V. On the Absorption and Radiation of Heat by Gaseous Matter.—Second Memoir. By John Tyndall, F.R.S., Member of the Academies and Societies of Holland, Geneva, Göttingen, Zürich, Halle, Marburg, Breslau, Upsala, la Société Philomathique of Paris, &c.; Professor of Natural Philosophy in the Royal Institution.

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#### § 1. Instruments.

The apparatus made use of in this inquiry is the same in principle as that employed in my last investigation\*. It grew up in the following way:—A tube was first procured to receive the gases through which radiant heat was to be transmitted, but it was necessary to close the ends of this tube by a substance pervious to all kinds of heat, obscure as well as luminous. Rock-salt fulfils this condition, and accordingly plates of the substance an inch in thickness, so as to be able to endure considerable pressure, were resorted to. In the earliest experiments a cube of boiling water was placed before one end of this tube, and a thermo-electric pile connected with a galvanometer at the other; it was found that if the needle pointed to any particular degree when the tube was exhausted, it pointed to the same degree when the tube was filled with air. Thus tested, the presence of dry air, oxygen, nitrogen, or hydrogen had no sensible influence on the radiant heat passing through the tube.

In some of these trials the needle stood at 80°, in some at 20°, and in others at intermediate positions. I reasoned thus:—The quantity of heat which produces the deflection of 20° is exceedingly small, and hence a minute fraction of this quantity, even if absorbed, might well escape detection. On the other hand, the quantity of heat which produces the deflection of 80° is comparatively large, but then it would require a large absorption to move the needle even half a degree in this position. A deflection of 20° is represented by the number 20, but a deflection of 80° is represented by the number 710. While pointing to 80, therefore, an absorption capable of producing a deflection of 15 or 20 degrees on the lower part of the scale, would hardly produce a sensible motion of the needle. The problem then was, to work with a copious radiation, and at the same time to preserve the needle in a position where it would be sensitive to the slightest fluctuations in the absolute amount of heat falling upon the pile.

This problem was finally solved by converting the pile into a differential thermometer. Its second face was exposed, and a second source of heat was placed in front of that face. A moveable screen was interposed between the two, by the motion of which the same amount of heat could be caused to fall upon the posterior surface of the pile as

\* Philosophical Transactions, 1861.

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that received from the experimental tube by its anterior surface. When this was effected, no matter how high the previous deflection might be, it was completely neutralized, and the needle descended to zero.

Supposing this equality to have been established when the tube was exhausted, it is manifest that any gas, capable of absorbing even an extremely small proportion of radiant heat, would, if introduced into the tube, destroy the equilibrium of both sources. The second source of heat would now predominate, and a deflection of the galvanometer needle would be the consequence. The magnitude of this deflection would depend on the quantity of heat cut off by the gas, and properly reduced it became a strict measure of the absorption.

But in these experiments my first source of heat stood at some distance from the anterior end of the tube, and the heat, previously to entering the latter, had to cross a space of air which was not the subject of examination. This air-space I wished to abolish, so as to allow the calorific rays to enter the gas with all the qualities which they possessed at the moment of emission. I first thought of soldering the end of the experimental tube direct to the radiating surface, thus allowing the air to come into direct contact with the source. But it immediately occurred to me that the introduction of cool air into the tube would lower the temperature of the source, and that I could never know how far the indication of my galvanometer under such circumstances could be regarded as a true effect of absorption; hence I abandoned the idea of bringing the gases into contact with the radiating surface.

Instead of this arrangement an independent tube, 8 inches long, and of the same diameter as the experimental tube, was soldered on to the radiating plate. By means of a screw joint, the free end of this tube was connected air-tight with the experimental tube. Thus a chamber, from which the air could be removed, was introduced between the first plate of salt and the radiating surface. Two objects were thus secured; firstly, my source of heat was withdrawn from the action of irregular currents of air; and, secondly, the radiant heat entered the tube unchanged in quality save the infinitesimal change due to its passage through the diathermic salt.

To save the trouble and expense of a new Plate, I will ask permission to reprint in this memoir the Plate made use of in my last; a verbal reference will in most cases be sufficient to indicate the changes recently introduced. SS' (Plate I.) it will be remembered represented the experimental tube, which was then made of brass polished within. Such a tube could not be used for any gases or vapours capable of attacking brass; and though I combated this difficulty, to some extent, by blackening the tube within, I could never feel at ease regarding the action of the gases upon the blackening substance. Many gases, moreover, present great difficulties on account of their affinity for atmospheric moisture. Hydrobromic and hydrochloric acid, for example, form dense fumes in the air, and however carefully they might have been dried, I should have been reluctant to base any inference on their deportment without actually having them under my eyes during experiment.

The brass tube, then, which stretched from S to S' in the figure is now replaced by one of glass, 2 feet 9 inches long, and 2.4 inches in diameter. The source of heat in my last-published inquiry was the cube of hot water C; but glass being far inferior to brass in reflecting power, I was unable with this source to bring out with due force the vast differences existing between various kinds of gaseous matter. I therefore had a copper hood constructed, and united by brazing with a tube 8 inches long, which was destined to form the vacuous chamber in front of the first plate of rock-salt. To heat the copper plate, a lamp formed on the principle of Bunsen's burner was made use of. The gas passed upwards by four hollow columns, each perforated for the admission of air. mixture of air and gas escaped from these columns into a chamber shaped like the frustum of a cone, and over this chamber was placed a shade of thin sheet-iron, the top of which was narrowed to a slit one-eighth of an inch wide and 2 inches long. From this slit the mixture of gas and air issued, and formed upon ignition a sheet of flame. was caused to glide along the back of the copper plate before referred to, which was thereby raised to a temperature of about 270°C. To preserve this source constant was one of the greatest difficulties of the investigation; for the slightest agitation of the surrounding air, or the slightest flickering of the flame itself, was sufficient to disturb the steadiness of the galvanometer and to render experiments in delicate cases impossible. The flame was surrounded by screens of pasteboard, these being again encompassed by towels, through the meshes of which the flame was fed; a suitable chimney produced a gentle draught and carried off the products of combustion; the rhythmic jumping of the flame itself was destroyed by screens of wire-gauze; in short, six weeks' practice was required to master all the difficulties of this portion of the apparatus. The "compensating cube" C', the double screen H, and the thermo-electric pile P remain as before. They are exposed in the figure, but during the experiments they were surrounded by a close hoarding, all the chinks of which were stuffed with tow, so as to protect the cube and pile from the disturbing action of the air. To protect the anterior plate of rock-salt from the heat which might have been conducted to it from the source, the front chamber passed as before through a vessel V in which a current of cold water, constantly renewed, was caused to circulate.

# § 2. Experiments.

On two points I wished to set my mind at rest previous to starting on my vacation tour this year. These were the absorption of chlorine gas and of ozone. On the 16th, 17th, and 18th of June, I experimented on these two substances, and satisfied myself that chlorine was far outstripped by many colourless gases, and that ozone had a power of absorption very much greater than common oxygen.

The work was resumed on the 12th of September, and my first care was to examine whether my published experiments on moist and dry air stood the test of repetition. Professor Magnus had experimented on dry air and on air saturated with moisture, and found that the presence of the moisture had no influence on the absorption. I, on the

contrary, had previously found, and stated, that dry air had only a small fraction of the absorptive energy of the same air when even partially saturated. I commenced my researches in September with a few experiments on this subject.

Half an atmosphere of the undried air of the laboratory admitted directly into the tube cut off an amount of heat which produced a deflection of 30 degrees.

My drying apparatus at this time consisted of a U-tube filled with fragments of pumicestone wetted with sulphuric acid. Associated with this was a similar tube filled with like fragments, but moistened with caustic potash solution, to remove the carbonic acid of the air.

The air of the laboratory passed through both these tubes in succession, till a tension of 15 inches was attained, gave a deflection of 26 degrees.

This result surprised me, showing, as it seemed to do, a very close agreement between dry and moist air. On examining the drying-tubes, however, I found that by a mistake of arrangement the air had entered the sulphuric acid tube first, and passed straight from the potash into the experimental tube; thus partially reloading itself with moisture after it had been dried.

The air was now sent through both tubes, commencing with the potash—the deflection fell instantly to less than 5 degrees. Hence this experiment showed the absorption due to the moisture and carbonic acid of the air to be more than six times greater than that of the atmosphere itself. It will presently be seen that the difference here stated falls far short of the truth.

The potash and sulphuric acid were now abandoned, and the air was dried by passing it through a U-tube filled with fragments of chloride of calcium, which had lain in the tube for some months. The deflection produced by air thus dried was 40 degrees; that is to say, 10 degrees more than that produced by the undried air.

This result, and many others of a similar nature, were due to the imperfection of the chloride of calcium. I think chemists ought to be very cautious in the use of this substance as a drying agent. When pure and newly fused it may answer for this purpose, but when old it yields an impalpable powder, which proved in the highest degree perplexing to me in my first experiments. It is generally found, I believe, that a drying-tube of sulphuric acid gains more in weight than one of chloride of calcium, and from this it has been inferred that the quantity of moisture taken up by the former is greater than that taken up by the latter. The difference, however, may really be due to the mechanical carrying away of a portion of the chloride by the current of air.

On the 13th of September these experiments were resumed. The dry air then gave a deflection of less than 2 degrees; the air direct from the laboratory caused, in one experiment, the needle to move from 20 degrees on one side of zero to 28 on the other. In a second experiment the undried air caused the needle to move from 18° on one side of zero to 32° on the other.

Experiments made on the 17th entirely corroborated this result. Three successive trials made the action of the undried air of the laboratory 29°, 31°, and 30° respectively;

the deflection produced by the dried air being less than a single degree. On this day, therefore, the action of the aqueous vapour of the air was at least thirty times that of the air itself.

Almost every week-day during the last four months experiments similar to the above have been executed, and in no case have I observed a deviation from the result that the absorptive action of the aqueous vapour of the air is quite enormous in comparison with that of the air itself. Further on I will give an array of figures illustrating this point.

