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XXIII. On the Absorption and Radiation of Heat by Gases and Vapours, and on the Physical Connexion of Radiation, Absorption, and Conduction.—The Bakerian Lecture. By JOHN TYNDALL Esq., F.R.S. &c.*

[With a Plate.]

§ 1. THE researches on glaciers which I have had the honour of submitting from time to time to the notice of the Royal Society, directed my attention in a special manner to the observations and speculations of De Saussure, Fourier, M. Pouillet, and Mr. Hopkins, on the transmission of solar and terrestrial heat through the earth's atmosphere. This gave practical effect to a desire which I had previously entertained to make the mutual action of radiant heat and gases of all kinds the subject of an experimental inquiry.

Our acquaintance with this department of Physics is exceedingly limited. So far as my knowledge extends, the literature of the subject may be stated in a few words.

From experiments with his admirable thermo-electric apparatus, Melloni inferred that for a distance of 18 or 20 feet the absorption of radiant heat by atmospheric air is perfectly insensible[†].

With a delicate apparatus of the same kind, Dr. Franz of Berlin found that the air contained in a tube 3 feet long absorbed 3.54 per cent. of the heat sent through it from an Argand lamp; that is to say, calling the number of rays which passed through the exhausted tube 100, the number which passed when the tube was filled with air was only 96.46[±].

* From the Philosophical Transactions, Part I. for 1861, having been read at the Royal Society February 7, 1861.

t La Thermochrose, p. 136. ‡ Pogg. Ann. vol. xciv. p. 342. Phil. Mag. S. 4. Vol. 22. No. 146. Sept. 1861. N In the sequel I shall refer to circumstances which induce me to conclude that the result obtained by Dr. Franz is due to an inadvertence in his mode of observation. These are the only experiments of this nature with which I am acquainted, and they leave the field of inquiry now before us perfectly unbroken ground.

§ 2. At an early stage of the investigation, I experienced the need of a first-class galvanometer. My instrument was constructed by that excellent workman, Sauerwald of Berlin. The needles are suspended independently of the shade; the latter is constructed so as to enclose the smallest possible amount of air, the disturbance of aërial currents being thereby practically avoided. The plane glass plate, which forms the cover of the instrument, is close to the needle; so that the position of the latter can be read off with ease and accuracy either by the naked eye or by a magnifying lens.

The wire of the coil belonging to this instrument was drawn from copper obtained from a galvano-plastic manufactory in the Prussian Capital; but it was not free from the magnetic metals.

In consequence of its impurity in this respect, when the needles were perfectly astatic they deviated as much as 30° right and left of the neutral line. To neutralize this, a "compensator" was made use of, by which the needle was gently drawn to zero in opposition to the magnetism of the coil.

But the instrument suffered much in point of delicacy from this arrangement, and accurate quantitative determinations with it were unattainable. I therefore sought to replace the Berlin coil by a less magnetic one. Mr. Becker first supplied me with a coil which reduced the lateral deflection from 30° to 3° .

But even this small residue was a source of great annoyance to me; and for a time I almost despaired of obtaining pure copper wire. I knew that Professor Magnus had succeeded in obtaining it for his galvanometer, but the labour of doing so was immense*. Previous to undertaking a similar task, the thought occurred to me, that for my purpose a magnet furnished an immediate and perfect test as to the quality of the wire. Pure copper is *diamagnetic*; hence its repulsion or attraction by the magnet would at once declare its fitness or unfitness for the purpose which I had in view.

Fragments of the wire first furnished to me by M. Sauerwald were strongly attracted by the magnet. The wire furnished by Mr. Becker, when covered with its green silk, was also attracted, though in a much feebler degree.

I then removed the green silk covering from the latter and tested the naked wire. It was repelled. The whole annoyance

* Pogg. Ann. vol. lxxxiii. p. 489; and Phil. Mag. 1852, vol. iii. p. 82.

was thus fastened on the green silk; some iron compound had been used in the dyeing of it; and to this the deviation of my needle from zero was manifestly due.

I had the green coating removed and the wire overspun with white silk, clean hands being used in the process. A perfect galvanometer is the result. The needle, when released from the action of a current, returns accurately to zero, and is perfectly free from all magnetic action on the part of the coil. In fact while we have been devising agate plates and other elaborate methods to get rid of the great nuisance of a magnetic coil*, the means of doing so are at hand. Nothing is more easy to be found than diamagnetic copper wire. Out of eleven specimens, four of which were furnished by Mr. Becker, and seven taken at random from our laboratory, nine were found diamagnetic and only two magnetic.

Perhaps the only defect of those fine instruments with which Du Bois Raymond conducts his admirable researches in animal electricity is that above alluded to. The needle never comes to zero, but is drawn to it by a minute magnet. This defect may be completely removed. By the substitution of clean white silk for green, however large the coil may be, the compensator may be dispensed with, and a great augmentation of delicacy secured. The instrument will be rendered suitable for quantitative measurements; effects which are now beyond the reach of experiment will be rendered manifest; while the important results hitherto established will be obtained with a fraction of the length of wire now in use[†].

§ 3. Our present knowledge of the deportment of liquids and solids, would lead to the inference that, if gases and vapours exercised any appreciable absorptive power on radiant heat, the absorption would make itself most manifest on heat emanating from an obscure source. But an experimental difficulty occurs at the outset in dealing with such heat. How must we close the receiver containing the gases through which the calorific rays are to be sent? Melloni found that a glass plate one-tenth of an inch in thickness intercepted all the rays emanating from a source of the temperature of boiling water, and fully 94 per cent. of the rays from a source of 400° Centigrade. Hence a tube closed with glass plates would be scarcely more suitable for the purpose now under consideration, than if its ends were stopped by plates of metal.

* See Melloni upon this subject, Thermochrose, pp. 31-33.

