 in.	144.5	48.0	
Acetate of Potash	"	113.5?	17.0?	
Acetate of Ammonia.....	"	144.5	48.0	
Acetate of Baryta	"	115.5?	19.0?	
Acetate of Lime	"	115.5?	19.0?	
Acetate of Lead	"	130.5	34.0	
Tartaric Acid.....	"	127.5	31.0	} Very faint brownish tinge in liquid.
Tartrate of Soda	"	144.5	48.0	
Tartrate of Potash.....	"	144.5	48.0	
Rochelle Salt (NaO, KO, } C ₈ H ₄ O ₁₀)	"	144.5	48.0	
Tartar Emetic (KO, SbO ₃ } C ₈ H ₄ O ₁₀)	"	131.5	35.0	
Citric Acid.....	"	133.5	37.0	
Oxalic Acid	"	114.5	18.0	Slightly opalescent.
Oxalate of Potash	"	117.5	21.0	
Oxalate of Ammonia.....	"	124.5	27.0	
Sugar-candy	60 grains in 200 grains of water.	156.5	60.0	
Milk-sugar		151.5	55.0	
Gum-arabic		113.5?	16.0	
Silicate of Soda.....	Sat. soln. 0.75 in.	108.5	12.0	Pale yellow.
Faraday's Optical Glass.....	0.54	101.5	5.0	
Flint-glass	0.68	105.5	9.0	
Window Sheet-glass	0.07	112.5	16.0	
Hard Bohemian Glass	0.18	114.5	18.0	
Plate-glass	0.22	111.5	15.0	
Crown-glass	0.74	106.5	10.0	
Thin Glass for Microscope ...	0.009	116.5	20.0	Greenish.

The photographic impression of each spectrum in every case quoted in this Table commences at 96.5, and the number inserted in the Table in the second column of figures indicates the point at which the most refrangible rays transmitted by the compound under examination ceased. The numbers in the third column of figures represent the length of the spectrum, the unit of the scale being one millimetre.

9. In the majority of cases of saline compounds in the foregoing Table the results given are those obtained by forming a saturated solution of the compound in distilled water, and decanting the liquid after it had become clear by standing. It is not advisable to filter in these cases, as the introduction of minute quantities of certain compounds, especially of some of organic origin, greatly impairs the transparency of the liquid to the rays which produce chemical action.

The solution, duly prepared, was then placed in a small trough made by cutting a notch in a piece of plate-glass $\frac{3}{4}$ inch in thickness, the sides of the trough being completed by thin plates of polished quartz, which were pressed by means of bands of

caoutchouc against the ground surfaces of the plate-glass. No cement was employed, and the trough was taken to pieces and cleansed between each experiment—a stratum of liquid 0.75 inch thick being used in each case.

10. In the preparation of the various compounds for examination, much care was taken to employ the materials in a state of purity. In one or two instances, however, it has happened that an acid which usually forms highly diactinic salts has exhibited an anomalous and excessive absorptive power, although in combination with a base which in other instances furnishes strongly diactinic salts. Here some impurity, in quantity so small as to escape the tests in ordinary use, but sensitive to the action of light, has probably been present, and has impaired the diactinic capacity of the substance. Cases in which such impurity is suspected are indicated in the Table by the mark (?) subjoined to them. I intended to have prepared fresh portions of each of these substances with a view to their re-examination; but by the time I had arrived at this stage of my experiments I learned from my friend Professor STOKES that he had been engaged in a similar inquiry, but had been turning to account for this purpose the property of fluorescence; and as I found that my results, where both of us had employed the same substance, were in close accordance with those which he had obtained, I determined to postpone the further examination of these bodies till after the details of Professor STOKES's experiments have appeared. I have also refrained from extending my observations to the compounds of organic chemistry, many of which I had otherwise proposed to submit to a similar investigation.

It may here be observed that the solution of a salt in water always to a certain extent impairs the diactinic quality of the liquid, however limpid the solution may be, producing an effect which may be compared to opalescence or turbidity in a liquid employed in the transmission of luminous rays.

11. I have not been able to trace any special connexion between the chemical complexity of a substance and its diactinic power. Carbon in its pure form as diamond we regard as an element. In thin slices it transmits portions of the chemical rays of nearly all degrees of refrangibility, though none of the specimens which I examined exhibited any approach to the actinic limpidity of quartz. Phosphorus, on the other hand, though transparent to light in its melted condition, and equally regarded as elementary, appears to be nearly *adiactinic*, or impermeable to the chemical rays. In many cases the peculiar diactinic or *adiactinic* action of an element is traceable in its simpler chemical compounds. Thus the simpler combinations of sulphur, such as sulphuretted hydrogen, sulphurous acid gas, bisulphide of carbon, and chloride of sulphur, are all powerful actinic absorbents, while in the more complicated form of sulphuric acid and the sulphates of certain bases the compounds are highly diactinic. On the other hand, the silicates are much less diactinic than silica in the form of quartz, or the bases which enter into the formation of the silicates: probably this may arise, as Professor STOKES suggests, from the difficulty of obtaining silicates, either natural or artificial, after fusion, perfectly free from iron.

12. No solid or liquid substance that I have as yet tried surpasses rock-crystal in

permeability to the rays which excite chemical action. Ice (and water), as well as white fluor-spar, rival it; and pure rock-salt approaches it very closely *. White topaz is a little inferior to the preceding bodies in diactinic capacity.

Amongst the various compounds submitted to examination, the *fluorides* rank first in diactinic power; then follow the *chlorides* of the metals of the alkaline earths. The *bromides* of the same metals appear to be less diactinic than the fluorides and chlorides, and this decline in power is still more marked in the case of the *iodides*. The short spectrum of these last-mentioned salts is interrupted by a well-marked absorption-band at a point beyond H, represented on the arbitrary scale at 103·5, beyond which the spectrum is again faintly renewed to 113·5, and then it terminates abruptly. The *cyanides* appear to be considerably diactinic; but further experiments upon these salts, as well as upon the *sulphocyanides*, are desirable. *Sulphuric*, *carbonic* and *boracic* acids furnish salts with the alkalies and alkaline earths, which are also largely diactinic: the *phosphates* seem to be less so, and the *arsenates* still less. It is remarkable that though the sulphates are so diactinic, the *sulphites* are considerably less so, and the *hyposulphites* are more opaque than the sulphites. The *hydrates* of the alkaline earths are also transparent. It is very difficult to obtain the alkaline hydrates perfectly pure; but a solution of hydrate of soda and one of potash, furnished by precipitation of their respective sulphates by means of baryta, and concentrated in a silver dish, gave a very fair result in each case.

The diactinic capacity of the *tartrates* and *citrates* is less than that of the carbonates. That of the *acetates* appears to be about the same as that of the tartrates; but the results obtained with the acetates are somewhat uncertain, as it is difficult to procure these salts absolutely free from the empyreumatic products which accompany the acid as it is usually prepared. The *oxalates* have a low diactinic power.

But the group most remarkable for its absorptive action is formed by the *nitrates*. Nitric acid, whether dissolved in water or in combination with a metallic oxide, has a specific action in arresting the chemical rays: the more refrangible portion it transmits freely, and then intercepts the spectrum abruptly at the same point whatever base be united with the acid, provided the base be capable of forming diactinic salts. The *chlorates*, on the contrary, are strongly diactinic.