As I became more and more master of my apparatus, and more acquainted with the precautions necessary in delicate cases, the absorption of air and the elementary gases diminished more and more. I was induced to abandon the use of pumice-stone as well as of chloride of calcium, and to construct my drying apparatus in the following way. The internal portion of a massive block of pure glass was pounded to small fragments in a mortar; these were boiled in pure nitric acid, and afterwards washed several times with distilled water so as to remove all trace of the acid. They were then dried, afterwards moistened with pure sulphuric acid, and introduced by means of a funnel into a U-tube. The funnel was necessary to preserve the neck of the tube from all contact with the acid, the least action of which upon the corks used to close the tube was sufficient to entirely vitiate the experiments. At the top of each arm of the U-tube a quantity of dry fragments of glass was placed, so that if any dust or particles from the cork or sealingwax chanced to reach the interior they fell upon the dry glass.

Similar precautions were taken with the caustic potash tube. Pure white marble was pounded to fragments and subjected to the action of a dilute acid, which removed the outer surface of the fragments. These were afterwards washed in distilled water and dried, then moistened with pure caustic potash, and introduced into the U-tube in the manner already described. It was sometimes necessary to perform this operation daily, and never on any occasion have I used tubes to dry a feeble gas which had been previously used to dry a powerful one.

In the present communication I shall have to touch upon many subjects which for want of time I have been unable to develope. The following is an example of these. Choosing a day of suitable temperature and moisture—a day on which the human breath shows no signs of precipitation—the action of the substances expired from the lungs may be most strictly determined by our apparatus. By breathing directly into the experimental tube, the action produced by the sum of the products of respiration might be accurately measured; by breathing through the sulphuric acid tube, the moisture of the breath would be withdrawn, and the difference between the action then observed and the former action would give that of the carbonic acid. In this way the products of respiration might be estimated singly, and the influence of various kinds of food and drink, or of physical exertion, on the respiration might be investigated in a manner hitherto unthought of.

I have to record the following experiments only in connexion with this subject. Placing a suitable tube between my lips, I filled my lungs with air; a stopcock which was interposed between me and the experimental tube being partially opened, I breathed through it slowly into the latter until the mercury gauge of the pump was depressed 15 inches. I had, at the time, two assistants, C. A. and R. C., and they subsequently breathed into the experimental tube the same quantity as myself. In the following Table the absorption produced by the breath of each is stated.

#### Action of the Products of Respiration on Radiant Heat.

Initials	of person	's na	ame.				A	bsorptic	on.
	J. T.	•	٠.					62	
	J. T.	• .						62	
	R. C.	٠.		•				66	
	R. C.			•			•	68	
	J. T. a	gaiı	ı.	•				<b>5</b> 9	
	J. T.	•					•	59	
	R. C.							63	
	C. A.				٠.			62	
	J. T.			•				60.5	

The absorption of dry air on the day that these results were obtained was found to be 1. The same dry air inhaled, underwent a chemical change which augmented its absorptive energy at least 60 times. I give this as a minor limit, and will not say how much I regard it as falling short of the truth.

The day afterwards the following results were obtained, the same amount as before being exhaled:—

Initials.				$\mathbf{A}$ b	sorpti	on
J. T.				•	56	
R. C.		•	• /	•	62	
J. T.				•	56	
R. C.					<b>59</b>	

In all cases R. C., who is the smallest and least robust man of the three, appeared to have the advantage. I will only add a few results obtained on the 6th of October, the quantity of air expired on the occasion depressing the mercurial column 5 inches.

Initials.																			A	bsorption.
J. T.				•				•	•	•		•	•		•	•	•	•	•	33.5
R. C.										•									•	35
R. C.	After 1	half	a gla	ss o	f Tı	rinit	у А	udit	t A	le				•		٠	•		•	41
	Again						•				•				•	•			•	35
	After a	a tea	spoor	nful	of l	bran	dy		•						•					35
	After of	$\operatorname{chew}$	ing a	$\mathbf{nd}$	swa	llow	ing	a sı	mal	l q	uan	tity	y of	on	ior	ι.			•	40

After taking the ale and brandy my assistant washed his mouth and gargled his throat several times with cold water. I give these results merely as illustrative of one of the

numerous applications of the apparatus. In all the experiments the tube remained perfectly transparent throughout, and, on pumping, the needle in each case returned accurately to zero.

**§** 3.

In my last paper I brought the fact somewhat prominently forward that the elementary bodies which I had then examined were far less hostile to the passage of the longer undulations than the compound ones; and I founded at the time certain theoretic considerations on this fact\*. I was desirous this year to extend the experiments to one or two of the coloured gases and vapours, and on the 20th of September resumed my experiments on chlorine. This gas is itself highly coloured, and of a specific gravity of 2·45; one of its compounds, hydrochloric acid, is quite transparent, and of specific gravity of only 1·26. Does the act of combination with hydrogen which renders chlorine gas more transparent to light render it also more transparent to heat? Chlorine prepared from hydrochloric acid and peroxide of manganese, and dried by passing it through sulphuric acid, was admitted into the tube till it depressed the mercury gauge 21 inches; the absorption of the gas was expressed by the number 44.

Hydrochloric acid was admitted till it depressed the gauge 19 inches; the absorption was 68. This experiment indicates that transparency to light and opacity to heat accompany the same act of chemical union.

The following results were afterwards obtained. I may remark that a subsidiary gauge was used, so as to prevent the destructive gases from entering the air-pump.

	$\mathbf{A}\mathbf{b}$	sorption.
Chlorine 15 inches		$3\overline{2}$
Chlorine 14 inches		30
Chlorine 14 inches		30
Hydrochloric acid 14 inche	s.	47
Chlorine again		30
Hydrochloric acid		56

In all cases the effect of the compound gas was found to exceed that of the elementary one; so that the chemical change which renders chlorine more transparent to light renders it more opake to obscure heat.

Great care is required in experiments on hydrochloric acid, and great care was bestowed on the above. Previously to the introduction of the gas the experimental tube was filled with perfectly dry air, so as to leave a perfectly dry residue on exhaustion. The gas was allowed to stream through the drying-tube until all traces of air were expelled; then a joint was suddenly broken, and the retort was connected with the experimental tube. The gas thus passed directly from the retort through the drying apparatus into the vacuum. It was difficult to avoid sending in with the gas a few particles of moisture; but these, if such existed, appeared to be dissipated by the dynamic

<sup>\*</sup> Philosophical Transactions, 1861.

heating of the gas on entering the tube, and kept dissipated by the flux of heat passing through it. At all events the closest scrutiny could detect no trace of mist or turbidity within the tube; it was perfectly transparent throughout. The chlorine, on the contrary, was intensely coloured.

I made many experiments with chlorine which had been collected over water, but something (what I know not yet) appeared to be in all cases carried along with the gas from the water into the tube, which materially augmented its absorption.

The above experiments were made in the early part of this inquiry, and before I had become aware of all the peculiarities of my apparatus. Subsequent experiments reduced in some degree the absorption both of chlorine and hydrochloric acid. Very careful experiments made on the 29th of October gave the following absorption for these two gases, at a tension of 30 inches:—

The chlorine and hydrochloric acid were removed from the experimental tube in the following manner:—A cock and connecting piece were attached to one end of the experimental tube, and from them a length of india-rubber tubing led to the flue of the laboratory stove. A gas-holder of air was put in connexion with the other end of the experimental tube, a system of drying-tubes intervening between the latter and the holder. By a slight water-pressure a stream of dry air was carried gently through the tube to the flue, and in this way the gases, which if pumped out would have injured the pistons, were speedily removed. As the dry air replaced the gases, the needle gradually descended to zero, its arrival there being indicative of the complete displacement of the gas. The perfect dryness of the air thus made use of was beautifully proved. Had the air contained moisture, it would instantly on its mixture with hydrochloric acid have rendered the medium within the tube turbid. However slight this turbidity might be, and however invisible to the eye, the galvanometer would have revealed it. But there was no movement in an upward direction; the needle gradually sunk from the moment the air entered.

As regards the influence of chemical union in the absorption of radiant heat, a still more severe test than that furnished by the substances last examined is presented by bromine and hydrobromic acid; for the opacity of the former to light is far greater than that of chlorine, while the two compounds are equally transparent. The density of bromine, moreover, is 5·54, whereas that of hydrobromic acid is only 2·75. The difficulty of operating with the acid compound of bromine is at least equal to that attendant on hydrochloric acid, and several successive days were spent in endeavouring to arrive at safe conclusions in connexion with this subject. Bromine dried with phosphoric acid was introduced into a flask furnished with a screw cap, which enabled it to be attached to the experimental tube. By turning a stopcock, the pure vapour was allowed slowly to enter until the mercury column was depressed two inches. From more than twenty experiments made with this substance, I should infer that the absorption of the quantity

mentioned does not exceed

11,

while the absorption of hydrobromic acid of the same tension amounts to 30.

The hydrobromic acid was prepared by the action of glacial phosphoric acid (for a pure specimen of which I have to thank my friend Dr. Frankland) on bromide of potassium. If the above figures represent the truth (and I have spared no pains to arrive at a right conclusion), we have here a most striking instance of transparency to light and opacity to obscure heat being promoted by the self-same chemical act\*.

§ 4.

In the following Table is given the absorption of a number of gases at a common tension of one atmosphere.

		,	TAI	BLE	I.			
1	Tame	<b>.</b>						Absorption.
Air .							•	1
Oxyge	n			•		•		1
Nitrog	en	•						1
$\mathbf{H}\mathbf{y}\mathbf{d}\mathbf{r}\mathbf{o}$	gen						•	1
Chlori	ne						•	39
Hydro	chlo	ric	ac	$\operatorname{id}$				62
Carbon	nic (	xi	le			٠.		90
Carbon	ic a	cic	ĺ					90
Nitrou	s ox	$\operatorname{cid}\epsilon$	·					355
Sulphi	iret	ted	hy	dro	oge:	n		390
Marsh	-gas					•		403
Sulphu	irou	ıs a	$\operatorname{cid}$					710
Olefiar	ıt ga	as						970
Ammo	nia							1195

Air, oxygen, nitrogen, and hydrogen are all set down as equal to unity in the above Table. I do not mean thereby to affirm that there are no differences between these gases as regards their powers of absorption, but that the most powerful and delicate tests which I have hitherto applied have failed to establish a difference in a satisfactory manner. It is not improbable that the action of these gases may turn out to be less even than I have found it. For who can say that the best-constructed drying apparatus is really perfect? Besides, stopcocks must be greased, and hence may contribute an infinitesimal impurity to the air passing through them. I cannot even say that sulphuric acid, however pure, may not deliver a modicum of vapour to the current of air passing through it. At all

<sup>\*</sup> A layer of liquid bromine, sufficiently opake to intercept the entire luminous rays of a gas-flame, is highly diathermanous to its obscure rays. An opake solution of iodine in bisulphide of carbon behaves similarly.—The details of these experiments shall be published in due time: they were publicly shown in my lectures many months ago.—June 13th, 1862.

events, if any further advance should be made in the purification of the gases, it will certainly only tend to augment the enormous differences exhibited in the above Table.