 \dagger Mr. Becker, to whose skill and intelligence I have been greatly indebted, furnished me with several specimens of wire of the same fineness as that used by Du Bois Raymond, some covered with green silk and others with white. The former were invariably attracted, the latter invariably repelled. In all cases the *naked* wire was repelled. Rock-salt immediately suggests itself as the proper substance; but to obtain plates of suitable size and transparency was exceedingly difficult. Indeed, had I been less efficiently seconded, the obstacles thus arising might have been insuperable. To the Trustees of the British Museum I am indebted for the material of one good plate of salt; to Mr. Harlin for another; while Mr. Lettsom, at the instance of Mr. Darker*, brought me a piece of salt from Germany from which two fair plates were taken. To Lady Murchison, Sir Emerson Tennant, Sir Philip Egerton, and Mr. Pattison my best thanks are also due for their friendly assistance.

The first experiments were made with a tube of tin polished inside, 4 feet long and $2\cdot 4$ inches in diameter, the ends of which were furnished with brass appendages to receive the plates of rock-salt. Each plate was pressed firmly against a flange by means of a bayonet joint, being separated from the flange by a suitable washer. Various descriptions of leather washers were tried for this purpose and rejected. The substance finally chosen was vulcanized india-rubber very lightly smeared with a mixture of bees-wax and spermaceti. A T-piece was attached to the tube, communicating on one side with a good air-pump, and on the other with the external air, or with a vessel containing the proper gas.

The tube being mounted horizontally, a Leslie's cube containing hot water was placed close to one of its ends, while an excellent thermo-electric pile, connected with its galvanometer, was presented to the other. The tube being exhausted, the calorific rays sent through it fell upon the pile, a permanent deflection of 30° being the consequence. The temperature of the water was in the first instance purposely so arranged as to produce this deflection.

Dry air was now admitted into the tube, while the needle of the galvanometer was observed with all possible care. Even by the aid of a magnifying lens I could not detect the slightest change of position. Oxygen, hydrogen, and nitrogen, subjected to the same test, gave the same negative result. The temperature of the water was subsequently lowered so as to produce a deflection of 20° and 10° in succession, and then heightened till the deflection amounted to 40° , 50° , 60° and 70° ; but in no case did the admission of air, or any of the above gases into the exhausted tube, produce any sensible change in the position of the needle.

It is a well-known peculiarity of the galvanometer, that its higher and lower degrees represent different amounts of calorific

* During the course of the inquiry, I have often had occasion to avail myself of the assistance of this excellent mechanician.

action. In my instrument, for example, the quantity of heat necessary to move the needle from 60° to 61° is about twenty times that required to move it from 11° to 12°. Now in the case of the small deflections above referred to, the needle was, it is true, in a sensitive position; but then the total amount of heat passing through the tube was so inconsiderable that a small per-centage of it, even if absorbed, might well escape detection. In the case of the large deflections, on the other hand, though the total amount of heat was large, and though the quantity absorbed might be proportionate, the needle was in such a position as to require a very considerable abstraction of heat to produce any sensible change in its position. Hence arose the thought of operating, if possible, with large quantities of heat, while the needle intended to reveal its absorption should continue to occupy its position of maximum delicacy.

The first attempt at solving this problem was as follows :---My galvanometer is a differential one-the coil being composed of two wires wound side by side, so that a current could be sent through either of them independent of the other. The thermoelectric pile was placed at one end of the tin tube, and the ends of one of the galvanometer wires connected with it. A copper ball heated to low redness being placed at the other end of the tube, the needle of the galvanometer was propelled to its stops near 90°. The ends of the second wire were now so attached to a second pile that when the latter was caused to approach the copper ball, the current thus excited passed through the coil in a direction opposed to the first one. Gradually, as the second pile was brought nearer to the source of heat, the needle descended from the stops, and when the two currents were nearly equal the position of the needle was close to zero.

Here then we had a powerful flux of heat through the tube; and if a column of gas four feet long exercised any sensible absorption, the needle was in the position best calculated to reveal it. In the first experiment made in this way, the neutralization of one current by the other occurred when the tube was filled with air; and after the exhaustion of the tube had commenced, the needle started suddenly off in a direction which indicated that a less amount of heat passed through the partially exhausted tube, than through the tube filled with air. The needle, however, soon stopped, turned, descended quickly to zero, and passed on to the other side, where its deflection became per-The air made use of in this experiment came direct manent. from the laboratory, and the first impulsion of the needle was probably due to the aqueous vapour precipitated as a cloud by the sudden exhaustion of the tube. When, previous to its admission, the air was passed over chloride of calcium, or pumice-stone moistened with sulphuric acid, no such effect was observed. The needle moved steadily in one direction until its maximum deflection was attained, and this deflection showed that in all cases radiant heat was absorbed by the air within the tube.

These experiments were commenced in the spring of 1859, and continued without intermission for seven weeks. The course of the inquiry during this whole period was an incessant struggle with experimental difficulties. Approximate results were easily obtainable; but I aimed at exact measurements, which could not be made with a varying source of heat like the copper ball. T resorted to copper cubes containing fusible metal, or oil, raised to a high temperature; but was not satisfied with their action. I finally had a lamp constructed which poured a sheet of gas-flame along a plate of copper; and to keep the flame constant, a gas regulator specially constructed for me by Mr. Hulet was made It was also arranged that the radiating plate should use of. form one of the walls of a chamber which could be connected with the air-pump and exhausted, so that the heat emitted by the copper plate might cross a vacuum before entering the experimental tube. With this apparatus I determined approximately the absorption of nine gases and twenty vapours during the summer of 1859. The results would furnish materials for a long memoir; but increased experience and improved methods have enabled me to substitute for them others of greater value; I shall therefore pass over the work of these seven weeks without further allusion to it.

On the 9th of September of the present year (1860) I resumed the inquiry. For three weeks I worked with the plate of copper as my source of heat, but finally rejected it on the score of insufficient constancy. I again resorted to the cube of hot oil, and continued to work with it up to Monday the 29th of October. During the seven weeks just referred to, I experimented from eight to ten hours daily; but these experiments, though more accurate, must unhappily share the fate of the former ones. In fact the period was one of discipline—a continued struggle against the difficulties of the subject and the defects of the locality in which the inquiry was conducted.