13. From the observations above detailed, it appears that the following acids may be considered as possessing high diactinic capacity,—viz. the sulphuric, hydrochloric, hydrofluoric, chloric, carbonic, and boracic acids. Inferior to these are hydrobromic, phosphoric, arsenic, tartaric, citric, acetic and oxalic, hydriodic, sulphurous and hyposulphurous acids, whilst nitric acid is still less diactinic. Chromic acid arrests all the chemical rays; and the presence of a tinge of yellow or green colour in any compound is immediately apparent in a great reduction in the amount of its diactinic power.

14. Among the bases, potash, soda, ammonia, baryta, lime, strontia, magnesia, and alumina are eminently diactinic. Oxides of zinc, mercury, and lead approach them in

* A specimen of sea-water which had been standing for some months in my laboratory, furnished a result identical with that obtained by using a strong solution of pure chloride of sodium.

power; but coloured bases, like oxide of iron, nickel, cobalt, or copper, are very inferior; and when the salts which they form are green or yellow, they are nearly opaque.

It is remarkable that, notwithstanding the high diactinic quality of silica, none of the different varieties of glass transmit rays extending beyond one-fifth or one-sixth of the range afforded by quartz. This absorptive action is produced by a lamina of glass less than the one-hundredth of an inch in thickness, which cuts off the more refrangible rays nearly as completely as a piece of glass of twenty times the thickness. All glass apparatus must therefore be abandoned in these experiments, and apparatus of quartz substituted for them.

15. I had no encouragement in my attempts to construct prisms of other materials than rock-crystal. Rock-salt offers no advantage, and it is too soft and deliquescent to yield prisms or lenses comparable with those of quartz. I did indeed make a considerable number of experiments with a hollow prism furnished with thin quartz sides, and filled with water. But the refractive power of water is less than that of rock-crystal, and its dispersive power is not higher. The addition of pure chloride of sodium till the water is saturated does not materially increase the refractive or dispersive power, whilst it appeared (in a very slight degree it is true) to diminish the amount of the more refrangible rays, so that, on the whole, I found it more convenient to work with a quartz prism, the double refraction of which in the position in which I used it, was so slight that it was not a source of any inaccuracy of importance.

b. *Absorption by transmission through Liquids.*

16. In the experiments with liquids, the same plate-glass trough with quartz sides was used as when solutions were employed, and the apparatus was arranged in exactly the same manner. Great care was taken in the purification of each specimen. The *wood-spirit* was prepared from oxalate of methyl by WÖHLER's method, and it, as well as the *alcohol* and *fousel oil* employed, was in the anhydrous state. The *glycerin* was perfectly colourless, and was prepared by Mr. GEO. WILSON by distillation with superheated steam; it retained about 4 per cent. of water. The specimen of *glycol* was the only one about which I had any doubt; it had a barely perceptible yellowish tinge, and a very slight empyreumatic odour. The *carbolic acid*, given me by Mr. CRACE-CALVERT, was a beautiful colourless specimen, which, by a slight reduction of temperature, solidified to a mass of delicate white needles. The *benzol* was a specimen prepared from benzoate of lime, purified by congelation at 32°, and carefully rectified. The *paraffin oil* was a perfectly limpid colourless specimen obtained from Rangoon petroleum; it had a specific gravity of 0.831, and boiled steadily at 360° F. The *bisulphide of carbon*, and indeed most of the other liquids, were rectified immediately before proceeding to experiment upon them.

The following Table contains a list of the liquids operated on, and the lengths of the different spectra, in terms of the scale already explained (par. 7). The compounds included in the following Table, with the exception of nitric and hydrochloric acids, are not simply solutions, but liquids to which a definite chemical formula may be assigned.

TABLE II.—Diactinic Power of Liquids.

Thickness of stratum 0·75 inch.

Name of substance.	Termination of spectrum.	Relative lengths of spectra.	Remarks.
Water.....	170·5	74·0	With a faint impression of the rays about 156.
Wood-spirit	116·5	20·0	
Alcohol	159·5	63·0	
Fousel Oil	116·5	20·0	Slight empyreumatic odour.
Glycol	107·5?	11·0?	
Glycerin.....	114·5	18·0	
Ether	112·5	16·0	
Chloroform	122·5	26·0	
Dutch Liquid	132·5	36·0	
Oxalic Ether	115·5	19·0	
Carbolic Acid	104·5	8·0	
Benzol ($C_{12}H_6$).....	117·5	21·0	
Paraffin Oil, $n(C_2H_2)$	111·5	15·0	Specific gravity 0·831. Boiling-point 360°.
Oil of Turpentine	104·5	8·0	Slight yellowish tinge.
Phosphorus (melted).....	0	
Bisulphide of Carbon	102·5	6	
Oxychloride of Phosphorus	0	Retaining a little phosphorus in solution.
Terchloride of Phosphorus	0	
Terchloride of Arsenic	101·5	5·0	
Acetic Acid	112·5	16·0	Glacial.
Sulphuric Acid	160·5	64·0	Specific gravity 1·3.
Nitric Acid	106·5	10·0	
Hydrochloric Acid.....	152·5	56·0	Specific gravity 1·1.

The starting-point for each spectrum was 96·5 upon the scale already adopted.

Of all these liquids, water and alcohol are the only two, except sulphuric and hydrochloric acids, which are strongly diactinic; water is eminently so, alcohol in a much less degree. No relation in this respect is traceable between common alcohol and the other alcohols examined, viz., wood-spirit, fousel oil, glycol, glycerin, and the phenic alcohol carbolic acid. Bisulphide of carbon, the refractive medium employed in my earlier experiments, is singularly deficient in diactinic power, and is therefore eminently unfit for such researches.

c. Absorption of Chemical Rays by transmission through Gases and Vapours.

17. In the experiments upon the absorbent action of aëriform media, the gas or vapour under trial was introduced into a brass tube 2 feet long, blackened on the inside, and closed at the end by plates of quartz, which were fitted on so as to form air-tight joints. The tube could be attached by a stopcock to the plate of the air-pump, and after exhausting the air any gas could be easily introduced. In cases in which the gas was liable to act upon the metal, a glass tube was substituted for the metallic one, and the gas was introduced by displacement. The tube when prepared was interposed at *t*, fig. 1 (par. 6), between the slit *s* and the prism *b*, and the rays emanating from the electric spark were, after traversing the column of gas contained in the tube, received first upon the prism and lens, and then upon the excited collodion surface, in the usual manner.

When the vapour of a volatile liquid was to be examined, a few drops of it were generally allowed to fall into the tube filled with air, through which the vapour was allowed to diffuse itself at the ordinary temperature. The action of such vapours was therefore compared at a great disadvantage with that of the various gases, particularly where the volatility of the liquid was rather low. The results, however, even under these disadvantageous circumstances, were well marked, as may be seen by examining the subjoined Table of gases and vapours submitted to experiment, in which the comparative lengths of the different spectra are shown in the second column of figures.

TABLE III.—Absorbent action of Gases and Vapours on the Chemical Rays.

Length of column of gas 2 feet.