Ammonia, of the tension mentioned, stands highest in the above list as regards absorptive energy. I believe that a length of less than 3 feet of this gas, which to the vision is as transparent within the tube as the vacuum itself, is *perfectly black* to the rays emanating from the source here made use of. When the gas was in the tube, the interposition of a double metallic screen between the pile and source augmented the deflection very slightly. But I shall show further on that the ammonia in this experiment could not exhibit the full energy of its absorption, and that the length indicated is in all probability absolutely impervious to the heat issuing from our source.

It would be a mere affectation of accuracy to try to deal with smaller quantities of the first four substances mentioned in the Table than those with which I have here operated. Still, if such small quantities could be directly measured, the action of air, oxygen, hydrogen, and nitrogen, in comparison with that of the other substances at the same tension, would doubtless be greatly reduced. With the energetic gases the rays are most copiously struck down by the quantities which first enter the tube, the quantities which enter last producing in many cases an infinitesimal effect. Now I have shown in my last paper that for very small absorptions the effect is sensibly proportional to the quantity of gas present, and this would seem to justify us in assuming that for 1 inch of tension the absorption of air, oxygen, nitrogen, and hydrogen would be  $\frac{1}{30}$ th of the absorption at 30 inches. With all the other gases I have measured directly the absorption of a quantity possessing in each case a single inch of tension. Assuming the proportionality just referred to, and again calling the effect of air unity (the unit, however, being only  $\frac{1}{30}$ th of that in the last Table), the following are the relative absorptions:—

			T	`ABI	Œ]	II.			
$\operatorname{Air}$									1
Oxy	gen	L							1
Nitr	oge	$\mathbf{e}\mathbf{n}$			:			•	1
Hyd	lrog	gen						•	1
Chlo	orin	e		•			•		60
Bro	min	ıe							160
Hyd	lrol	oroi	$_{ m nic}$	ac	$\operatorname{id}$				1005
Carl	bon	ic c	oxid	le					750
Nita	ric (	oxi	de						1590
Niti	ous	s ox	$\operatorname{cid}\epsilon$	e .					1860
Sul	phi	de d	of l	ıyd	rog	en			2100
Am	$\mathbf{mo}$	nia						•	7260
Ole	fian	t g	as						7950
Sul	phu	rou	ıs a	cid					8800

Here we have the extraordinary result that for tensions of 1 inch of mercury the

absorption of ammonia is over seven thousand times, the absorption of olefant gas seven thousand nine hundred and fifty times, while the action of sulphurous acid is eight thousand eight hundred times that of air.

It is impossible not to be struck by the position of chlorine and bromine in this Table. They are elements, and notwithstanding their colour and density, they take rank after the transparent elementary gases. The perfectly transparent elementary gases. more than one hundred and thirty times the amount absorbed by the untransparent chlorine, and nearly fifty times the quantity absorbed by the intensely brown vapour of bromine. I cannot think this fact insignificant. Hitherto chemists have spoken to us of elements, and we have helped ourselves to conceptions regarding them and their compounds in the only way possible to our mental constitution. But our conceptions remained purely subjective, nor were we acquainted with any physical trait which would in any degree justify these conceptions. Here, however, we seem to touch the ultimate particles of matter. Starting from the idea that a gas absorbs such vibrations as are isochronic with its own, in all cases the compound gas reveals itself to the mind's eye with its molecules on the whole swinging more slowly than the uncombined atoms of which it is composed. Their absorption of the longer undulations proves their general coincidence in period with those undulations. We load the atom by the act of chemical union, and thereby render its vibrations more sluggish, that is to say, more fit to synchronise with the slowly recurrent waves of obscure heat.

In the foregoing Table I have given the absorption of nitric oxide as 1590, which is less than that of nitrous oxide, though the molecule of the former contains a greater number of atoms than that of the latter. It will be noticed that those gases which on combining suffer no condensation are less energetic absorbers than those which suffer a reduction of volume. Whether this rule is universal I am as yet unable to say.

It is very difficult to operate with nitric oxide; the affinity of the gas for oxygen is so enormous that the slightest trace of this substance gives rise to the brown fumes of nitrous acid. On first sending this gas into the experimental tube, 1 inch of it gave an absorption of 2040; but the needle slowly went up afterwards, until it finally indicated an absorption of 5100. On looking across the tube at this time, the brown hue of nitrous acid was discernible.

In a second experiment I made the vacuum as perfect as possible; on allowing nitric oxide to enter, the absorption was 1860, but the needle soon afterwards declared an absorption of 3060, the brown fumes appearing as before.

On filling the experimental tube with nitrogen, then exhausting, and allowing nitric oxide to enter, the absorption of 1 inch of the gas was 1680. On filling the experimental tube previously with hydrogen the absorption was 1590, which is that given in the Table. On letting in a mixture of air and nitric oxide till the tube was filled, the action last mentioned was augmented nearly twentyfold. Nitrous acid is therefore an extremely energetic gas. The difference between it and bromine is enormous when the colours of both are equally dense.

A close inspection of Melloni's Table \* reveals, I think, the tendency of solid bodies also to become more transparent to heat as their composition becomes more simple. After rock-salt itself comes the element sulphur, and after it fluor-spar. But the case of lampblack will here occur to many, who regard it as the most powerful absorber and radiator yet discovered. No doubt the grouping of the atoms of an elementary substance may make it tantamount to a compound, and no doubt this is actually the case with lampblack; another eminent example of this kind is referred to in this paper in the section on ozone. Leslie, however, found water to be a better radiator than lampblack, and Wells found several substances which were more capable of being chilled by nocturnal radiation. On reflection, moreover, the following considerations arise. lampblack of commerce and the soot of a lamp or candle, that is to say, the substances which have been hitherto employed in experiments on radiant heat, are copiously mixed with hydrocarbons, which are the most powerful absorbers and radiators in Nature. might fairly be questioned whether the reputed experiments with lampblack really dealt with lampblack at all. But even the impure substance is to some extent transparent to radiant heat.

I have plates of black glass, rendered so by the solution of carbon in the glass while in a state of fusion, and which, though they are impervious to the rays of the most intense electric light, allow of a copious transmission of the rays of obscure heat. Melloni's beautiful experiments on glass of this character are well known; indeed mine are but repetitions of his. Another of Melloni's experiments which I have recently verified is the following. A plate of transparent rock-salt was placed over a smoky camphine lamp, and soot was deposited on its surface until it intercepted every ray of a brilliant jet of gas. The plate was placed between a source of heat possessing a temperature of 100° C., and a thermo-electric pile, a polished screen being placed between the salt and the source. As long as the screen remained, the needle of the galvanometer connected with the pile stood at zero; but the moment the screen was removed the needle promptly advanced, showing the instantaneous transmission across the layer of soot of a portion of the heat incident upon the salt. The actual numbers obtained in this experiment are these:—The deflection produced by the heat transmitted through the soot was 52°; which is equal to 90 units. The deflection produced when the layer of soot had been carefully removed, so as to leave both surfaces of the salt smooth and transparent, was 71°, which is equal to 300 units. The quantity transmitted through the soot is therefore to the total quantity as

that is to say, the lampblack, which was perfectly opake to the light of a gas-jet, was transparent to fully 30 per cent. of the incident heat. On consulting Melloni's Table, I was gratified to find that he made the transmission by a plate similarly prepared

<sup>\* &#</sup>x27;La Thermochrôse,' p. 164.

27 per cent.; while a layer so opake that it cut off the beams of the sun itself transmitted 23 per cent. of the rays emitted by a source heated to 100° C.

At page 93 of 'La Thermochrôse,' Melloni examines the absorption of this substance for all sorts of rays, and by a series of ingenious experiments, and reasonings remarkable for their clearness and precision, he arrives at the conclusion that lampblack absorbs with the same intensity all descriptions of radiant heat\*. At page 284, however, he cites and discusses with the same precision a series of experiments made with smoked rock-salt, in which he shows that the same layer of lampblack transmits 8 per cent. of the rays from a lamp of Locatelli, 10 per cent. of those of incandescent platinum, 18 per cent. of those from copper heated to 400° C., and fully 23 per cent. of those emitted by a source of 100° C. Now a transmission of 8 per cent. implies an absorption of 92; while transmissions of 10, 18, and 23 per cent. imply absorptions of 90, 82, and 77. But that the self-same layer of lampblack absorbs 77 per cent. of the rays from one source and 92 per cent. of the rays from another, is at variance with the statement that lampblack absorbs heat from all sources with the same intensity. Suppose the surface of a thermo-electric pile to be coated by a layer of lampblack of the same thickness as that which coated Melloni's plate of salt; 23 per cent. of the rays from a source of 100°C. would go right through such a layer and impinge upon the metal face of the pile; and if the latter were a good reflector, the heat incident upon it would be in great part retransmitted through the lampblack and lost to the instrument. For a source of 100° C., this loss would be many times greater than for a Locatelli lamp. Possibly, however, Melloni meant simply to assert that for practical purposes the absorption by the face of his pile might be considered to be the same for all kinds of heat †.

§ 5.

I have now to record some new experiments on the action of vapours upon radiant heat. A number of glass flasks were prepared, of the shape and size of common test-tubes, each of which was furnished with a brass cap carefully cemented on to it. By means of this it could be attached to a stopcock, and thus connected with the experimental tube. The mode of operation was this. The liquid was introduced into the flask by means of a small glass funnel; the stopcock (S) was then attached to the flask and connected with a second air-pump, which was always kept at hand. The air above the liquid was removed, and the air dissolved in it was allowed to bubble away, until nothing remained but the pure liquid below and the pure vapour above it. The stopcock S was now shut off, and the flask united to the experimental tube. The exhaustion of the tube and stopcocks being complete, and the needle of the galvanometer at zero, the cock S was turned on and the mercury-gauge carefully observed at the same time.