My reason for making use of the high sources of heat above referred to was, that the absorptive power of some of the gases which I had examined was so small that, to make it clearly evident, a high temperature was essential. For other gases, and for *all* the vapours that had come under my notice, a source of lower temperature would have been not only sufficient, but far preferable. I was finally induced to resort to boiling water, which, though it gave greatly diminished effects, was capable of being preserved at so constant a temperature that deflections which, with the other sources, would be masked by the errors of observation, became with it true quantitative measures of absorption.

§ 4. The entire apparatus made use of in the experiments on absorption is figured on Plate III. S S' is the experimental tube, composed of brass, polished within, and connected, as shown in the figure, with the air-pump, AA. At S and S' are the plates of rock-salt which close the tube air-tight. The length from S to S' is 4 feet. C is a cube containing boiling water, in which is immersed the thermometer t. The cube is of cast copper, and on one of its faces a projecting ring was cast to which a brass tube of the same diameter as SS', and capable of being connected air-tight with the latter, was carefully soldered. The face of the cube within the ring is the radiating plate, which is coated with lampblack. Thus between the cube C and the first plate of rock-salt there is a front chamber F, connected with the air-pump by the flexible tube D D, and capable of being exhausted independently of SS'. To prevent the heat of conduction from reaching the plate of rock-salt S, the tube F is caused to pass through a vessel V, being soldered to the latter where it enters it and issues from it. This vessel is supplied with a continuous flow of cold water through the influx tube *ii*, which dips to the bottom of the vessel; the water escapes through the efflux tube e e, and the continued circulation of the cold liquid completely intercepts the heat that would otherwise reach the plate S.

The cube C is heated by the gas-lamp L. P is the thermoelectric pile placed on its stand at the end of the experimental tube, and furnished with two conical reflectors, as shown in the figure. C' is the compensating cube, used to neutralize by its radiation* the effect of the rays passing through SS'. The regulation of this neutralization was an operation of some delicacy; to effect it the double screen H was connected with a winch and screw arrangement, by which it could be advanced or withdrawn through extremely minute spaces. For this most useful adjunct I am indebted to the kindness of my friend Mr. Gassiot. NN is the galvanometer, with perfectly astatic needles and perfectly non-magnetic coil; it is connected with the pile P by the wires w w; Y Y is a system of six chlorideof-calcium tubes, each 32 inches long; R is a U-tube containing fragments of pumice-stone, moistened with strong caustic potash; and Z is a second similar tube, containing fragments of pumice-stone wetted with strong sulphuric acid. When drying only was aimed at, the potash tube was suppressed. When, on

* It will be seen that in this arrangement I have abandoned the use of the differential galvanometer, and made the thermo-electric pile the differential instrument.



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the contrary, as in the case of atmospheric air, both moisture and carbonic acid were to be removed, the potash tube was included. G G is a holder from which the gas to be experimented with was sent through the drying-tubes, and thence through the pipe p p into the experimental tube S S'. The appendage at M and the arrangement at OO may for the present be disregarded; I shall refer to them particularly by and by.

The mode of proceeding was as follows :- The tube S S' and the chamber F being exhausted as perfectly as possible, the connexion between them was intercepted by shutting off the cocks m, m'. The rays from the interior blackened surface of the cube C passed first across the vacuum F, then through the plate of rock-salt S, traversed the experimental tube, crossed the second plate S', and being concentrated by the anterior conical reflector, impinged upon the adjacent face of the pile P. Meanwhile the rays from the hot cube C' fell upon the opposite face of the pile, and the position of the galvanometer needle declared at once which source was predominant. A movement of the screen H back or forward with the hand sufficed to establish an approximate equality; but to make the radiations perfectly equal, and thus bring the needle exactly to 0°, the fine motion of the screw above referred to was necessary. The needle being at 0°, the gas to be examined was admitted into the tube; passing, in the first place, through the drying apparatus. Any required quantity of the gas may be admitted; and here experiments on gases and vapours enjoy an advantage over those with liquids and solids, namely, the capability of changing the density at pleasure. When the required quantity of gas had been admitted, the galvanometer was observed, and from the deflection of its needle the absorption was accurately determined.

Up to about its 36th degree, the degrees of my galvanometer are all equal in value; that is to say, it requires the same amount of heat to move the needle from 1° to 2° as to move it from 35° to 36° . Beyond this limit the degrees are equivalent to larger amounts of heat. The instrument was accurately calibrated by the method recommended by Melloni (*Thermochrose*, p. 59); so that the precise value of its larger deflections are at once obtained by reference to a table. Up to the 36th degree, therefore, the simple deflections may be regarded as the expression of the absorption; but beyond this the absorption equivalent to any deflection is obtained from the table of calibration.

Oxygen obtained from chlorate of potash and peroxide of manganese produced a deflection of about $\ldots \ldots \ldots 1^{\circ}$.

One specimen of nitrogen, obtained from the decomposition of nitrate of potash, produced a deflection of about \ldots 1° .

Oxygen obtained from the electrolysis of water, and sent through a series of eight bulbs containing a strong solution of iodide of potassium, produced a deflection of about . . 1°.

Hence the small quantity of ozone which accompanied the oxygen in this case trebled the absorption of the oxygen itself*.

I have repeated this experiment many times, employing different sources of heat. With sources of high temperature the difference between the ozone and the ordinary oxygen comes out very strikingly. By careful decomposition a much larger amount of ozone might be obtained, and a corresponding large effect on radiant heat produced.

In obtaining the electrolytic oxygen, I made use of two different vessels. To diminish the resistance of the acidulated water to the passage of the current, I placed in one vessel a pair of very large platinum plates, between which the current from a battery of ten of Grove's cells was transmitted. The oxygen bubbles liberated on so large a surface were extremely minute, and the gas thus generated, on being sent through iodide of potassium, scarcely coloured the liquid; the characteristic odour of ozone was also almost entirely absent. In the second vessel smaller plates were used. The bubbles of oxygen were much larger, and did not come into such intimate contact with either the platinum or the water. The oxygen thus obtained showed the characteristic reactions of ozone; and with it the above result was obtained.