Name of gas.	Termination of spectrum.	Relative lengths of spectra.	Remarks.
Atmospheric Air	170·5	74·0	
Hydrogen	170·5	74·0	
Carbonic Acid	170·5	74·0	
Carbonic Oxide.....	170·5	74·0	
Olefiant Gas	162·5	66·0	
Marsh-gas	159·5	63·0	
Coal-gas.....	133·5	37·0	Cut off abruptly.
Protoxide of Nitrogen	159·5	63·0	
Cyanogen	159·5	63·0	
Ammonia	170·5	74·0	
Sulphurous Acid	110·5	14·0	Cut off abruptly.
Sulphuretted Hydrogen	110·5	14·0	Cut off abruptly.
Bisulphide of Carbon	101·5	6·0	{ A few of the strongest lines between 140 and 152 are seen.
Dichloride of Sulphur	108	10	
Benzol	131·5	35·0	Faint beyond 111·5.
Oil of Turpentine	152·0	55·5	
Chloroform	152·0	55·5	
Ether	163·5	67·0	
Terchloride of Phosphorus	131·5	35	Very feeble spectrum.
Oxychloride of Phosphorus	141·5	45	Fades out very gradually.
Hydrochloric Acid	151·5	55·0	
Hydrobromic Acid	119·5	23	Cut off abruptly.
Hydriodic Acid.....	111·5	15	Cut off abruptly.
Peroxide of Nitrogen	0	0	
Peroxide of Chlorine	0	0	

18. The absorbent action disclosed by the foregoing experiments on the colourless gases and vapours is very interesting, as it proves that differences exist in the diactinic power of these substances quite as marked as in the case of liquids and solids. Some of the *elementary* gases, oxygen, hydrogen, and nitrogen, appear to possess a diactinic capacity greater than any solid or liquid body. Many *compound* gases, such as ammonia, carbonic acid, and carbonic oxide, appear to rival them. Olefiant gas, cyanogen, and hydrochloric acid exhibit a decided but not great absorptive power, with which that of the vapours of ether, chloroform, and oil of turpentine at the atmospheric tension, and when diffused through air, may be compared. Doubtless if these vapours were tried at a tension of 30 inches, they would exhibit greater absorptive power. The absorptive

action of hydrobromic acid much exceeds that of the hydrochloric, and that of hydriodic acid is greater than of either.

The abrupt termination of the spectrum in coal-gas is remarkable. The absorption appears to be due not to the permanent gases, but to the vapours of benzol and other heavy hydrocarbons which it contains. The four compounds of sulphur, viz., sulphurous acid*, sulphuretted hydrogen, bisulphide of carbon, and dichloride of sulphur, are especially active in absorbing the chemical rays; and the vapours of the terchloride and oxychloride of phosphorus exhibit a similar though less intense absorptive power.

19. Coloured gases, whether elementary or compound, such as chlorine, bromine, and nitrous gas, have long been known to exert an absorptive action upon the luminous rays†; and their effect is not less marked upon the invisible prolongation of the electric spectrum.

The effects of the three halogens, chlorine, bromine, and iodine, in the form of vapour, are particularly remarkable. As a general rule, when a body exerts an absorptive influence the absorption is greatest in the most refrangible portions; but the reverse of this occurs in the case of chlorine and of bromine. A column of *chlorine* two feet in depth, cuts off the whole of the *less* refrangible portion as far as 143·5; beyond that a distinct impression is obtained as far as about 159. With *bromine* diffused in the form of diluted vapour, the impression commences at 106, and is continued distinct, though rather feeble, to the extreme end of the spectrum. The apparatus required a slight modification to adapt it for the experiment with *iodine*. I had a glass tube 6 inches long, the open ends of which were ground flat so as to admit of being closed by thin plates of quartz; this was enclosed in a brass tube; a few grains of iodine were introduced, and the quartz plates fixed by metallic caps perforated to admit the passage of the rays; this tube could then be supported as usual between the spark and the prism, and could be raised to and kept at a temperature beyond that necessary for the volatilization of the iodine. The electric light, after traversing such a column of vapour of an intensely deep violet colour, gave a strong spectrum, extending from 96·5 as far as 112, then it gradually faded till it disappeared at about 118; the impression became again rather faintly but distinctly visible at 142, and gradually disappeared at about 156. It is interesting to notice a somewhat similar interrupted absorption of the rays, though at a different part of the spectrum, in the case of the metallic iodides.

Both peroxide of nitrogen and peroxide of chlorine, in a stratum of 2 feet in depth, wholly absorb the chemical rays; but when more dilute or in shorter columns, they each give characteristic absorption-bands.

20. There appears to be little or no connexion between the absorptive power of any particular gas for the chemical rays, and its power of absorbing radiant heat as determined by the experiments of Dr. TYNDALL‡. Aqueous vapour is highly diactinic, though not diathermic; olefiant gas exhibits a similar difference; and various other instances might be pointed out.

* An aqueous solution of sulphurous acid cuts off the spectrum at the same point as the gas itself does.

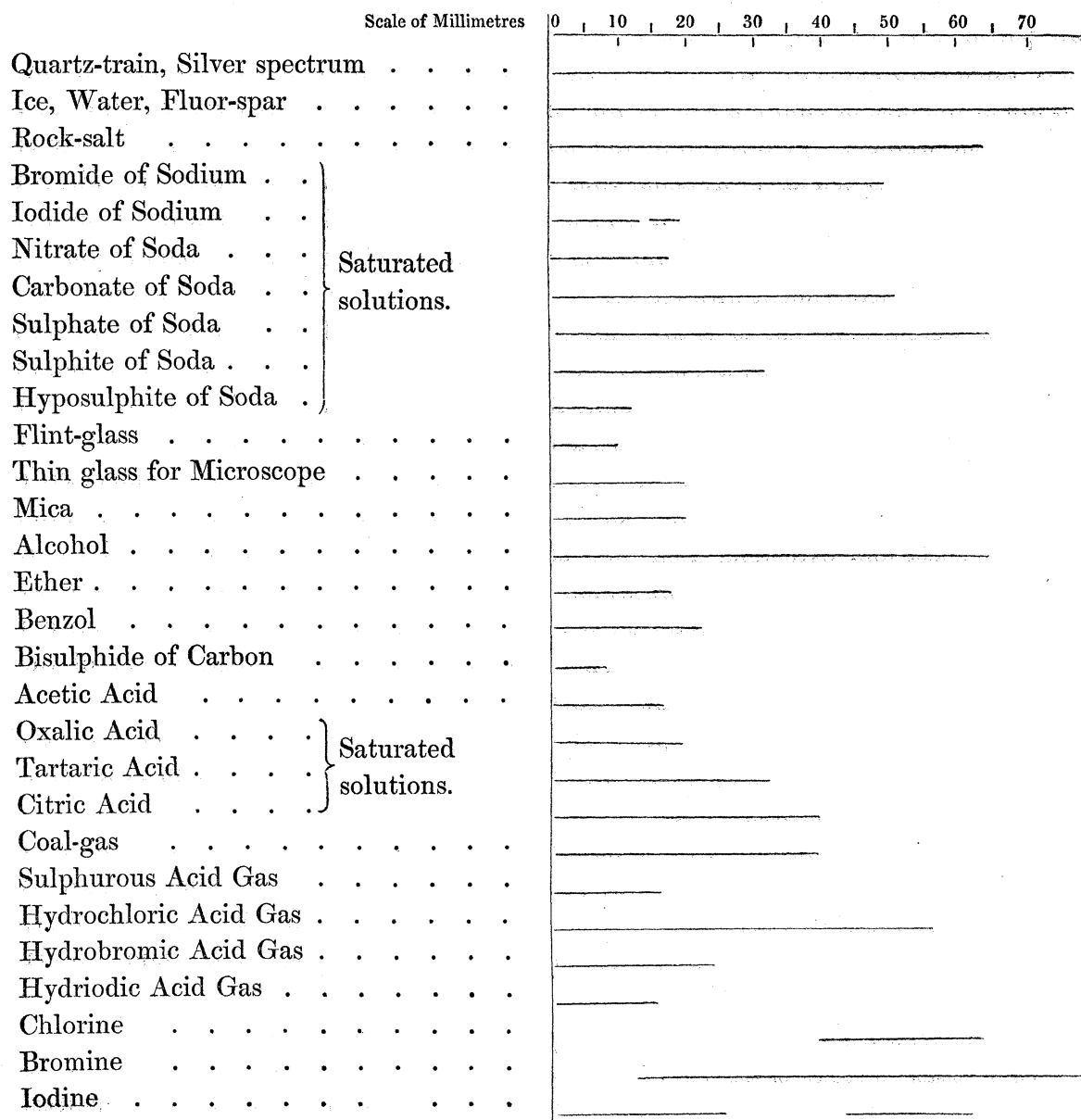
† For an historical sketch of the progress of discovery in relation to the production of bands in the spectrum, the reader is referred to a paper by the author in the 'Pharmaceutical Journal,' February 1862, p. 17 *et seq.*