<sup>\* &</sup>quot;Donc, le noir de fumée absorbe avec la même intensité toute sorte de rayonnements calorifiques" (p. 101).

<sup>†</sup> The sun, through the floating carbon of the London atmosphere, sometimes presents a most instructive appearance. Entirely shorn of his rays and of perfectly uniform brightness, his colour at times is as red as blood. This is doubtless mainly due to the comparative transparency of the floating carbon for the longer undulations.

No bubbling of the liquid was in any case permitted. The vapour entered silently and without the slightest commotion, and when the mercurial column was depressed to the extent required, the cock S was promptly turned off.

The energy with which the needle moves the moment a strong vapour enters is so extraordinary, that I was compelled to remove the stops which arrested the swing of the needle at 90°, lest the shock against them should derange the equilibrated magnetism of the astatic pair. The needle often swung far beyond a quadrant; and after it had come finally and permanently to rest, its position was observed in the following manner:— The dial of the galvanometer being well illuminated, a looking-glass was placed behind the instrument, at such an angle that when looked at horizontally the image of the dial was clearly seen. This image was observed by an excellent telescope, fixed at a distance of 11 feet from the galvanometer. Attached to the needle, and in continuation of it, was a bit of glass fibre of extreme fineness, which ranged over the graduated circle, and by means of it a very small fraction of a degree could be easily read off. I resorted to the expedient of observing from a distance, because I found that the approach of my person, perhaps through the diamagnetic action of my own body, had a sensible effect upon the needle of my instrument, which, I believe, surpasses in delicacy any hitherto constructed.

The permanent deflection of the needle was noted in all these experiments, and the value of the deflection, expressed in terms of one of the lower degrees of the galvanometer, was obtained from a table of calibration. To spare unnecessary labour, I omit the deflections in the following Table, and give the absorptions only produced by the vapours mentioned, at 0·1, 0·5, and 1·0 inch of tension.

	7	AB	LE	III.		
					Tensions.	
Name of substance.			(	Of inch.	0.5 inch.	1.0 inch.
Bisulphide of carbon .			•	15	47	62
Iodide of methyl	÷			35	147	242
Benzol				66	182	267
Chloroform				85	182	236
Methylic alcohol		•,		109	390	590
Iodide of ethyl				158	290	390
Amylene				182	535	823
Sulphuric ether				300	710	870
Alcohol				325	622	
Formic ether				480	870	1075
Acetic ether			٠	590	980	1195
Propionate of ethyl	•			596	970	
Boracic ether		,		620		

Let us compare some of the results of this Table of transparent vapours with the action of the highly coloured vapour of bromine. The absorption of bromine vapour at 1 inch

tension is about 6, and at 0·1 of an inch tension would probably not exceed 1; hence, at 0·1 of an inch tension, bisulphide of carbon has probably 15 times the absorbent power of bromine; but bisulphide of carbon is the feeblest of the compound vapours that I have yet discovered. The strongest of these, boracic ether, has, according to the above estimate, and at the tension stated, more than 600 times the absorbing energy of the strongly coloured bromine.

The whole of the numbers in the above Table are referred to atmospheric air as unity; 0.1 of an inch of bisulphide of carbon vapour, for example, absorbs 15 times as much as a whole atmosphere of air. Let us compare, for an instant, the action of boracic ether with that of air. We arrive at an approximate comparison in this way. The absorption of the tenth of an inch of boracic ether is something more than that of a whole inch of methylic alcohol; by diminishing the quantity of methylic alcohol to one-tenth, we reduce its absorption from 590 to 109. The absorption of one-tenth of an inch of boracic ether is  $620^{\circ}$ ; suppose it to diminish in the proportion above found for methylic alcohol, we should have for 0.01 of an inch of boracic ether an absorption of 111; that is to say, for  $\frac{1}{3000}$ th of an atmosphere of boracic ether, we should have an absorption 111 times that of a whole atmosphere of oxygen, nitrogen, hydrogen, or atmospheric air.

With the transparent elementary gases it is impossible to measure directly the absorption of 0·1 of an inch; but assuming, as before, that up to an absorption of 1 the effect is proportional to the quantity of gas present, the absorption of each of the elementary gases, at a tension of 0·1 of an inch, would be about 0·0033; hence the absorption of boracic ether of 0·1 of an inch tension is to that of air at the same tension as

620:0.0033,

which would give to the ether an energy 186,000 times that of air.

I have already spoken of the blackness of ammonia at 30 inches tension. Referring to Table I., its absorption is found to be 1195. In the last Table the vapour of acetic ether, possessing only one-thirtieth of the tension of the ammonia, produces apparently the same effect; its absorption is also 1195. Such facts give one entirely new ideas of the capabilities of matter, and our wonder will not be diminished by the results to be recorded further on.

With both gases and vapours we find that it does not follow that a gas which produces a larger effect than another at one tension should surpass that other at all tensions. Some gases start from a lower level than others, but finally attain an equal, or even a greater elevation. If their absorptions were represented by curves plotted from the same datum-line, these curves would in some cases approach, and in some cases cross each other. At a tension of 1 inch, for example, carbonic acid has more than double the absorptive power of carbonic oxide, whereas at a tension of 30 inches they are equal; indeed some of my experiments show carbonic oxide to have the advantage. On the 22nd of October, for example, I found the deflection produced by 2 inches of carbonic oxide to be 15°, while that of 2 inches of carbonic acid was 38°. The two gases

at a tension of 30 inches gave these results:—

Carbonic	oxide				$5 {2}$
Carbonic	acid .		_		51.5

And again, on the 4th of November I obtained the following relative effects:—

			T	ensions.
			1.2 inches	. 24 inches.
Carbonic oxide	٠		. $1\mathring{2}$	$5\r7$
Carbonic acid .			. 37	54

The same remarks apply to vapours. Methylic alcohol, for example, starts at a lower level than the iodide of ethyl, but ascends more quickly, and finally reaches a much higher elevation. The same observation may be made of chloroform in comparison with benzol and the iodide of ethyl.

**§** 6.

I have now to refer to a class of facts which surprised and perplexed me when I first observed them. As an illustration, I will first take the case of alcohol vapour. A quantity of this substance, sufficient to depress the mercury gauge 0.5 of an inch, produced an absorption which caused a deflection of 72° of the galvanometer needle.

While the needle pointed to this high figure, and previously to pumping out the vapour, I allowed dry air to stream into the tube, and happened while it entered to observe the effect upon the galvanometer. The needle, to my astonishment, sank speedily to zero, and went to 25° at the opposite side. The entry of the almost neutral air here not only abolished the absorption previously observed, but left a considerable balance in favour of the face of the pile turned towards the source. A repetition of the experiment brought the needle down to zero, and sent it to 38° on the opposite side. In like manner a very small quantity of the vapour of sulphuric ether produced a deflection of 30°; on allowing dry air to fill the tube the needle descended speedily to zero, and swung to 60° at the opposite side.

These results both perplexed and distressed me, for I imagined, on first observing them, that I had been throughout dealing with an effect totally different from absorption. I thought, at first, that my vapours had deposited themselves in opake films on my plates of rock-salt, and that the dry air on entering had cleared these films away, and allowed the heat from the source free transmission.

But a moment's reflection dissipated this supposition. The clearing away of such a film could at best but restore the state of things existing prior to its formation. It might be conceived of as bringing the needle again to 0°; but it could not possibly produce the negative deflection, which, in the case of ether vapour, amounted to the vast amplitude of 60°. Nevertheless I dismounted the tube, and subjected the plates of salt to a searching examination. I satisfied myself thus that no such deposition as that

above surmised took place. The salt remained perfectly transparent while in contact with the vapour.

Some of the experiments recorded in the Bakerian Lecture for this year (1860) had taught me that the dynamic heating of the air when it entered the exhausted tube was sufficient to produce a very sensible radiation on the part of any powerful vapour contained within the tube, but I was slow to believe that the enormous effect above described could be thus accounted for. My first care was to determine the difference of temperature between a thermometer placed within the tube at the end furthest from the source, and one placed without it. I then examined, by an extremely sensitive thermometer, the increase of temperature produced by the admission of dry air into the tube, and the decrease consequent on pumping out; and found the former to be a considerable fraction of the total heat transmitted from the source. Could it be that the heat thus imparted to the alcohol and ether vapours, and radiated by them against the adjacent face of the pile, was more than sufficient to make good the loss by absorption? The experimentum crucis at once suggested itself here. If the effects observed be due to the dynamic heating of the air, we ought to obtain them even when the sources of heat made use of in the experiments are entirely abolished; and we should thus arrive at the solution of the novel, and at first sight utterly paradoxical problem, To determine the radiation and absorption of gases and vapours without any source of heat external to the gaseous body itself.

For the sake of brevity, I will call the heating of gas by its admission into a vacuum, the dynamic heating of the gas; and the chilling accompanying its pumping out, dynamic chilling. It would also contribute to brevity if I were allowed to call the radiation and absorption of the gaseous body, consequent on such heating and chilling, dynamic radiation and dynamic absorption, though I fear the terms are not unobjectionable.

# § 7. On Dynamic Radiation and Absorption.

Both the source of heat and the compensating cube were dispensed with, and the thermo-electric pile was presented to the end of the cold experimental tube. By a little management, the slight inequality of radiation against both faces of the pile, arising from differences in the various parts of the laboratory, was obliterated, and the needle of the galvanometer thus brought to 0°.

The vapours were admitted in the manner already described, until a tension of 0.5 of an inch was obtained. The air was then allowed to enter through a drying apparatus by an orifice of a constant magnitude. Two stopcocks, in fact, were introduced between the drying-tube and the experimental tube; one of these was kept partially turned on, and formed the gauge for the admission of the air. When the tube was to be exhausted, the second stopcock was turned quite off. When the tube was to be filled, this stopcock was turned full on; but the gauge-cock was never touched during the entire series of experiments.

Before, however, the mode of experiment was thus strictly arranged, a few preliminary trials gave me the following results:—

Nitrous oxide on entering caused the needle to swing in a direction which indicated the heating of the gas; the limit of its excursion was 28°, after which it slowly sunk to 0°.