Taking as unit of heat the quantity necessary to cause the needle to move from 0° to 1° , the number of units expressed by the above deflection is $\ldots \ldots 308$.

Hence the absorption by the above gases amounted to about 0.33 per cent.

I am unable at the present moment to range with certainty oxygen, hydrogen, nitrogen, and atmospheric air in the order of

* It will be seen further on that this result is in harmony with the supposition that ozone, obtained in the manner described, is a *compound* body. their absorptive powers, though I have made several hundred experiments with the view of doing so. Their proper action is so small that the slightest foreign impurity gives one a predominance over the other. In preparing the gases, I have resorted to the methods which I found recommended in chemical treatises, but as yet only to discover the defects incidental to these methods. Augmented experience and the assistance of my friends will, I trust, enable me to solve this point by and by. An examination of the whole of the experiments induces me to regard hydrogen as the gas which exercises the lowest absorptive power.

We have here the cases of minimum gaseous absorption. It will be interesting to place in juxtaposition with the above results some of those obtained with olefant gas—the most highly absorbent permanent gas that I have hitherto examined. I select for this purpose an experiment made on the 21st of November.

The needle being steady at zero in consequence of the equality of the actions on the opposite faces of the pile, the admission of olefiant gas gave a permanent deflection of $...70^{\circ}3.$

Now a deflection of $70^{\circ}3$ is equivalent to 290 units, and a deflection of 75° is equivalent to 360 units; hence more than seven-ninths of the total heat was cut off by the olefiant gas, or about 81 per cent.

The extraordinary energy with which the needle was deflected when the olefiant gas was admitted into the tube, was such as might occur had the plates of rock-salt become suddenly covered with an opake layer. To test whether any such action occurred, I polished a plate carefully, and projected against it for a considerable time a stream of the gas; there was no dimness produced. The plates of rock-salt, moreover, which were removed daily from the tube, usually appeared as bright when taken out as when they were put in.

The gas in these experiments issued from its holder, and had there been in contact with cold water. To test whether it had chilled the plates of rock-salt, and thus produced the effect, I filled a similar holder with atmospheric air and allowed it to attain the temperature of the water; but its action was not thereby sensibly augmented.

In order to subject the gas to ocular examination, I had a glass tube constructed and connected with the air-pump. On permitting olefiant gas to enter it, not the slightest dimness or opacity was observed. To remove the last trace of doubt as to the possible action of the gas on the plates of rock-salt, the tin tube referred to at the commencement was perforated at its centre and a cock inserted into it; the source of heat was at one end of the tube, and the thermo-electric pile at some distance from the other. The plates of salt were entirely abandoned, the tube being open at its ends and consequently full of air. On allowing the olefiant gas to stream for a second or two into the tube through the central cock, the needle flew off and struck against its stops. It was held steadily for a considerable time between 80° and 90°.

A slow current of air sent through the tube gradually removed the gas, and the needle returned accurately to zero.

The gas within the holder being under a pressure of about 12 inches of water, the cock attached to the cube was turned quickly on and off; the quantity of gas which entered the tube in this brief interval was sufficient to cause the needle to be driven to the stops, and steadily held between 60° and 70°.

The gas being again removed, the cock was turned once half round as quickly as possible. The needle was driven in the first instance through an arc of 60° , and was held permanently at 50° .

The quantity of gas which produced this last effect, on being admitted into a graduated tube, was found not to exceed onesixth of a cubic inch in volume.

The tube was now taken away, and both sources of heat allowed to act from some distance on the thermo-electric pile. When the needle was at zero, olefiant gas was allowed to issue from a common argand burner into the air between one of the sources of heat and the pile. The gas was invisible, nothing was seen in the air, but the needle immediately declared its presence, being driven through an arc of 41° . In the four experiments last described, the source of heat was a cube of oil heated to 250° Centigrade, the compensation cube being filled with boiling water*.

Those who like myself have been taught to regard transparent gases as almost perfectly diathermanous, will probably share the astonishment with which I witnessed the foregoing effects. I was indeed slow to believe it possible that a body so constituted, and so transparent to light as olefant gas, could be so densely opake to any kind of calorific rays; and to secure myself against error, I made several hundred experiments with this single substance. By citing them at greater length, however, I do not think I

* With a cube containing boiling water I have since made this experiment visible to a large audience.

could add to the conclusiveness of the proofs just furnished, that the case is one of true calorific absorption*.

§ 6. Having thus established in a general way the absorptive power of olefiant gas, the question arises, "What is the relation which subsists between the density of the gas and the quantity of heat extinguished?"

I sought at first to answer this question in the following way:— An ordinary mercurial gauge was attached to the air-pump; the experimental tube being exhausted, and the needle of the galvanometer at zero, olefiant gas was admitted until it depressed the mercurial column 1 inch, the consequent deflection being noted; the gas was then admitted until a depression of 2 inches was observed, and thus the absorption effected by gas of 1, 2, 3, and more inches tension was determined. In the following Table the first column contains the tensions in inches, the second the deflections, and the third the absorption equivalent to each deflection.

Tensions in inches.	Deflections.	Absorption
1	56	90
$\hat{2}$	58.2	123
3	59.3	142
4	60.0	157
5	6 0·5	168
6	61.0	177
7	61.4	182
8	61.7	186
9	62.0	190
10	62.2	192
20	66·0	227

TABLE I.—Olefiant Gas.

No definite relation between the density of the gas and its absorption is here exhibited. We see that an augmentation of the density *seven times* about *doubles* the amount of the absorption; while gas of 20 inches tension effects only $2\frac{1}{2}$ times the absorption of gas possessing 1 inch of tension.