‡ Phil. Trans. 1861.

21. The most interesting fact, however, disclosed by these various experiments is the persistence of either the diactinic or the absorbent property in the compound, whatever be its physical state—a circumstance which proves that the property under consideration is intimately connected with the atomic or chemical nature of the body, and not merely with its state of aggregation.

The following diagram represents approximatively the relative position of the portions of the spectrum transmitted in a few of the cases described in the foregoing section of this paper. No attempt is made to indicate partial absorption of the rays. In one or two instances, where complete absorption at a particular part of the spectrum occurs, this has been indicated by an interruption in the line.

Relative absorptive action of various Media upon the Electric Spectrum of Silver.



§ 2. THE ABSORPTION OF THE CHEMICAL RAYS BY REFLEXION FROM POLISHED SURFACES.

22. In my earlier experiments I had much difficulty in obtaining a spectrum all the parts of which were even approximatively in focus in the same plane, and, with the view of remedying this defect, I tried the effect of substituting specular reflexion for the refracting action of a lens. This led me to compare the reflecting-power of different polished surfaces for the chemical rays. With this object in view, a small polished plate of the material under experiment was supported at an angle of 45° , as shown in fig. 3 (par. 6), opposite the vertical slit of the apparatus, so that when the source of light *e*, was placed at right angles to the axis of the tube, the rays were reflected down the tube in the direction of that axis. The arrangement of the prism, lens, and camera was the same as that already described (6). As, however, much less light was reflected upon the prism from the polished surface than that which fell upon the prism when the direct rays of the spark were employed, the exposure of the sensitive plate in the camera was prolonged from 5 minutes to 10.

23. Among the metals and alloys thus submitted to trial were platinum, gold, silver, mercury, contained in a trough with quartz faces, lead, copper, tin, cadmium, zinc, aluminum, steel, brass, and speculum-metal. In addition to these, the reflecting-power of quartz, window-glass, and Iceland spar was also tried.

No judgment of the perfection of the reflecting-power could be formed from the colour of the metal. *Gold* possesses the power of reflecting all the rays, even the most refrangible, very equally, though somewhat feebly. Next to gold ranks burnished *lead*, some part of the spectrum of the electric spark reflected from lead being more intense than that from gold. The length of the spectrum obtained from the light of the electric spark between silver points, by reflexion from the surface of these two metals, extended from 96·5 to 170·5, or over the full distance of that obtained by the direct light of the spark, viz. 74 divisions of the scale which I have adopted. With all the other metals the spectrum of the same reflected spark terminated at 159·5, covering only 63 divisions of the scale.

The spectrum from a *silver* surface was remarkable. The impressed image was strong up to 112·5; then an abrupt cessation of the reflected rays occurred for a distance of 1·5 division; beyond this the reflexion gradually returned, and continued tolerably intense till it reached 159·5, covering 63 divisions of the scale.

The reflexion from *mercury* was weak in the middle, but strong towards each extremity. *Platinum*, *zinc*, and *aluminum* resembled mercury in their effects, but the spectrum was much less intense. The reflexion from *cadmium* was similar, but still weaker.

The spectrum of the rays reflected from *copper* was deficient in strength for the last half of the more refrangible portion; and that of *brass* was similar to it, but weaker. The reflexion from a surface of *steel* was more intense than that from any surface which I employed, but it ended abruptly at 159·5, or at the 63rd division of the scale. The spectrum reflected from *tin* was nearly as complete as that from steel.

A small concave mirror of *speculum-metal* gave an intense spectrum for the first half;

but the more refrangible portion was deficient in power, and no rays were reflected beyond 159·5 (63 divisions), the point at which the other metals also failed. I therefore abandoned the attempt to substitute a speculum for the lens, with which latter I succeeded subsequently in obtaining a field sufficiently flat for the purpose.

24. The reflexion from the surface of transparent objects was so scanty that, of course, no idea was entertained of using such bodies as mirrors; but it may be worthy of notice that a feeble spectrum was obtained from surfaces of *quartz*, *window-glass*, and *Iceland spar* extending to 159·5, or over a length of 63 divisions of the scale—that is to say, fully as far as the majority of the metals. The quantity of the reflected rays was small, but its quality was similar to that of the rays reflected from metallic surfaces.

§ 3. PHOTOGRAPHIC EFFECTS OF THE ELECTRIC SPECTRA OF DIFFERENT METALS TAKEN IN AIR.

a. *Pure Metals.*

25. I have spent a considerable time in endeavouring to procure exact photographs of these spectra, inasmuch as the spectrum of a metal is a constant not less important than its density or its fusing-point; and it frequently furnishes the means of identifying an element under circumstances in which no other method at present known is practicable.

KIRCHHOFF, in his elaborate and masterly researches on the constitution of the solar spectrum, has, as is well known, published in minute detail a map including the lines of a large number of the metals. He has, through a limited portion of the visible spectrum, laid down the position of the bright lines of certain metals coincident with particular dark lines of FRAUNHOFER, with a precision best appreciated by those who have followed him with most minuteness.

Much yet, however, remains to be done even for the rays which fall within the range of the visible spectrum; and for those which are beyond the limits of ordinary vision, the whole yet remains to be examined.

The lines of each spectrum are so numerous and so close together, that it would be impossible without a sacrifice of time, that would scarcely be justifiable, to obtain accurate impressions of them by eye-drawing. Indeed, except by the process of photography, these lines can only be rendered visible by the aid of a fluorescent screen, under which circumstances the minute details are almost necessarily lost even by the most careful observer.