The pump was now worked; the propulsion of the first portions of the gas from the tube was so much work done by the residue. That residue became consequently chilled; into it the face of the pile adjacent poured its heat, and a swing of the needle on the negative side of 0° was the consequence. The limit of the excursion was 20°.

Olefiant gas, operated on in the same manner, produced on entering the tube a swing of  $67^{\circ}$ , showing radiation; and on pumping out, a swing of  $41^{\circ}$ , showing absorption. After the pumping out of the gas, and without introducing a fresh quantity, dry air was again admitted; the swing produced by the dynamic radiation of the residue of the gas (0.2 of an inch intension) was  $59^{\circ}$ . On pumping out very quickly, the dynamic absorption produced a deflection of nearly  $40^{\circ}$ .

A little of the vapour of sulphuric ether was admitted into the tube; on the admission of dry air afterwards the needle swung from  $0^{\circ}$  to  $61^{\circ}$ ; on pumping out, the needle ran up to  $40^{\circ}$  on the opposite side.

These and other experiments, which I confess gratified me exceedingly, showed that, without resorting to any source of heat external to the gaseous body itself, its radiation and absorption might be determined with extreme accuracy, and the reciprocity of both phenomena rendered strikingly clear. In fact, at this very time I had been devising an elaborate apparatus for the purpose of examining the radiation of gases and vapours, with a view to comparing it with their absorption; but no such apparatus would have given me results equal in accuracy to those placed within reach by the discovery of dynamic radiation and absorption.

The following Table is the record of a series of experiments in connexion with this subject. The vapour in each case was admitted till the mercury column fell half an inch, and dry air was admitted afterwards.

Table IV.—Dynamic Radiation and Absorption of Vapours.

				flections.	
			$\mathbf{R}$	adiation.	Absorption.
				$1\mathring{4}$	$ m \mathring{6}$
	•			19.5	8
				30	14
				34	15.5
				36	
				41	23
		•	•	48	
		•		50	27.5
				64	34
				68.5	<b>3</b> 8
•		ø		70	43
	•		· · · · · · · · · · · · · · · · · · ·		Radiation.

The paradox already referred to is here solved, and the explanation given of the extraordinary effect observed in the case of the alcohol and ether vapours when dry air entered the experimental tube. Dynamic radiation, moreover, and dynamic absorption go hand in hand; and if we compare both with Table III., we shall find the order of the substances precisely the same, although one set of results are obtained with a source of heat external to the gaseous body, and the other with a source of heat and cold within the body itself. Had I sufficient time at my disposal, I could develope this subject with advantage. The results just recorded constitute my first regular series of experiments, and no doubt augmented experience will enable me to attain more perfect results.

I could not well obtain half an inch of my most energetically acting vapour, namely, boracic ether; but one-tenth of an inch admitted into the tube and dynamically heated and chilled, gave—

Radiation. Absorption. 56° 28°

Seeing the astonishing energy with which some of these vapours absorb and radiate heat, it may be asked how far the quantity of vapour may be reduced before its action becomes insensible. At present I will not venture to answer this question fully; certainly we should be dealing at least with millionths of our smallest weights. But I will here lay before the Society an account of one experiment, the result of which can hardly fail to excite astonishment. The experimental tube being exhausted, one-tenth of an inch of boracic ether vapour was admitted into it; the barometer stood at 30 inches at the time, hence the tension of the vapour within the tube was  $\frac{1}{300}$ th of an atmosphere.

Dynamically heated by dry air, the radiation of this vapour produced a deflection of 56°.

The tube was then exhausted to 0.2 of an inch, and the quantity of vapour reduced thereby to  $\frac{1}{150}$ th part of its first amount; the needle was allowed to come to zero, and the residue of vapour was dynamically heated as before: its radiation produced a deflection of  $42^{\circ}$ .

The pump was again worked till a vacuum of 0.2 of an inch was obtained, this residue containing of course  $\frac{1}{150}$ th of the quantity of ether present in the last. On dynamically heating this residue, its radiation produced a deflection of  $20^{\circ}*$ .

Two additional exhaustions, succeeded by dynamic heating, gave the deflections 14° and 10° respectively.

Tabulating the results so as to place each deflection beside the vapour-tension which produces it, we have the following view of the experiment:—

\* This is less than the truth; my assistant having executed three or four strokes of the pump inadvertently while the dry air was not shut off, removing thereby a considerable proportion of the vapour which ought to be present at this stage of the experiment.

Table V.—Dynamic Radiation of Boracic Ether.

Tension in parts of an atmosphere.	Deflection.
of an atmosphere.	0
$\frac{1}{300}$ th	56
$\frac{1}{150} \times \frac{1}{300} = \frac{1}{45000} \text{th}$	42
$\frac{1}{150} \times \frac{1}{150} \times \frac{1}{300} = \frac{1}{6750000}$ th	20
$\frac{1}{150} \times \frac{1}{150} \times \frac{1}{150} \times \frac{1}{150} \times \frac{1}{300} = \frac{1}{1012500000} th$	14

The air itself, slightly warming the apparatus near the pile, produces a feeble radiation, amounting to 6° or 7°. I have purposely excluded the deflection 10°, in order to show that the effect was still diminishing when the experiment ended, the constant effect due to the air itself being not yet attained. I thus exclude two 0s from the denominator of my fraction which might fairly have appeared in it. The above result is, however, sufficiently extraordinary, showing as it does that the radiation of an amount of vapour possessing in our tube a tension of less than the thousand millionth of an atmosphere is perfectly measurable. It will also be borne in mind that the temperature imparted to this infinitesimal quantity of matter did not exceed 0.75 of a Centigrade degree.

These experiments, which I intend to develope on a future occasion, seem to give us new ideas as to the nature and capabilities of matter. A platinum wire raised to whiteness in a vacuum by an electric current, becomes comparatively cold in a second after the current has been interrupted; yet that wire, while ignited, was the repository of an immense amount of mechanical force. What has become of this? It has been conveyed away by a substance so attenuated that its very existence must for ever remain an hypothesis. But here is matter that we can weigh, measure, taste, and smell; that we can reduce to a tenuity, which, though expressible by numbers, defeats the imagination to conceive of it. Still we see it competent to arrest and originate quantities of force, which on comparison with its own mass are almost infinite, a small fraction of this force causing the double needle of the galvanometer to swing through considerable arcs. When we find common ponderable matter producing these effects, we have less difficulty in investing the luminiferous ether with those mechanical properties which have long excited the interest and wonder of all who have reflected upon the circumstances involved in the undulatory theory of light.

In the foregoing experiments dry air was used to warm the vapours, but similar differences ought to be exhibited by gases when heated by their own dynamic action. This is the case, as the following experiments show:—

Table VI.—Dynamic Radiation of Gases.

Name.				$\mathbf{R}$	adiation
Air			•		$\mathring{7}$
Oxygen					7
Hydrogen .					7
Carbonic oxide					19
Carbonic acid					21
Nitrous oxide		•			31
Olefiant gas .		46			63

I also satisfied myself of the energetic radiation of the two following gases, which, however, were used in irregular quantities. They were admitted into the tube from a large bolthead, until a common tension was established between the gas in the tube and the gas in the bolthead.

		Radiation.	Absorption.
Ammonia 15 in. tension		. 56.5	$3\mathring{3}\cdot 5$
Sulphurous acid 16 in. tension		. 45	24

Let us reflect for an instant on the condition of our tube with its  $\frac{1}{2}$  inch of vapour at the moment when the latter has been heated by the entrance of the air. The gaseous column is heated throughout to the same temperature; the elastic condition of the luminiferous ether is the same for all the particles, and consequently their periods of vibration are all the same. Hence each molecule is in that precise condition which enables it to absorb most effectually the undulations emanating from its neighbours. The rays from the particles at the end of the tube most distant from the pile have to cross a space of nearly 3 feet before they reach the latter, this space being partially filled with molecules circumstanced as just described. Hence absorption to a comparatively greater extent must occur; and indeed we can imagine the tube so long that its frontal portion should furnish a vapour screen absolutely opake to the radiation of its hinder portion. Comparing ether vapour with olefant gas, it is, I think, evident that the radiant points of the attenuated vapour which depresses the mercury column only 0.5 of an inch, are further apart than those of the gas which depresses the column 30 inches. Consequently there is a wider door open for the radiation of the distant ether particles towards the pile than for the distant particles of olefiant gas. The length of the whole column, in fact, might be available for the radiation of the vapour, and a part of it only available for the gas. Cut off this unavailable portion from the gas column, and we do not injure its efficacy; but cut off a similar length from the vapour column, and we may materially diminish its effect. Speaking generally, by reducing the column of ether and that of gas by the same amount, the diminution of radiation will be most sensibly felt where the radiant points are furthest asunder. Reasoning thus, it becomes evident that in a long tube the vapour may excel the gas in its amount of radiation, while with a short tube the gas may excel the vapour. Let us now test this reasoning by experiment.

The dynamic radiation of the following four substances has been tabulated thus:—

Sulphuric ethe	er					$6\overset{\circ}{4}$
Formic ether			•			68.5
Acetic ether						70
Olefiant gas	_	_				63

The action of olefant gas is therefore smallest when the length of the radiating column is 2 feet 9 inches.

Experiments of the same character were made with a tube 3 inches long, or of the

former length, and the following results were obtained:-

Sulphuric ether				$1\mathring{1}$
Formic ether .				12
Acetic ether .				15
Olefiant gas .				39

The verification of the above theoretic reasoning is here complete. It is proved that in a long tube the dynamic radiation of the vapour exceeds that of olefant gas, while in a short tube the dynamic radiation of the gas far exceeds that of the vapour.

§ 8.

The apparatus with which these experiments were made is capable of very diverse uses. Attached to a compression pump, with it the relation between the mechanical force expended in compressing a gas and the heat developed might be accurately determined. If oxygen, hydrogen, nitrogen, or air were the body compressed, the conversion of vis viva into heat might be declared by a modicum of vapour always kept in the tube, while a compound gas would tell its own tale.