But here the following reflections suggest themselves :—It is evident that olefant gas of 1 inch tension, producing so large a deflection as 56°, must extinguish a large proportion of the rays which are capable of being absorbed by the gas, and hence the succeeding measures having a less and less amount of heat to act upon must produce a continually smaller effect. But sup-

* It is evident that the old mode of experiment might be applied to this gas. Indeed, several of the solids examined by Melloni are inferior to it in absorptive power. Had time permitted, I should have checked my results by experiments made in the usual way; this I intend to do on a future occasion. posing the quantity of gas first introduced to be so inconsiderable that the number of rays extinguished by it is a vanishing quantity compared with the total number capable of absorption, we might reasonably expect that in this case a double quantity of gas would produce a double effect, a treble quantity a treble effect, or in general terms, that the absorption would, for a time, be proportional to the density

To test this idea, a portion of the apparatus, which was purposely omitted in the description already given, was made use of. OO, Plate III., is a graduated glass tube, the end of which dips into the basin of water B. The tube can be stopped above by means of the stopcock r; dd is a tube containing fragments of chloride of calcium. The tube OO being first filled with water to the cock r, had this water displaced by olefiant gas; and afterwards the tube S S', and the entire space between the $\operatorname{cock} r$ and the experimental tube, was exhausted. The $\operatorname{cock} n$ being now closed and r' left open, the cock r at the top of the tube OO was carefully turned on and the gas permitted to enter the tube S S' with extreme slowness. The water rose in O O, each of whose smallest divisions represents a volume of $\frac{1}{30}$ th of a cubic inch. Successive measures of this capacity were admitted into the tube and the absorption in each case determined.

In the following Table the first column contains the quantity of gas admitted into the tube; the second contains the corresponding deflection, which, within the limits of the Table, expresses the absorption; the third column contains the absorption, calculated on the supposition that it is proportional to the density.

TABLE II.—Olefiant Gas.

Unit-measure $\frac{1}{50}$ th of a cubic inch. Absorption.

Measures of gas.	Observed.	Calculated.	
1	2.2	2.2	
2	4.2	4.4	
3	6.6	6.6	
4	8.8	8.8	
5	11.0	11.0	
6	12.0	13.2	
7	14.8	15.4	
8	16·8	17.6	
9	19.8	19.8	
10	22.0	22.0	
11	24.0	24.2	
12	25.4	26.4	
13	29 ·0	28.6	
14	30.5	29.8	
15	33·5	33.0	

This Table shows the correctness of the foregoing surmise, and proves that for small quantities of gas the absorption is exactly proportional to the density.

Let us now estimate the tensions of the quantities of gas with which we have here operated. The length of the experimental tube is 48 inches, and its diameter 2.4 inches; its volume is therefore 218 cubic inches. Adding to this the contents of the cocks and other conduits which led to the tube, we may assume that each fiftieth of a cubic inch of the gas had to diffuse itself through a space of 220 cubic inches. The tension, therefore, of a single measure of the gas thus diffused would be $\frac{1}{11,000}$ th of an atmosphere,—a tension capable of depressing the mercurial column connected with the pump $\frac{1}{367}$ th of an inch, or about $\frac{1}{15}$ th of a millimetre !

But the absorptive energy of olefiant gas, extraordinary as it is shown to be by the above experiments, is far exceeded by that of some of the vapours of volatile liquids. A glass flask was provided with a brass cap furnished with an interior thread, by means of which a stopcock could be screwed air-tight on to the Sulphuric ether being placed in the latter, the space flask. above the liquid was completely freed of air by means of a second air-pump. The flask, with its closed stopcock, was now attached to the experimental tube; the latter was exhausted and the needle brought to zero. The cock was then turned on so that the ether-vapour slowly entered the experimental tube. An assistant observed the gauge of the air-pump, and when it had sunk an inch, the stopcock was promptly closed. The galvanometric deflection consequent on the partial cutting off of the calorific rays was then noted; a second quantity of the vapour, sufficient to depress the gauge another inch, was then admitted, and in this way the absorptions of five successive measures, each possessing within the tube 1 inch of tension, were determined.

In the following Table the first column contains the tensions in inches, the second the deflection due to each, and the third the amount of heat absorbed, expressed in the units already referred to. For the purpose of comparison I have placed the corresponding absorption of olefant gas in the fourth column.

Tensions in inches.	Deflections.	Absorption.	Corresponding absorption by olefiant gas.
1	64.8	214	90
2	70.0	282	123
3	72.0	315	142
4	73 .0	330	154
5	73·0	330	163

TABLE III .- Sulphuric Ether.

For these tensions the absorption of radiant heat by the vapour of sulphuric ether is more than twice the absorption of olefiant gas. We also observe that in the case of the former the successive absorptions approximate more quickly to a ratio of equality. In fact the absorption produced by 4 inches of the vapour was sensibly the same as that produced by 5.

But reflections similar to those which we have already applied to olefiant gas are also applicable to ether. Supposing we make our unit-measure small enough, the number of rays first destroyed will vanish in comparison with the total number, and for a time the fact will probably manifest itself that the absorption is directly proportional to the density. To examine whether this is the case, the other portion of the apparatus, omitted in the general description, was made use of. K is a small flask with a brass cap, which is closely screwed on to the stopcock c'. Between the cocks c' and c, which latter is connected with the experimental tube, is the chamber M, the capacity of which was accurately determined. The flask k was partially filled with ether, and the air above the liquid removed. The stopcock c'being shut off and c turned on, the tube S S' and the chamber M are exhausted. The cock c is now shut off, and c' being turned on, the chamber M becomes filled with pure ether vapour. By turning c' off and c on, this quantity of vapour is allowed to diffuse itself through the experimental tube, and its absorption determined; successive measures are thus sent into the tube. and the effect produced by each is noted. Measures of various capacities were made use of, according to the requirements of the vapours examined.

In the first series of experiments made with this apparatus, I omitted to remove the air from the space above the liquid; each measure therefore sent in to the tube was a mixture of vapour and air. This diminished the effect of the former; but the proportionality, for small quantities, of density to absorption exhibits itself so decidedly as to induce me to give the observations. The first column, as usual, contains the measures of vapour, the second the observed absorption, and the third the calculated absorption. The galvanometric deflections are omitted, their equivalents being contained in the second column. In fact as far as the eighth observation, the absorptions are merely the record of the deflections.