The photographs of these spectra were obtained by an arrangement of the quartz prism and lens, identical with that already described (6), wires, plates, or irregular fragments of the metal, according to circumstances, being supported in brass forceps connected with the secondary wires of the induction-coil. The interval traversed by the spark was in each case about a quarter of an inch, and the slit was placed at a distance of half an inch from the line traversed by the spark.

The specimens of gold, silver, mercury, copper, bismuth, antimony, zinc, tellurium, thallium, and lithium employed are believed to have been pure. The tungsten,

molybdenum, chromium, and manganese were reduced from pure oxides in crucibles lined with charcoal. The other metals were as they are furnished in commerce as pure.

26. Each metal gives its own distinctive spectrum; but it is remarkable that these differences are not obvious in the less refrangible end. The true metallic spectrum, when the sparks pass in air, is in fact combined with that due to atmospheric air, as has already been pointed out for the visible rays by ÅNGSTRÖM and by ALTER. The photographic lines of the air-spectrum are most marked in the less refrangible portion, whilst the characteristic lines of the metals are particularly evident in the more refrangible parts. Hence the photographs which I formerly obtained by the use of a prism of bisulphide of carbon, which transmits rays of low refrangibility only, represent, as I then correctly pointed out, lines which are chiefly atmospheric; and consequently they exhibit appearances which are almost identical whatever be the metal employed.

In describing the spectra of the different metals, I shall employ the same arbitrary scale that I have hitherto used in this paper.

27. It will be observed that generally the lines as they advance towards the less refrangible extremity become less intense in their central portion, until towards the extreme limit of the spectrum, the two marginal ends of the lines alone are visible, though these terminations are often rather intense. Indeed, throughout the whole length of the impressed photograph, the marginal extremities of the metallic lines leave a stronger image than their central portions, as though the incandescence of the volatilized portions of the electrodes, owing to their high radiating power, did not continue sufficiently intense during their transfer across the interval between the two electrodes, to enable them to produce a continuous line. Evidently the cause of this diminution of action operates more powerfully upon the more refrangible rays; and a higher temperature, as the experiments of other observers have abundantly proved, is necessary to the production of radiations of these high degrees of refrangibility.

Exceptions to this remark occur in the lines due to the atmosphere; this is well seen in the strong line at 110·5, which is in marked contrast to some of the metallic lines in its vicinity, particularly in the spectrum of silver (Plate XXXIX. fig. 9), where this nitrogen-line is included between two pairs of very intense lines due to the metal itself, and which are each interrupted in the middle.

In order to abbreviate the description of the various spectra, I shall generally speak of these interrupted lines as "*dots*"; they, indeed, constitute the characteristic features of the different metallic spectra. These dots, if the image be exactly in focus, may usually be seen to consist of groups of very short lines closely aggregated. This is well shown in some parts of Plate XL. fig. 39, which represents the spectrum of silver; and it is less distinctly shown in the spectra of palladium (fig. 38), of copper (fig. 40), of antimony (fig. 41), and of cadmium (fig. 42). These spectra were taken with the screen, lens, and prism at a distance from the slit different from those with which the other impressions were procured; some parts are consequently out of focus, but the details of other portions are shown more fully.

As might be anticipated, the spectra of the more volatile metals are the most intense—those of bismuth and antimony, of cadmium, zinc, and magnesium being especially remarkable in this respect.

A certain similarity is also observable in the spectra of allied metals, as in the case of the three metals last mentioned, also in those of iron, cobalt, and nickel, of bismuth and antimony, as well as of chromium and manganese.

It should further be observed that, in estimating the apparent length of the different spectra, considerable difficulty is frequently experienced owing to the extremely faint impressions which the most refrangible rays commonly occasion; in some experiments this portion of the spectrum with the same metal appears to be longer than in others made under apparently similar conditions.

28. *Platinum*.—The characters of the spectrum of platinum are feebly marked. The *atmospheric lines* are well developed. It is important to remark that the *continuous spectrum* which forms the background to all the metallic spectra in their less refrangible portion, appears to be due to the oxygen and nitrogen of the atmosphere. Between 96.5 and 103.6 this spectrum is intense, and is crossed by a strong pair of compound lines followed by three strong groups of lines, ending in two other groups, each successively of less intensity than the preceding ones. At 107.5 is a well-defined line, and a strong band at 110.5. Three others, nearly equidistant, follow at 114, 117.3, and 121.7: at 137 and 138.2 are two faint lines, and beyond these, at 142.5, is a very faint pair of lines. All these are atmospheric lines. The true metallic spectrum of platinum (Plate XXXIX. fig. 5) gradually fades out with a series of groups of dots, and terminates at about 162.

29. *Iridium*.—The spectrum of this metal, for a fine sample of which I am indebted to my friend Professor WHEATSTONE, scarcely differs sensibly from that of platinum. The lines apparently most prominent are atmospheric. (See Plate XL. fig. 44.)

30. *Palladium*.—This spectrum is much more uniform in intensity than that of platinum. Besides the usual atmospheric lines, groups of dots commence at 103.5, and continue at irregular intervals. Four of the strongest of these groups occur at 138.5, 143, 148, and 152.5, measuring at about the centre of each group. The spectrum terminates rather abruptly at about 162.5. (Plate XXXIX. fig. 6, & Plate XL. fig. 38.)

31. *Gold*.—The spectrum of this metal has about the same degree of intensity as that of palladium, and it is almost exactly equal to it in length. Amongst its numerous lines, the most characteristic are two pairs of dots very close together at 124, and three groups of dots, commencing at 130.0, 143.5, and 153.5 respectively; the last is faint. (Plate XXXIX. fig. 7.)

32. *Silver*.—The spectrum of this metal is very characteristic. It is intense for the first third of its length, then becomes much fainter, after which several remarkable and very strong groups of lines are observed, beyond which the impression disappears at 170.5. The most conspicuous lines are a pair of double lines interrupted in the middle groups of dots rather strong, at 126.8, 129.0, and 131.0; between 140.5 and 144.5 are three very strong groups of dots. About 148 is another broad strong group; beyond

which, and terminating at about 159·5, is another strong triple group of dots,—the spectrum terminating at 170·5, with six nearly equidistant but rather faint groups of dots *. (Plate XXXIX. fig. 9, & Plate XL. fig. 39.)

The strongly marked character of the spectrum of silver, and particularly the renewal of its intensity towards the more refrangible end, rendered it very appropriate for the purpose of testing the diactinic quality of different media; and accordingly I have used it more extensively than any other metal in the experiments already detailed upon this subject.

[33. *Thallium*.—The spectrum of thallium (for a specimen of which in a pure state I am indebted to the kindness of Mr. CROOKES, its discoverer) is particularly interesting, as in its visible portion it is remarkably simple, the single intense green line being the only one visible, even when heated in the intense flame of the oxyhydrogen jet. When, however, the sparks of the secondary coil are transmitted, not only do new lines make their appearance in the visible spectrum, but also in the extra-violet portion, and the complex impression shown at Plate XL. fig. 45 is developed. This character of its spectrum † separates thallium from the metals of the alkalies. In the less refrangible portion are two strong groups of lines at about 103 and 106; three other groups occur at 116, 121, and 126 respectively, the two first less intense, the third of about the same strength as the first pair of groups. Several feebler pairs of dots follow; and the spectrum terminates with four nearly equidistant groups, commencing respectively at 136, 141, 145, and 151: the first of these groups is very strongly marked, the others are fainter but of nearly equal intensity.—Feb. 1863.]