Another interesting point might be, and indeed has been settled by the apparatus. Some years ago a discussion was carried on between Professors Challis and Stokes on Laplace's correction for the velocity of sound, Professor Challis contending that LAPLACE had no right to his correction, inasmuch as the heat developed by the local compression of a mass of air of indefinite extension would be instantly wasted by radiation. Experiments, he argued, conducted in confined vessels furnish no ground for drawing conclusions regarding what occurs in the atmosphere, where the heat developed has an indefinite space to lose itself. In our experimental tube, though it is mechanically closed, indefinite extension, as regards the radiation of heat, is secured in one direction, and the means also exist of measuring the flux of heat in this direction. is true for one direction is of course true for all, so that the apparatus will inform us of what must occur in the open atmosphere. Now with the most powerful radiating gases which I have examined the radiation continues a very sensible time, while the heat acquired by air on entering the tube is often a source of inconvenience on account of the inability of the air to disperse its heat by radiation. The question is therefore experimentally decided in favour of LAPLACE and his supporter.

I would here dwell for a moment on this comparative absence of radiating power on the part of air, and of the elementary gases generally. The air is the sole source of the heat which has warmed the vapours in our experiments on dynamic radiation; it is related to them precisely as a hot polished metal plate is to the coat of varnish which makes it a radiator. The air and the metal, both elements or mixtures of elements, are incompetent to impart motion to the luminiferous ether without the intermediation of a second body. They possess the motion, but they are so related to the ether that they cannot communicate this motion to it directly, or only in an extremely feeble degree. The atoms of

air oscillate, but the ether does not swell. We have here a definite picture before the mind's eye, which, if the theory of an ether be true, is as certain as any conclusion of mathematics, and would hardly be rendered more certain if the physical vision were so sharpened as to be able to see the oscillating atom and the fluid in which it swings. I write thus strongly and definitely lest it should be imagined that I am dealing in vague conjectures in connexion with this subject. If I am vague, the mechanical theory of an ether must in reality bear the reproach. So far, however, from having a reproach to bear, the whole body of facts is in complete harmony with this theory.

Further, if, as all the facts declare, radiation and absorption are complementary acts, the one consisting in communication, the other in reception, and the one being strictly proportional to the other, no coincidence in period between the vibrations of a radiating body and those of oxygen, hydrogen, or air, could make any one of these substances a good absorber. The form of the atom, or some other attribute than its period of oscillation, must enter into the question of absorption. It is physically incapacitated from communicating motion, and hence in an equal degree incapacitated from accepting motion. The neutrality of elementary gases in the experiments on absorption already recorded does not arise from my accidentally choosing a source of heat whose periods do not synchronise with those of the gas; for however they might synchronise, the gas would still be a bad absorber. Even when the motion which their own absorbent power does not enable them to take up is mechanically imparted, or is communicated to them by contact, they are still incompetent to expend it upon the ether, which accepts all vibrations alike\*.

§ 9.

Scents and effluvia generally have long excited the attention of observant men, and they have formed favourite illustrations regarding the divisibility of matter. Several chapters in the works of the celebrated Robert Boyle are devoted to this subject, and eminent men in all countries have speculated more or less upon the extraordinary tenuity of the matter which is competent to produce sensible effects upon our organs of smell. Such a subject would of course in itself form a wide inquiry, which it is quite out of my power to develope at present. I think, however, that the apparatus which we have thus far made use of enables us to deal with the question in a manner hitherto unattainable.

A number of dry aromatic plants† were obtained from Covent Garden, the leaves and flowers of which were stuffed into glass tubes 18 inches long and a quarter of an inch in diameter. By means of my second air-pump, a current of dry air was first passed

- \* I can hardly imagine the bands in the spectra of metallic compounds to be produced by the vibration of the compound atom. All my experiments show the vast influence of chemical union on the rate of oscillation; the metal itself and the compound of that metal could hardly, in my opinion, oscillate alike. Hence I infer that decomposition has occurred when the bright and constant spectral bands are seen.—June 20th.
- † I mean "dry" in the common acceptation of the term. They were not green, but withered; doubtless, strictly speaking, they contained aqueous vapour.

MDCCCLXII. M

over them for some minutes. They were then connected with the experimental tube, which had its sources of heat arranged as already described. The tube was first exhausted and the needle brought to 0°, and dry air was then passed over the scented herbs until the tube was filled. The consequent deflection was noted, and from it the absorbent action of the odorous substance was deduced.

Thyme thus treated exercised thirty-three times the absorption of the air in which it was diffused.

Peppermint exercised thirty-four times the action of the air.

Spearmint exercised thirty-eight times the same action.

Lavender produced thirty-two times the action of the air.

Wormwood forty-one times the action of the air.

The following perfumes were obtained from Mr. Atkinson of Bond Street, and examined in this manner. Small squares of dried bibulous paper, all of the same size, were rolled into cylinders about 2 inches in length; each of these was moistened by an aromatic oil, and introduced into a glass tube between the drying apparatus and the experimental tube. The latter being first exhausted, was afterwards filled by a current of dry air which had passed over the scented paper. Calling the action of the air which formed the vehicle of the perfumes 1, the following absorptions were observed in the respective cases:—

#### TABLE VII.

Name of perfume.					A	bsorption.
Pachouli .			•			$3\overline{0}$
Sandal Wood	•		۰		•	32
Geranium .						33
Oil of Cloves			•			33.5
Otto of Roses						36.5
Bergamot .						44
Neroli						47
Lavender .	•					60
Lemon						65
Portugal .				•		67
Thyme		•	•,			68
Rosemary .	. •				*	74
Oil of Laurel		•				80
Cassia						109

It would be interesting to examine the absolute weights of the substances which produced these effects; but this I suppose is a task which chemistry is unable to accomplish. In comparison with the air which carried the odours into the tube, their weight must be almost infinitely small. Still we find that the least energetic in the list has thirty times the effect of the air, while the most energetic produces 109 times the same

effect. As regards the absorption of radiant heat, the perfume of a flower-bed may be more efficacious than the entire oxygen and nitrogen of the atmosphere above it.

After each scent had been introduced a stream of dry air was admitted at one end of the tube, while the pump was worked in connexion with the other. The perfume was thus cleared out until the needle returned to 0°. This was often a long operation, the odours clung with such tenacity to the apparatus. After the zero had been attained in the case of a strong perfume, a few minutes' rest of the pump sufficed to bring the scent from its hiding-places in the crevices and cocks of the apparatus, and almost to restore the original deflection. The quantity of those residues must be left to the imagination to conceive. If they were multiplied by billions they probably would not reach the density of the air.

Fearing that the more active perfumes might possibly prejudice the action of the more feeble ones which succeeded them, I made a series of experiments with the following essences, and obtained the results recorded:—

${\bf Camomile}$	flow	ers		•	•	٠	87
Spikenard		٠,	•			•	355
Aniseed .	•			٠			372

After this enormous effect I repeated the experiment with bergamot, and found its action to be exactly the same as that recorded in the Table.

I made a few experiments on musk, but obtained different results with it at different times. On the 16th of October I obtained some fresh musk from the perfumer's, placed it in a small glass tube, and carried dry air over it into the experimental tube. The first experiment gave me an absorption of

74,

the air which carried the perfume being unity. A second experiment, in which the air was admitted more quickly, the absorption was

72.

It would be idle to speculate upon the quantity of matter which produced this result. The stories regarding the unwasting character of this substance are well known; suffice it to say, that a quantity of its odour carried into the tube by a current of air of a minute's duration, produced an effect seventy-two times that of the air which carried it. Long-continued pumping failed to cleanse the tube and passages of the musk. It cannot be volatile, for an amount of ether vapour which produces a far greater action is speedily cleared away, while the cocks and connecting pieces of the air-pump had to be boiled in a solution of soda before they were fit for use after the experiments with this substance.

Two perfectly concurrent experiments with ordinary cinnamon, in which fragments of the substance were placed in a tube and had dry air passed over them, gave an absorption of

Several kinds of tea, treated in the same manner, produced absorptions which varied between 20 and 28.

In the teas, cinnamon, musk, and the odorous plants already referred to, dry air had been passed over them for some time before they were examined. Still a small amount of aqueous vapour may have entered with the odours, and thus rendered the results to some extent of a mixed character.

### § 10. Ozone.

In my last memoir I alluded briefly to the action of ozone; but the experiments then made having been executed with a brass tube, I was very desirous of repeating them with a tube which could not be attacked by this extraordinary substance. Experiments with the glass tube, performed on the 16th, 17th, and 18th of last July, satisfied me that I had not over-estimated its power as an absorber of radiant heat.

In my first experiments I made use of large electrodes for the purpose of lessening the resistance to the passage of the current through the decomposing liquid. The oxygen thus obtained differed but little from ordinary oxygen.

This year I had three decomposing vessels constructed: in the first (No. 1) the platinum plates had about four square inches of surface, being rolled up to economise space; the plates of the second (No. 2) had two square inches of surface, while those of the third (No. 3) had only a square inch of surface each. Numerous experiments with these gave me the following constant results. Calling the absorption of ordinary oxygen 1,—

### Electrolytic Oxygen.

From plat	es			Ab	sorptio	n.
No. 1	٥				20	
No. 2					34	
No. 3			•		47	

A series of experiments made on the following day gave these results:—

No.	I.	•	•	•	•	•	21
No.	II.						36
No.	III.		٠				47

I now cut away a portion of the plates of No. II. so as to make them smaller than those of No. III. The oxygen obtained with these plates gave an absorption of

65,

thus exceeding No. III. considerably. The plates of No. III. were now reduced so as to make them smallest of all; the oxygen which they delivered gave an absorption of 85.

I feared the development of heat with these smallest plates, and knowing heat to be very destructive of ozone, I surrounded the apparatus by a mixture of pounded ice and

salt. The absorption of the oxygen thus obtained with the smallest plates amounted to 136.

By the results already recorded we have been prepared for the effect of minute quantities of matter; otherwise we could not fail to be struck with astonishment on finding a quantity of this substance, which would elude all attempts on the part of the chemist to determine its amount, producing an effect so stupendous in comparison with common oxygen. I have, moreover, strong reason to believe that I understate considerably the effect of the ozone. The experiments exhibit in an extremely striking manner the great influence of the density of the current at the place where the oxygen is liberated on the amount of ozone developed.

#### § 11.

All the results here recorded had been obtained, when, turning to De LA RIVE'S excellent treatise on Electricity, I found an allusion to the experiments of M. Meidinger on ozone. I had never previously heard any allusion made to this investigation, and was gratified to find in it the record of a very interesting piece of work.