	Abso	orption.
Measures.	Observed.	Calculated.
1	4.2	4.2
2	9.2	9.0
3	13·5	13.2
4	18.0	18.0
5	22.8	23.5
6	27.0	27.0
7	31.8	31.2
8	36.0	36.0
9	39.7	40.0
10	45.0	45.0
20	81 0	90.0
21	82.8	95 ·0
22	84.0	9 9·0
23	87.0	104.0
24	88.0	108.0
25	90.0	113·0
26	93·0	117.0
27	94 ·0	122.0
28	95.0	126.0
29	98.0	131.0
30	100.0	135.0

TABLE IV.—Mixture of Ether Vapour and Air.

Unit-measure $\frac{1}{50}$ th of a cubic inch.

Up to the 10th measure we find that density and absorption augment in precisely the same ratio. While the former varies from 1 to 10, the latter varies from 4.5 to 45. At the 20th measure, however, a deviation from proportionality is apparent, and the divergence gradually augments from 20 to 30. In fact 20 measures tell upon the rays capable of being absorbed,—the quantity destroyed becoming so considerable, that every additional measure encounters a smaller number of such rays, and hence produces a diminished effect.

With ether vapour alone, the results recorded in the following Table were obtained. Wishing to determine the absorption exercised by vapour of very low tension, the capacity of the unitmeasure was reduced to $\frac{1}{100}$ th of a cubic inch.

TABLE V.-Sulphuric Ether.

Unit-measure	100 th	of a	cubic	inch.	
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	Absor	ption.	1	Absor	ption.
Measures.	Observed.	Calculated.	Measures.	Observed.	Calculated.
1	5.0	4.6	17	65.5	77.2
2	10.3	9.2	18	68·0	83.0
4	19.2	18.4	19	70·0	87.4
5	24.5	23.0	20	72.0	92.0
6	29.5	27.0	21	73.0	96·7
7	34.2	32.2	22	73.0	101-2
8	38.0	36 ·8	23	73.0	105.8
9	4 4·0	41.4	24	77.0	110.4
10	46.2	46.2	25	7 8·0	115.0
11	50·0	50.6	26	78·0	119.6
12	52.8	55.2	27	80.0	124.2
13	55·0	5 9·8	28	80.2	128.8
14	57.2	64.4	29	81.0	133•4
15	59.4	69.0	30	81.0	138.0
16	62.5	73.6			

We here find that the proportion between density and absorption holds sensibly good for the first eleven measures, after which the deviation gradually augments.

I have examined some specimens of ether which acted still more energetically on the thermal rays than those above recorded. No doubt for smaller measures than $\frac{1}{100}$ th of a cubic inch the above law holds still more rigidly true; and in a suitable locality it would be easy to determine with perfect accuracy $\frac{1}{10}$ th of the absorption produced by the first measure; this would correspond to $\frac{1}{1000}$ th of a cubic inch of vapour. But on entering the tube the vapour had only the tension due to the temperature of the laboratory, namely 12 inches. This would require to be multiplied by 2.5 to bring it up to that of the atmosphere. Hence the $\frac{1}{1000}$ th of a cubic inch, the absorption of which I have affirmed to be capable of measurement, would, on being diffused through a tube possessing a capacity of 220 cubic inches, have a tension of $\frac{1}{220} \times \frac{1}{2\cdot 5} \times \frac{1}{1000} = \frac{1}{500,000}$ th part of an atmosphere !

I have now to record the results obtained with thirteen other vapours. The method of experiment was in all cases the same as that just employed in the case of ether, the only variable element being the size of the unit-measure; for with many substances no sensible effect could be obtained with a unit volume so small as that used in the experiments last recorded. With bisulphide of carbon, for example, it was necessary to augment the unit-measure 50 times to render the measurements satisfactory.

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TABLE VI.—Bisulphide of Carbon.

Unit-measure $\frac{1}{2}$ a cubic inch.

	Absorption.		
Measures.	Observed.	Calculated.	
1	2.2	2.2	
$\overline{2}$	4.9	4.4	
3	6.2	6.6	
4	8.8	8.8	
5	10.7	11.0	
$\overline{6}$	12.5	13.0	
7	13.8	15.4	
8	14.5	17.6	
9	15.0	19.0	
10	15.6	22.0	
11	16.2	24.2	
12	16.8	26 ·4	
13	17.5	28.6	
14	18.2	30.8	
15	19 ·0	33.0	
16	20.0	35.2	
17	20.0	37.4	
18	20.2	39·6	
19	21.0	41.8	
20	21.0	44.0	

As far as the sixth measure the absorption is proportional to the density; after which the effect of each successive measure diminishes. Comparing the absorption effected by a quantity of vapour which depressed the mercury column half an inch, with that effected by vapour possessing one inch of tension, the same deviation from proportionality is observed.

By	mercurial	gauge.
Tension.		Absorption.
🚽 inch		14.8
1 inch		18.8

These numbers simply express the galvanometric deflections, which, as already stated, are strictly proportional to the absorption as far as 36° or 37° . Did the law of proportion hold good, the absorption due to 1 inch of tension ought of course to be 29.6 instead of 18.8.

Whether for equal volumes of the vapours at their maximum density, or for equal tensions as measured by the depression of the mercurial column, bisulphide of carbon exercises the lowest absorptive power of all the vapours which I have hitherto examined. For very small quantities, a volume of sulphuric ether vapour, at its maximum density in the measure, and expanded thence into the tube, absorbs 100 times the quantity of radiant heat intercepted by an equal volume of bisulphide of carbon vapour at its maximum density. These are the extreme limits of the scale, as far as my inquiries have hitherto proceeded. The action of every other vapour is less than that of sulphuric ether, and greater than that of bisulphide of carbon.

A very singular phenomenon was repeatedly observed during the experiments with bisulphide of carbon. After determining the absorption of the vapour, the tube was exhausted as perfectly as possible, the trace of vapour left behind being exceedingly minute. Dry air was then admitted to cleanse the tube. On again exhausting, after the first few strokes of the pump a jar was felt and a kind of explosion heard, while dense volumes of blue smoke immediately issued from the cylinders. The action was confined to the latter, and never propagated backwards into the experimental tube.