34. *Mercury*.—Experiments were made with this metal by soldering a platinum wire into a small glass tube which was filled with mercury and connected by means of the platinum wire with one end of the secondary wire of the coil; the other electrode consisted of a platinum wire. The spectrum obtained exhibited few lines, excepting those due to the mercurial electrode. The never-failing nitrogen line, 110·5, was evident; but there were numerous strong lines due to the mercury, the most distinct of which are those at 104, 114·5, 117·5, 119·0, 122·5, 131·0, 138, 156, 159, each of the two last forming a strong broad group of dots, the last group terminating the spectrum at 161·0. (Plate XXXIX. fig. 10.)

35. *Lead*.—This spectrum is very strong for rather more than one-third of its length; it then diminishes in strength, until the action ceases almost entirely at 146·5; at about 161 it is renewed abruptly by a strong group of dots, which terminate the spectrum at 162·5. The lines in this spectrum are numerous and complicated. It exhibits an at 109·5 and 111·5, equidistant from the nitrogen line 110·5; beyond this are three intense triple group of dots between 122 and 125, and two other strong groups at about 130 and 132. (Plate XXXIX. fig. 11.)

* In one or two instances, when using bromiodized collodion, I saw a *very* faint series of groups prolonged as far as 190·0.

† Proceedings of the Royal Society, January 1863, vol. xii. p. 407.

36. *Copper*.—The spectrum of this metal is considerably prolonged. The intensity of the light from copper points is liable to vary considerably during the course of an experiment, being apparently much influenced by the slight changes of form experienced by the electrodes in consequence of the action of the discharge upon them. In these experiments I always used thin sheets of electrotpe copper. The most marked lines in the spectrum of copper are the following: viz., two close together at 111·7 and 112·3; these are followed by three strong nearly equidistant groups of dots at 128, 136·5, and 146·7; a very strong group appears at 156·7; and the spectrum ends at about 181·5, with a series of much fainter groups. (Plate XXXIX. fig. 12, & Plate XL. fig. 40.)

37. *Tin*.—The spectrum of this metal shows at 107·0 and 112·5 a pair of strong double dots, at 114 another dotted line, at 118·0 a strong double line; characteristic groups of dots commence at about 122·0 and 129·5; between 130 and 134 it exhibits three strong groups, followed by several well-marked pairs of dots to about 154, after which it terminates rather abruptly by four nearly equidistant faint groups at about 163. (Fig. 13.)

38. *Bismuth*.—This metal furnishes a strong and well-marked spectrum. Five pairs of dots show themselves between the line H and the nitrogen line 111·5; a strong pair is then seen at 115·3, followed by five strong groups, each of which is triple; the first of these is the most intense; these are followed by an intense group, which terminates at 122·0; beyond these the spectrum is continued by a numerous and intense series of groups of dots, particularly at 143 and 157, and terminates at about 158. (Fig. 14.)

39. *Antimony*.—The spectrum of antimony is also very characteristic. A triple series of groups of dotted lines commences at about 104·5; the nitrogen line at 110·5 is very intense; at 113 is a strong double line followed by seven or eight intense groups of dots which terminate at about 138·5; at 150·5 is a group of moderate intensity; and the last traces of lines disappear at about 164·0. (Figs. 15 & 41.)

40. *Arsenic*.—The characteristic dotted lines of this spectrum commence at 115·0; a series of groups occur very close together, ending at about 129·0; then follow six fainter irregular groups; and the spectrum terminates abruptly with three very strong groups—the first two of which nearly run into each other, succeeded by an interval, the last group ending at 155. (Fig. 16.)

41. *Tellurium*.—This spectrum is highly characteristic. It exhibits a close series of dots, commencing at about 106, and terminating by a very strong group at 147·5. There is then a complete blank, till at 156 another group is seen, then an interval, and the spectrum terminates abruptly with a well-defined group at 168·5. (Fig. 17.)

42. *Tungsten*.—This spectrum is not very intense. It shows a double dotted line at 114, and a stronger one at 125; it is prolonged by a distinct series of dots to about 145, and fades out at about 168. (Fig. 19.)

43. *Molybdenum*.—The spectrum of this metal resembles that of tungsten, but is more intense. It is prolonged by a very faint termination to about 157. (Fig. 20.)

44. *Chromium* shows a group of dots at 106·0, then a strong line at 114·5, then

three intense groups of dots between 122 and 131, beyond which it gradually fades till it is lost at 160·0. (Fig. 21.)

45. *Manganese*.—This spectrum is well-marked. A double group of dots appears at 107, then five strong groups of dots and lines between 119·4 and 135·5; the first is the most intense, and the last group is broad and complicated: beyond this the impression becomes gradually fainter, and disappears at about 152·0. (Fig. 22.)

46. *Iron*.—The spectrum of iron is intense, particularly in the more refrangible portion. Between 113 and 124 are three diffused groups of dots of moderate intensity; at 126 is a very intense group; then a series of numerous intense groups of dots, which terminate at 154; at 155·5 a series of fainter groups recommences, and fades away at about 162. (Fig. 23.)

47. *Cobalt*.—The spectrum of cobalt is very like that of iron in its general appearance; but it shows two or three rather strong groups of lines between 106 and 109; an increase of intensity commences at about 128, and is continued in a series of groups of very strong dots, the most intense of which are situated between 134 and 147: the spectrum terminates rather suddenly at about 163. (Fig. 24.)

48. *Nickel*.—This spectrum is not so intense as either that of iron or of cobalt, but it is like them in its intensity being greater near the more refrangible extremity (fig. 25). It is a very long one, extending to about 190, and exhibits an arrangement of groups of dots at its more refrangible end, resembling that of silver, but prolonged much further.

49. *Cadmium*.—This is a striking spectrum. The action is accumulated into intense bands with perfectly dark intervals. Two broad strong groups of lines occur at 105 and 107, then two other compound bands or groups of dots, one on each side of the nitrogen line 110·5; beyond this are two fainter lines, then at 118 and 121 two broad groups of dots, frequently prolonged into lines; at 126·3 a very strong group of dots, and another at 133·5; beyond this an almost entire cessation of action till it is resumed by three groups of dots, the first and last of which are the strongest in the entire spectrum. These groups commence at 149·5 and terminate at 155·5; beyond these are two other detached groups at 162·5 and 167, where the spectrum terminates abruptly. (Figs. 26 & 42.)

50. *Zinc*.—This spectrum is equally characteristic with that of cadmium. Between 109·5 and 112·5 is an intense double group of eight or nine distinct lines, then several well-marked lines in the interval between these and another double group, which commences at 125. An interval of diminished action follows; and then between 135 and 140 are two intense groups, the strongest in the spectrum. These are followed by a few feeble groups of dots, after which is a complete interval; and the spectrum terminates with four groups of equidistant lines, the first commencing at 167·5, the latest terminating at 183. (Fig. 27.)