M. Meidinger commences by showing the absence of agreement between theory and experiment in the decomposition of water, the difference showing itself very decidedly in a deficiency of oxygen when the current was strong. On heating his electrolyte, he found that this difference disappeared, the proper quantity of oxygen being liberated. He at once surmised that the defect of oxygen might be due to the formation of ozone; but in what way was still to be determined. If it were due to the great density of ozone in the tube which received the oxygen, the destruction of this substance by heat would restore the oxygen to its true volume. Strong heating, however, which destroyed the ozone, showed in repeated measurements no alteration of volume, hence M. MEIDINGER concluded that the defect which he had observed was not due to the ozone mixed with the oxygen itself. He finally concluded, and justified his conclusion by satisfactory experiments, that the loss of oxygen was caused by the formation of peroxide of hydrogen which was dissolved in the liquid, and thus withdrawn from the electrolytic gas. was further led to experiment with electrodes of different sizes, and found the loss of oxygen much more considerable when a small electrode was used than with a large one; whence he inferred that the formation of ozone was facilitated by augmenting the density of the current at the place where electrode and electrolyte meet. Nothing could be more different from the method pursued by M. Meidinger than that by which I arrived at the same conclusion; and though I had no doubt of the accuracy of my experiments, it was pleasant to find them corroborated in such a remarkable and unexpected way. I may add, that since the perusal of M. Meidinger's paper I have repeated his experiments with my decomposition cells, and find that those which gave me the greatest absorption also show the greatest deficiency in the amount of oxygen liberated\*.

<sup>\*</sup> I have recently learned that M. DE LA RIVE was the first to observe the influence of the size of the electrodes on the development of ozone.

The quantities of ozone with which I have operated must be perfectly unmeasurable The action of the substance is like that of olefant gas, or boracic by ordinary means. ether-bulk for bulk it might transcend either. No elementary gas that I have examined behaves at all like ozone. In its swing through the ether it must powerfully disturb the medium. If it be oxygen, it must be oxygen packed into groups of atoms, which encounter vast resistance in moving through the ether. I sought to decide the question whether it is oxygen or a compound of hydrogen in the following way. Heat destroys ozone. If it were oxygen only, heat would convert it into the common gas; if it were the hydrogen compound which some chemists consider it to be, heat would convert it into oxygen plus aqueous vapour. The gas alone admitted into my tube would give the neutral action of oxygen, but the gas plus the aqueous vapour I hoped might give a sensibly greater action. I caused the dry electrolytic gas to pass through a glass tube heated to redness direct into the experimental tube. I afterwards introduced a dryingtube between the place where the gas was heated and the experimental tube. Hitherto I have not been able to establish with certainty a difference between the dried and undried gas. Previously to heating, the electrolytic oxygen had been scrupulously dried; if the act of heating developed aqueous vapour, I can only say that the experimental means which I have employed are unable to detect it. For the present, therefore, I hold the belief that ozone is produced by the packing of the atoms of elementary oxygen into oscillating groups; and that heating dissolves the bond of union and allows the atoms to swing singly, thus disqualifying them for either intercepting or generating the motion, which as systems they were competent to intercept and generate.

# § 12.

Since these researches were commenced, an eminent experimenter has been led by his own inquiries in another field to enter upon the investigation of gaseous diathermancy. On the 7th of February of the present year (1861), Professor Magnus communicated to the Academy of Sciences in Berlin a memoir on the Transmission of Heat through Gases\*. The published notices of my experiments, commencing in May 1859, had escaped his attention, and his work is therefore to be regarded as independent of mine. Considering the very different methods which we have pursued, the general agreement between us must be regarded as remarkable.

The starting-point of Professor Magnus's investigation was the interesting experiment of Mr. Grove, in which a platinum wire raised to whiteness by an electric current is suddenly cooled by an atmosphere of hydrogen. This action, which we have hitherto been disposed to attribute to the mobility of hydrogen, and its consequent high convective power, Professor Magnus was led to regard as an effect of conduction; and the thought induced him to examine the conductibility of gases generally. The mode of experiment adopted led him, not I think to the establishment of gaseous conductivity, but to results substantially the same as those that I had previously obtained. In fact

<sup>\*</sup> Poggendorff's 'Annalen,' reprinted in Philosophical Magazine, S. 4. vol. xxii. p. 85.

the very experiments devised to show conductivity showed in a very striking manner the existence of athermancy, or opacity to radiant heat, in the case of a considerable number of gases.

The experiments on radiation, where obscure heat was made use of, were thus conducted. Two glass vessels, one much larger than the other, had their bottoms fused together; the larger one being turned upside down, the smaller one stood upright on the top of it. The mouth of the larger vessel was ground down, so that it could be placed like an ordinary receiver on the plate of an air-pump and exhausted, while through proper openings different gases could be afterwards admitted into it.

To the plate of the air-pump on which the above vessel was placed, was attached a thermo-electric pile with wires leading from it, through the plate, to a galvanometer; the axis of the pile was vertical, one face of it being turned downwards towards the plate, and the opposite face turned upwards towards the common surface of the two vessels which had been fused together.

Water was placed in the uppermost vessel, and caused to boil by conducting hot steam through it. Its under surface became thus heated to a temperature of 100°C. But this under surface constituted the upper surface of the vessel underneath. This latter, therefore, possessed a temperature of 100°C.; and it formed the source of heat made use of in the experiments.

Here Professor Magnus had a radiating surface of glass—a good radiator—kept at a constant temperature by the hot water above it; at a distance from this surface and turned towards it was the thermo-electric pile, defended from the radiation of the surface, or exposed to it, at pleasure, by the action of a moveable screen. The entire space between the pile and the radiating surface could either be rendered a vacuum, offering no resistance to the passage of the calorific rays, or else be filled by a gas the diathermancy of which was to be examined.

The concurrence of the experiments made with this apparatus and those made with mine is, as I have stated, remarkable. Some differences, however, exist between my friend and myself, a few remarks on which will not be without their use to those who may afterwards enter upon this extensive field of inquiry.

Experimenting in the ordinary way with his thermo-electric pile—using one of its faces only—Professor Magnus finds that air and oxygen cut off each more than 11 per cent. of the heat emanating from his source, while hydrogen cuts off more than 14 per cent.\* I, on the contrary, with the most delicate means I could apply, failed to establish the absorption of these gases by experiments made in the ordinary manner. In fact it was their neutrality that drove me to devise the principle of compensation, briefly referred to at the commencement of this memoir. I was so particular in the experiments which led me to the above negative result, that if the absorption amounted to one-tenth of that found by Professor Magnus I do not think it could have escaped me. Nor do I think that if such an action existed Melloni could have concluded that the absorption

of a column of air fifteen times the length of that employed by Professor Magnus was absolutely insensible.

In the account of the experiments already published, where my source of heat was also 100°C., I have set down the absorption of air, oxygen, and hydrogen at about 0.33 per cent.; which is for air and oxygen thirty times, and for hydrogen over forty times less than that found by Professor Magnus.

In fixing the above figure for the absorption of these gases, I protected myself by assigning what I knew to be the superior limit of the effect, but I was morally certain at the time, that as soon as I could combine sufficient power and delicacy I should make the effect less. This I have done in my present inquiry, and find the absorption of the above gases to be under 0.1 per cent., which in the case of oxygen is less than  $\frac{1}{100}$ th, and in the case of hydrogen less than  $\frac{1}{140}$ th of the effect obtained by Professor Magnus with a tube less than half the length of mine. Making every allowance for the difference between our two sources of heat, the discrepancy between us is still enormous. In fact my conclusion is that these gases are practical vacua to radiant heat, and that the mixture of oxygen and nitrogen which constitutes the body of our atmosphere is the same.

While, however, in the case of the elementary gases the discrepancy between Professor Magnus and myself consists in a defect on my part, or an excess on his, with the powerful gases I obtained a considerably stronger action than he does. Thus with olefiant gas his absorption amounts to less than 54 per cent., whereas in mine it amounts to more than 72. This last result is what might only be expected, inasmuch as the length of gas traversed by the radiant heat was in the one case a little under 15 inches, and in the other 33.

Professor Magnus has further published an account of experiments in which a powerful gas-flame surrounded by a glass cylinder furnished the source of heat; the latter being augmented by a parabolic mirror of polished metal, placed behind the lamp. In this case the gases were enclosed in a glass tube 1 metre long and 35 millims. in diameter, the two ends of which were stopped with plates of glass 4 millimetres thick.

Two series of experiments were executed with this tube, in one of which the interior surface was covered with black paper, while in the other the glass was uncovered within. The former method is that pursued by Dr. Franz, and the result obtained by Professor Magnus in the case of atmospheric air and oxygen closely agrees with that obtained for the same gases by Dr. Franz. Professor Magnus makes the absorption in the case of the blackened tube about  $2\frac{1}{2}$ , and Dr. Franz about 3 per cent. for air and oxygen.

In the case of the unblackened tube, however, the absorption was found to be much more considerable. Here the absorption by air and oxygen amounted to 14.75 per cent., and with hydrogen it reached 16.23. This great difference between the unblackened and the blackened tube is ascribed by Professor Magnus to a change of quality which the heat undergoes by its reflexion from the interior glass surface.

One of my motives in introducing a glass tube into the present inquiry was, that I

might be enabled to investigate the interesting question raised by this surmise of Professor Magnus. I have failed, however, to obtain his result. My naked glass tube, which is nearly of the same length as his, gives me a result which is more than 140 times less than his in the case of air and oxygen, and more than 160 times less than what he has obtained with hydrogen. Our sources of heat are, it is true, different, but the disadvantage is on my side; for assuredly the rays from a gas-jet are, if anything, less affected by the transparent elementary gases than those from my source. Had I time, I would repeat the experiments with a flame; but this, I regret to say, is out of my power at present.

Another difference between Professor Magnus and myself has reference to the influence of aqueous vapour. With both the gas-flame and the boiling water as sources of heat, he finds the effect of dry air to be precisely the same as that of air which he has allowed to pass in minute bubbles through water, and thus saturated with aqueous vapour.