It is only with bisulphide of carbon that this effect has been observed. It may, I think, be explained in the following manner:—To open the valve of the piston, the gas beneath it must have a certain tension, and the compression necessary to produce this appears sufficient to cause the combination of the constituents of the bisulphide of carbon with the oxygen of the air. Such a combination certainly takes place, for the odour of sulphurous acid is unmistakeable amid the fumes.

To test this idea I tried the effect of compression in the airsyringe. A bit of tow or cotton wool moistened with bisulphide of carbon, and placed in the syringe, emitted a bright flash when the air was compressed. By blowing out the fumes with a glass tube, this experiment may be repeated twenty times with the same bit of cotton.

It is not necessary even to let the moistened cotton remain in the syringe. If the bit of tow or cotton be thrown into it, and out again as quickly as it can be ejected, on compressing the air the luminous flash is seen. Pure oxygen produces a brighter flash than atmospheric air. These facts are in harmony with the above explanation.

TABLE VII.—Amylene.

Unit-m	easure <u>1</u> 0th of Absor	a cubic inch. ption.
Measures.	Observed.	Calculated.
1	3.4	4 ·3
2	8.4	8.6
3	12.0	12.9
4	16.2	17.2
5	21.6	21.2
6	26.5	25.8
7	30.6	30.1
8	35.3	34.4
9	39 ·0	38.7
10	44.0	43 [.] 0
	0.2	

For these quantities the absorption is proportional to the density, but for large quantities the usual deviation is observed, as shown by the following observations :---

By mercurial gauge.			
Tension.	Deflection.	Absorption.	
‡ inch Ì inch	60 65	157 216	

Did the proportion hold good, the absorption for an inch of tension ought of course to be 314 instead of 216.

TABLE VIII.-Iodide of Ethyle.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

	ADSO	rption.
Measures.	Observed.	Calculated.
1	5.4	5.1
2	10.3	10.2
3	16·8	15-3
4	22.2	20.4
5	26.6	25.5
6	31.8	30.6
7	35.6	35.9
8	40.0	40 ·8
9	44·0	45.9
10	47.5	51·0
]	By mercurial g	auge.

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Tension.	Deflection.	Absorption.
1/2 inch	56·3	94 190
1 men	58.2	120

TABLE IX.-Iodide of Methyle.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

...

Measures.	Absorption.	
	Observed.	Calculated.
1	3.2	3.4
2	7.0	6·8
3	10.3	10.2
4	15.0	13.6
5	17.5	17.0
6	20.5	20.4
7	24.0	23.8
8	26.3	27.2
9	30.0	30· 6
10	32.3	34.0

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	By mercurial ga	By mercurial gauge.	
Tension.	Deflection.	Absorption.	
1/2 inch	48.5	60	
l inch	56.2	96	

TABLE X.—Iodide of Amyle.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

	Absorption.	
Measures.	Observed.	Calculated.
1	0.6	0.57
2	1.0	1.1
3	1.4	1.7
4	2.0	2.3
5	3.0	2.9
6	3.8	3.4
7	4.2	4.0
8	5.0	4.6
9	5.0	5.1
10	5.8	.5.7

The deflections here are very small; the substance, however, possesses so feeble a volatility, that the tension of a measure of its vapour, when diffused through the experimental tube, must be infinitesimal. With the specimen which I examined, it was not practicable to obtain a tension sufficient to depress the mercury gauge $\frac{1}{2}$ an inch; hence no observations of this kind are recorded.

TABLE XI.—Chloride of Amyle.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

	Absorption.	
Measures.	Observed.	Calculated.
1	1.3	1.3
2	3.0	2.6
3	3.8	3.9
4	5.1	5.2
5	6.8	6.2
6	8.5	7.8
7	9.0	9.1
8	10.9	10.4
9	11.3	11.7
10	12.3	13.0
	By mercurial ga	uge.
Tension.	Deflection.	Absorption.
🕯 inch	59	137
1 inch	not practicable.	

TABLE XII.—Benzole.

Measures.	Absorption.	
	Observed.	Calculated.
1	4.5	4.2
2	9.5	9.0
3	14·0	13.5
4	18.2	18.0
5	22.5	22.5
6	27.5	27.0
7	31.6	31.2
8	35.5	36•0
9	39.0	40.0
10	44.0	45.0
11	47.0	49.0
12	49 ·0	54.0
13	51.0	58·5
14	54.0	63·0
15	56·0	67.5
16	59.0	72.0
17	63·0	76.5
18	67.0	81.0
19	69.0	85.2
20	72.0	90.0

Unit-measure $\frac{1}{10}$ th of a cubic inch.

Up to the 10th measure, or thereabouts, the proportion between density and absorption holds good, from which onwards the deviation from the law gradually augments.

By mercurial gauge.

Tension.	Deflection.	Absorption.
1 inch	54	78
1 inch	57	103

TABLE XIII.—Methylic Alcohol.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

Absorption.

	the second se	A
Measures.	Observed.	Calculated.
1	10.0	1 0 ·0
2	20·0	20.0
3	30.0	30.0
4	40.5	40 ·0
5	49.0	5 0 ·0
6	53·5	60.0
7	59.2	70.0
8	71·5	80.0
9	78.0	90.0
10	84.0	100· 0

By mercurial gauge.		
Tension.	Deflection.	Absorption.
inch	58.8	133
l mch	60.2	108

TABLE XIV .--- Formic Ether.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

Measures.	Aosorption.	
	Observed.	Calculated.
1	8.0	7.5
2	16.0	15.0
3	22.5	22.5
4	30.0	30.0
5	35.2	37.5
6	39.5	45.0
7	45·0	52.5
8	48 ·0	60.0
9	50.2	67.5
10	53.2	75.0

By mercurial gauge.