51. *Magnesium*.—This is another remarkable spectrum. An intense group of lines commences at 101; at 115 a bright group of dots is seen, and between 119 and 126·5 are three remarkably intense groups of lines: the first of these comprises at least four strong

lines, the second group three, and the third consists of eight or ten separate lines. This last is the most intense group that I have met with in the course of these experiments. Beyond this the spectrum is prolonged by a faint tail, which is strongest along the edges, and nearly vanishes midway between them; this tail disappears a little beyond 150. (Fig. 28.)

52. *Aluminum*.—This spectrum exhibits a characteristic group of dots at 106, another at 115·5, followed by others at irregular intervals as far as 155, beyond which no impression is visible. I have frequently repeated this experiment, as Professor STOKES informs me he that sees in the spectrum of aluminum lines which are beyond the limit of the zinc-spectrum, when the aluminum-spectrum is received upon a screen of uranium glass, or of a particular phosphate of uranium; but either the collodion plate is insensitive to rays of this extreme refrangibility, or, as I believe, the quartz prism which I employ begins to fail in transparency at about the end of the zinc-spectrum. (Fig. 29.)

53. *Sodium*.—The lines exhibited when sodium is employed appear to be mainly atmospheric; the usual nitrogen line at 110·5 is, however, developed into a broad band or group of nine or ten distinct lines, and the other atmospheric lines are very well marked; the spectrum is prolonged into a faint nearly continuous band at about 156, when it ceases to be visible. (Plate XL. fig. 47.)

54. *Potassium*.—The spectrum produced by potassium presents the same appearances as that of sodium, both being apparently only atmospheric (fig. 46).

[55. *Lithium*.—The spectrum of this metal differs from those of the other alkali-metals in presenting a single well-marked group of dots at about 123; it is prolonged into a tail, which resembles that of magnesium, and fades out at about 150. (Fig. 48.)—Feb. 1863.]

56. It is unnecessary to give any details of experiments made with electrodes one of which consisted of one metal and the other of a different metal. Under these circumstances the lines starting from the side corresponding to each metal are identical with those furnished by the particular metal. This mode of making the experiment is therefore frequently convenient when it is desirable to compare the spectrum of any given metal with another selected for comparison. When the difference in volatility between the two is extreme, as when platinum is opposed to mercury (fig. 10), it may happen that one spectrum only is seen, the lines starting from an edge of the photographic impression, and terminating at irregular distances before they reach the opposite edge.

b. *Spectra of Alloys.*

57. The principal object of these experiments was to determine the influence which small amounts of foreign metals exercise upon the photographic image. When equal weights of the two metals are employed (tin and lead, for example, or cadmium and lead), a compound spectrum exhibiting the lines due to both metals is produced; and it is not always the more volatile metal that predominates. An alloy containing 62 parts

of copper and 38 of zinc, gave a spectrum in which the lines due to copper predominated considerably. In an alloy of about 2 parts of zinc to 1 of cadmium the zinc-spectrum was the most strongly marked.

In another experiment an alloy of 990 parts of fine gold and 10 of fine silver was prepared; on taking the spectrum obtained by an exposure of 10 minutes, a distinct but feeble impression of the more refrangible lines due to silver was procured (see fig. 8). A contamination of gold with silver to an extent not exceeding 1 per cent. could therefore be recognized by this means; but prolonged exposure was necessary in order to develop the lines due to silver. An analogous result was obtained when the spectrum of plumbago was taken. In this case, in addition to the atmospheric lines, the spectrum of iron was distinctly impressed: the total amount of metallic iron in the plumbago was 3.94 per cent. Graphite deposited in the gas-retorts, which contained 0.23 per cent. of iron, gave very feeble indications of iron. On the other hand, no indication of iron was observable in the spectrum of brass which contained 0.23 per cent. of iron, nor was lead indicated in brass which contained 0.7 per cent. of this metal.

58. All the foregoing spectra were obtained either from the metals in their uncombined form, or else from their alloys. The electric spectra of a few other metals which admit of being submitted to experiment in their isolated form, still remain to be added. A considerable proportion of the metallic elements, however, are not included in the foregoing list. These it is almost impossible to examine, except in the form of some of their saline or other compounds. As, however, this portion of the inquiry is attended with some peculiar difficulties, I shall defer what I have to add upon this subdivision of the subject to a future occasion.

§ 4. PHOTOGRAPHIC EFFECTS OF ELECTRIC SPECTRA OF DIFFERENT METALS PRODUCED BY TRANSMITTING THE SPARKS THROUGH GASES OTHER THAN ATMOSPHERIC AIR.

59. In making experiments upon the influence of various gases upon the spectra of the electric spark, the arrangement of the apparatus was modified in the following manner:—The position of the slit, prism, lens, and camera was the same as in the preceding experiments (6); but the metallic electrodes were enclosed in a stout glass tube, shown at half its real size in Plate XL. fig. 49. *a* is the tube itself, *b* a hole drilled through the side of the tube, which upon this side is ground flat in order that it may be closed airtight by the thin plate of polished quartz *c*. This plate is kept in its place by means of an elastic band. *d, d* are brass forceps screwed into the brass plugs *e, e*, for holding the electrodes. The ends of the tube are closed by the brass plugs *e, e*, which are ground to fit the ends of the tube, and are pierced by small brass tubes for the conveyance of the gas. An elastic band, passing from one end of the glass tube to the other, keeps the brass plugs in their place. The tube is then connected with a gas-holder

filled with the gas under experiment (or, when practicable, the gas is disengaged during the experiment), and, after the apparatus has been connected with the induction-coil and adjusted in its proper position, a slow current of the gas at the atmospheric pressure is transmitted, the excess of gas as it passes out of the apparatus being conveyed into the chimney or out of the window by a suitable arrangement of tubes.

A simpler apparatus was admissible when the wires could, like those of platinum or of iron, be soldered into glass. Fig. 50 shows this modification. A piece of tubing *a*, about an inch and a half long and half an inch in internal diameter, is united at each extremity to a piece of quill tubing *e, e*; the wires *d, d* are then soldered through its sides. A portion of the wide tube is ground away as at *b*, leaving an opening to which the quartz plate *c* can be applied, and kept in its place by small rings of caoutchouc. The gas was transmitted through the tube as in the other form of apparatus.

60. In one or other of these modes the following gases were submitted to experiment:—hydrogen, carbonic acid, carbonic oxide, olefiant gas, marsh-gas, cyanogen, sulphurous acid, sulphuretted hydrogen, ammonia, protoxide of nitrogen, nitrogen, oxygen, chlorine, and hydrochloric acid.

The general results of these experiments on the invisible rays are in harmony with those already obtained for the visible ones by MM. ÅNGSTRÖM*, ALTER†, and PLÜCKER‡. The conclusions at which I have arrived may be thus summed up:—

1. Each gas tinges the spark of a characteristic colour; but no judgment can be formed from this colour of the kind of spectrum which the gas will furnish.

2. In most cases, in addition to the lines peculiar to the metal used as electrodes, new and special lines characteristic of the gas, if elementary, or of its constituents, if compound, are produced. When compound gases are employed, the special lines produced are not due to the compound as a whole, but to its constituents.