Tension.	Deflection.	Absorption.
1 inch	58 ⁸ .8	133
1 inch	62·5	19 3

TABLE XV.-Propionate of Ethyle.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

Measures.	Absorption.	
	Observed.	Calculated.
1	7.0	7:0
$\overline{2}$	14.0	14.0
3	21.8	21.0
4	28.8	28.0
5	34.4	35.0
6	38.8	42·0
7	41.0	49·0
8	42.5	56·0
9	44.8	63·0
10	46.2	70.0

By mercurial gauge.

Tension.	Deflection.	Absorption.	
1 inch	60.5	168	
1 inch	not practicable.		

TABLE XVI.-Chloroform.

Unit-measure $\frac{1}{10}$ th of a cubic inch.

Absorption,	
Observed.	Calculated.
4.2	4.2
9 ·0	9.0
13 [.] 8	13·5
18.2	18·0
$22 \cdot 3$	22.5
27.0	27.0
31.2	31.2
35.0	36.0
39.0	4 0·5
40.0	45·0
	Observed. 4·5 9·0 13·8 18·2 22·3 27·0 31·2 35·0 39·0 40·0

Subsequent observations lead me to believe that the absorption by chloroform is a little higher than that given in the above Table.

TABLE XVII.-Alcohol.

Unit-measure $\frac{1}{2}$ a cubic inch.

	Absorption.	
Measures.	Observed.	Calculated.
1	4 ·0	4.0
2	7.2	8.0
3	10.5	12.0
4	14.0	16.0
5	1 9·0	20.0
6	23.0	24.0
7	28.5	28.0
8	32.0	32.0
9	37.5	36.0
10	41.2	40.0
11	45.8	44.0
12	48 ·0	48·0
13	50.4	52.0
14	53·5	56.0
15	55.8	60.0

By mercurial gauge.				
Tension.	Deflection.	Absorption.		
‡ inch 1 inch	60 not practic	157 able.		

The difference between the measurements when equal *tensions* and when equal *volumes* at the maximum density are made use of is here strikingly exhibited.

In the case of alcohol I was obliged to resort to a unit-measure of $\frac{1}{2}$ a cubic inch to obtain an effect about equal to that

produced by benzole with a measure possessing only $\frac{1}{10}$ th of a cubic inch in capacity; and yet for equal tensions of 0.5 of an inch, alcohol cuts off precisely twice as much heat as benzole. There is also an enormous difference between alcohol and sulphuric ether when equal measures at the maximum density are compared; but to bring the alcohol and ether vapours up to a common tension, the density of the former must be many times augmented. Hence it follows that when equal tensions of these two substances are compared, the difference between them diminishes considerably. Similar observations apply to many of the substances whose deportment is recorded in the foregoing Tables; to the iodide and chloride of amyle, for example, and to the propionate of ethyle. Indeed it is not unlikely that with equal tensions the vapour of a perfectly pure specimen of the substance last mentioned would be found to possess a higher absorptive power than that of ether itself.

It has been already stated that the tube made use of in these experiments was of brass polished within, for the purpose of bringing into clearer light the action of the feebler gases and Once, however, I wished to try the effect of chlorine, vapours. and with this view admitted a quantity of the gas into the experimental tube. The needle was deflected with prompt energy; but on pumping out *, it refused to return to zero. To cleanse the tube, dry air was introduced into it ten times in succession; but the needle pointed persistently to the 40th degree from zero. The cause of this was easily surmised : the chlorine had attacked the metal and partially destroyed its reflecting power; thus the absorption by the sides of the tube itself cut off an amount of heat competent to produce the deflection mentioned above. For subsequent experiments the interior of the tube had to be repolished.

Though no other vapour with which I had experimented produced a permanent effect of this kind, it was necessary to be perfectly satisfied that this source of error had not vitiated the experiments. To check the results, therefore, I had a length of 2 feet of similar brass tube coated carefully on the inside with lampblack, and determined by means of it the absorptions of all the vapours which I had previously examined, at a common tension of 0.3 of an inch. A general corroboration was all I sought, and I am satisfied that the few discrepancies which the measurements exhibit would disappear, or be accounted for, in a more careful examination.

In the following Table the results obtained with the blackened and with the bright tubes are placed side by side, the tension

* Dense dark fumes rose from the cylinders on this occasion; a similar effect was produced by sulphuretted hydrogen.

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in the former being three-tenths, and in the latter five-tenths of an inch.

TABLE XVIII.

Absorption.

Vapour.	Bright tube, 0.5 tension.	Blackened tube, 0.3 tension.	Absorption with bright tube pro-
Bisulphide of Carbon .	. 5.0	21	23
Iodide of Methyle	. 15.8	60	71
Benzole	. 17.5	78	79
Chloroform	. 17.5	89	79
Iodide of Ethyle	. 21.5	94	97
Wood-spirit	. 26.5	123	120
Methylic Alcohol	. 29.0	133	131
Chloride of Amyle	. 30.0	137	135
Amylene	. 31.8	157	143

The order of absorption is here shown to be the same in both tubes, and the quantity absorbed in the bright tube is, in general, about $4\frac{1}{2}$ times that absorbed in the black one. In the third column, indeed, I have placed the products of the numbers contained in the first column by 4.5. These results completely dissipate the suspicion that the effects observed with the bright tube could be due to a change of the reflecting power of its inner surface by the contact of the vapours.

With the blackened tube the order of absorption of the following substances, commencing with the lowest, stood thus :---

Alcohol. Sulphuric ether, Formic ether. Propionate of ethyle; whereas with the bright tube they stood thus :----Formic ether, Alcohol. Propionate of ethyle, Sulphuric ether. As already stated, these differences would in all probability

disappear, or be accounted for on re-examination. Indeed very slight differences in the purity of the specimens used would be more than sufficient to produce the observed differences of absorption*.

[To be continued.]

* In illustration of this I may state, that of two specimens of methylic alcohol with which I was furnished by two of my chemical friends, one gave an absorption of 84 and the other of 203. The former specimen had been purified with great care, but the latter was not pure. Both specimens, however, went under the common name of methylic alcohol. I have had a special apparatus constructed with a view to examine the influence of ozone on the interior of the experimental tube.