3. The lines due to the gaseous medium are continuous, not interrupted or broken into dots.

61. *Hydrogen*.—The spectrum of the spark taken in this gas is not characterized by any new lines. The most remarkable effect is the disappearance of the atmospheric lines, together with the great lowering of the photographic intensity, whether the metal employed be platinum, gold, silver, copper, iron, or zinc. It is interesting to observe that the characteristic lines of highly oxidizable metals, such as iron and zinc, are visible in hydrogen, though the impression on the plate throughout is very greatly reduced in intensity.

62. *Carbonic Acid and Carbonic Oxide*.—The lines contained in the spectra of these two gases are identical; new lines characteristic of carbon occur in addition to the lines due to the nature of the metallic electrodes. The same lines are visible when other compounds of carbon, such as olefiant gas, marsh-gas, and cyanogen, are employed. The

* POGGENDORFF's *Annalen*, 1855, Bd. xciv. S. 141.

† SILLIMAN's *Journal*, 1855, vol. xix. p. 213.

‡ POGGENDORFF's *Annalen*, 1859, Bd. cvii. S. 497.

most characteristic lines in the spectrum of carbon are the following:—At 123 a strong line, a weaker one at 127, two strong compound lines at 138 and 140, and an intense compound line at 153.

With carbonic acid the special spectrum of silver appears much intensified. Some of the lines which appeared as dots in air are continued across the spectrum in carbonic acid. In carbonic oxide the intensity of the spectrum is less than in air; and this contrast between the two gases may be observed whatever be the nature of the metallic electrodes.

Fig. 35 exhibits the spectrum obtained between platinum points in carbonic acid. Fig. 36 shows the spectrum from gold points in carbonic oxide. Unfortunately in the Plate the figure is given a little too much to the right of its true position for accurate comparison with the spectrum above it; but the principal lines will at once be recognized as coinciding, if allowance be made for this displacement.

63. *Olefiant Gas*.—Some difficulty is experienced in observing the spectrum of this gas, owing to the copious deposition of carbon which occurs immediately that a current of sparks is transmitted. The nature of the electrodes employed seems to exert considerable influence upon this decomposition. It is extremely intense when aluminum electrodes are used, but comparatively slight with gold. Observations made when gold electrodes were employed exhibited a spectrum which could not be distinguished from that of carbonic acid or of carbonic oxide.

64. *Marsh-gas*.—Sparks pass freely in this gas. The spectra obtained with gold and copper electrodes cannot be distinguished from those of the same metals in carbonic acid and carbonic oxide. A scanty separation of carbon occurs during the passage of the spark. This is particularly evident when copper electrodes are used, the bluish light of the metallic spark being frequently accompanied by reddish yellow scintillations: the deposition of finely divided carbon upon the quartz plate on the side of the gas-tube impairs the intensity of the photograph.

65. *Cyanogen*.—A difficulty was experienced in this case also in obtaining intense photographs, particularly when silver electrodes were employed; a rapid deposition of a brown matter, probably paracyanogen, took place upon the interior of the tube. When copper electrodes were used, the light of the spark was sometimes of an intense green, at others of a pale blue. The photograph showed the particular lines due to carbon as well as those of nitrogen, and the special lines due to the metallic electrode employed.

66. *Sulphurous Acid*.—This gas offers unusual resistance to the passage of the electric sparks, the electrodes requiring to be brought very close to each other before the disruptive discharge passed freely. This difference in the power of different gases to modify the striking-distance has already been examined by Dr. FARADAY*. A strong spectrum was obtained with gold wires: it terminated abruptly at 113·5, a single spot of renewed action appearing at 143·0. This result is due no doubt to the absorbent action of the gas, which has been already shown in a former section of this paper (18) to be one of the least diactinic of gaseous bodies. In this form of experiment the stratum

* Philosophical Transactions, 1838, p. 103.

of gas traversed by the rays before they entered the air amounted to about half an inch in thickness.

67. *Sulphuretted Hydrogen*.—This gas also offers considerable resistance to the passage of the electric spark. It is decomposed by the spark with deposition of sulphur. When gold electrodes are used, it furnishes lines resembling those of the same metal in air. With silver electrodes the gas was decomposed very rapidly, and no lines were produced beyond 113·5, the absorbent action of the gas being strongly manifested.

68. *Ammonia*.—Sparks pass in this gas as freely as in air; the spectrum of each metal is the same as in nitrogen; no new lines are visible in the photograph. Most of the atmospheric lines are distinct.

69. *Protoxide of Nitrogen*.—The electric sparks pass in this gas with much greater difficulty than in air. The spectrum appears to be the same as that produced in air, and no new lines are apparent in the photograph.

70. *Nitrogen*.—The spectrum of this gas, when gold or platinum electrodes are used, commences with a pale continuous spectrum, which slowly diminishes in intensity; this continuous spectrum appears to increase in intensity with the volatility of the metal, being well-marked in the case of magnesium, sodium, and potassium: at about 151 it terminates abruptly. The spectrum of nitrogen is crossed between 96·5 and 100 by two strong double lines; it shows an indistinct line at 108·5, a strong one at 110·5, three feeble lines at 113·5, 118, and 122, a faint band at 138, and another at 150. Fig. 33 shows the lines obtained from platinum points in nitrogen.

71. *Oxygen*.—This gas was obtained from black oxide of manganese heated with sulphuric acid. It gave, after purification by passing through a solution of caustic soda, lines identical with many of those obtained in atmospheric air. When the gas contained traces of carbonic acid, the lines due to the compounds of carbon were distinctly visible in the impressed spectrum. With platinum electrodes and with pure oxygen a feeble, nearly continuous spectrum extends to about 122·5; it also contains numerous lines extending as far as 142·5; beyond that, the impression is more feeble, terminating at about 156. The principal lines due to the gas are the following:—A broad line about 100, then two faint lines, beyond which, at 101·5, is a double line; a strong complex group at 103·5; a feebler one at 105·5; one rather stronger at 107·5; a double group of considerable strength at 112; another stronger at 114; between 116 and 119 is a group of six rather faint lines; after this there are no prominent lines until 138·2 and 141·5; at 153 is a strong compound line, and beyond this only the dotted lines of platinum are seen. (Fig. 32.)

72. *Chlorine* and *Hydrochloric Acid* give spectra which can scarcely be distinguished one from the other. With platinum points these spectra terminate by an abrupt band at 156·5. Their most marked features are a strong compound band at 96·5, and one still more marked at 100; then two lines, of which the first at 103 is the stronger, followed by two others, of which the second at 108·5 is the stronger: several fainter lines follow these lines. A group of six between 126 and 133, the most marked of which is a broad

band terminating at about 130. Several faint lines intervene between this and another broad band at 140, followed by several others less distinctly defined. (Fig. 34.)

I attempted to obtain the spectra of iodine and bromine by employing a current of hydriodic and hydrobromic acid ; but the results were not satisfactory. It is very difficult to maintain a steady current of sparks through these gases, and not easy to keep up a continuous current of the pure and dry gases, which are immediately decomposed by the passage of the electric spark, with extrication of dense fumes of iodine or of bromine.