I was engaged in experiments on this substance when my other duties compelled me to close this inquiry for a time. I believe, however, I may safely say, that not only is the action of aqueous vapour on radiant heat measurable, but this action may be made use of as a measure of atmospheric moisture, the tube used in my experiments being thus converted into a hygrometer of surpassing delicacy. Unhappily, as in other cases touched upon in this memoir, I have been unable to give this subject the development I could wish; but the results which I am in a position to record are nevertheless interesting.

On a great number of occasions I compared the air sent in directly from the laboratory into the experimental tube with the same air after it had been passed through the drying apparatus. Calling the action of the dry air unity, or supposing it rather to oscillate about unity (for the temperature of my source varied a little from day to day), on the following days the annexed absorptions were observed with the undried air of the laboratory:—

## Absorptions by undried air.

October 23rd		•	•		63
October 24th		•			62
October 29th				.•	65
October 31st.					56
November 1st					50
November 4th					58
November 8th	• ,				<b>4</b> 9
November 12th				_	62

Nearly  $\frac{9}{10}$ ths of the above effects are due to aqueous vapour; which, therefore, in some instances exerted nearly sixty times the action of the air in which it was diffused.

The experiments which I have made on aqueous vapour have been very numerous and varied. Differing as I did from so cautious and able an experimenter, I deemed it due to Professor Magnus and myself to spare no pains in securing myself against error. I MDCCCLXII.

have experimented with air moistened in various ways, sometimes by allowing small bubbles of it to ascend through water, sometimes dividing it by sending it through the pores of common cane immersed in water. Between the drying apparatus and the experimental tube I have introduced tubes containing fragments of glass moistened with water, and allowed the air to pass over them; large effects were in all such cases obtained, the absorption being usually more than eighty times that of dried air. Fragments of unwetted glass, which had been merely exposed to the air of the laboratory, had dry air led over them into the experimental tube; the absorption was fifteen times that of dried air. A roll of bibulous paper, taken from one of the drawers of the laboratory, and to all appearance perfectly dry, was enclosed in a glass tube, and dry air carried between its leaves. The experiment was made five times in succession with the same paper, and the following absorptions were observed:—

				Al	sorption.
No. 1					$7\hat{2}$
No. 2					62
No. 3					62
No. 4	Į.			. •	47
No. 5		ě	•		47

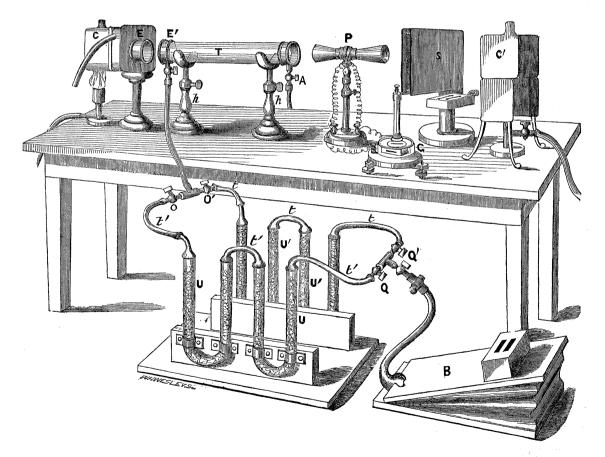
In fact, the action of aqueous vapour is exactly such as might be expected from the vapour of a liquid which Melloni found to be the most powerful absorber of radiant heat of all he had examined.

Every morning, on commencing my experiments, I had an interesting example of the power of glass to gather a film of aqueous vapour on its surface. Suppose the tube mounted, and the air of the laboratory removed as far as the air-pump was capable of On allowing dry air to enter for the first time, the needle would move removing it. from 0° to 50°. On pumping out it would return to 0°, and on letting in dry air a second time it would swing almost to 40°. Repeated exhaustions would cause this action to sink almost to nothing. These results were entirely due to the vapour collected during the night in an invisible film on the inner surface of the tube, and which was removed by the air on entering, and diffused through the tube. If the dry air entered at the end of the tube nearest to the source of heat, on the first and second admissions, and sometimes even on a third, the vapour carried from the warm end to the cold end of the tube was precipitated as a mist upon the latter, for a distance sometimes of nearly a foot. The mist always disappeared on pumping out. It is needless to remark that facts of this character, of which I could cite many, were not calculated to promote incautiousness or rashness on my part. I saw very clearly how easy it was to fall into the gravest errors, and I took due precautions to prevent myself from doing so.

Knowing that a solution of salt was almost as opake to radiant heat as water itself, I was careful to examine whether the effects which I had observed with aqueous vapour might not be due to the precipitation of the vapour on the surfaces of the plates of

salt used to stop my tube. The substance is well known to be very hygroscopic, and during the last three years the knowledge of this fact has rendered me careful to remove my polished plates every evening from the apparatus, and to keep them in perfectly dry air. Still, when it is remembered that the air on entering the tube is raised in temperature, and thus enabled to maintain a greater amount of vapour, and that the tube and plates of rock-salt form the channel for a flux of heat from the radiating source, the likelihood of precipitation occurring will seem but small. On examining the plates after the undried air of the laboratory was experimented with, no trace of precipitated moisture was observed upon their surfaces.

But to place the matter beyond all doubt, I abolished the plates of rock-salt altogether, and operated thus:—An india-rubber bag (B) was filled with air, and to its nozzle a T-piece, with the cocks Q Q', was attached. The cock Q' was connected with two tubes, U' U', each of which was filled with fragments of glass moistened with distilled water. The cock Q was connected with the tubes U U, each of which was filled with fragments of glass moistened by sulphuric acid. The other ends of these two series of tubes were connected with the cocks O O', and from the T-piece between these cocks



a tube led to the end E' of the open experimental tube T. The cock A at the other end of the experimental tube was placed in connexion with an air-pump. The pile P,

the screen S, and the compensating cube C' were used as in the other experiments. E is the end of the front chamber, and C the source of heat. In some experiments I had the end E closed by a plate of rock-salt, in others it was allowed to remain open; a distance of about 12 inches intervening between the radiating surface and the open end E' of the experimental tube.

Closing the cocks Q and O, and opening Q' and O', gentle pressure being applied to the bag B, a current of moist air was slowly discharged at the end E' of the experimental tube. The pump in connexion with A was then worked, and thus by degrees when the air was sucked into the tube T. The deflection of the galvanometer was 30°, the moist moist air filled the tube as completely as the arrangement permitted\*; this deflection being due to the predominance of the compensating cube over the radiating source C.

The cocks Q' and O' were now closed, and Q and O opened; proceeding as before, a current of dry air was discharged at E', and this air was drawn into the tube T in the manner just described. The moist air was thus displaced by dry; and, while the displacement was going on, the galvanometer was observed through the distant telescope. The needle soon commenced to sink, and slowly went down to zero; proving that a greater quantity of heat passed through the dry than through the moist air. The wet air was substituted for the dry, and the dry for the wet twenty times in succession, with the same constant result; the entrance of the humid air caused the needle to move from 0° to 30°, while the entrance of dry air caused it to fall from 30° to 0°. The air-pump was resorted to, because I found that when I attempted to displace the air by the direct force of the current from B, the temperature of the pile, or of the source, was so affected by the fresh air as to confuse the result. I may remark, that not only have I operated thus for days with aqueous vapour, but every result which I have obtained with vapours generally has been thus confirmed, so that all doubt as to the applicability of the rock-salt plates to researches of this nature may, I think, be abandoned †.

### § 13.

Whence, then, arise those differences between Professor Magnus and myself? I have no doubt that every one of his published results is the record of an experiment made with the utmost care which it is possible to bestow upon scientific work. The differences between us are, I imagine, to be referred to a radical defect in his apparatus. His desire was to do away with plates of all kinds between his source of heat and his pile, and hence he brought his gas into direct contact with his source of heat. The same thought had occurred to myself, and I was on the point of falling into the same error; but a series of experiments executed with reference to this point so early as the 26th of July, 1859, showed me that the accuracy of the results was entirely compromised by bringing

<sup>\*</sup> Still, of course, only partially.

<sup>†</sup> It is sheer want of time that prevents me from describing more particularly the numerous experiments executed with open tubes.

the gas to be examined into contact with the source. I obtained thus an action forty times what I knew it ought to be, and was confirmed in the view which caused me to interpose a vacuous chamber in front of the experimental tube. Let me here record a few experiments made on the 4th of last November in connexion with this subject.

I first satisfied myself that the drying apparatus was in perfect condition, the air of the laboratory producing, when sent through it, an absorption of 1. This same air was sent into the front chamber, that is, into direct contact with the source. The galvanometer needle moved as it does in the case of absorbent gases, and at the end of two minutes declared a loss of heat equivalent to an absorption of 50. The front chamber is 8 inches in length; the experimental tube is 33 inches long; hence a column of 8 inches, in contact with the radiating surface, produced at least fifty times the effect of a column more than four times as long when the air was separated from the radiating surface.

I made the foregoing experiment three times in succession, and after two minutes found the needle pointing to precisely the same degree; the lowering of the source was perfectly constant and regular, and in all cases showed a loss equivalent to an absorption of 50.

It will be remembered that Professor Magnus obtained a greater absorption with hydrogen than with either oxygen or air. This result is perfectly explained by reference to the quicker convection of this gas. I operated with hydrogen as I did with air, first satisfying myself that a column of it 33 inches long exercised an absorption less than unity. In fact it could not be measured. The same hydrogen introduced into the first chamber, and allowed to remain there for two minutes, caused a withdrawal of heat from the source equivalent to an absorption of

65.

Now the absorption of air in Professor Magnus's experiments is to that of hydrogen as

11.12:14.21,

or as 50:64,

while my results of convection are as 50:65.

The coincidence is so perfect that I am disposed to regard it as in part accidental.

Substantially the same remarks apply to the experiments with the glass tube stopped with plates of glass 4 millimetres thick. According to Melloni, 61 per cent. of the rays of a Locatelli lamp are absorbed by a plate of glass only 2.6 millimetres thick. Professor Magnus surrounded his flame by a glass cylinder, and this, it may be urged, partially sifted the heat of the lamp before it reached the end of the tube. But in so doing the glass cylinder itself must become intensely heated, and to the heat of the cylinder the glass ends of the tube would be *opake*. They would absorb it all. Cold air admitted into such a tube is exactly similar to cold air let into my front chamber, it chills what is in part the source of heat, and maintains that chill by convection. The heat applied

may, in fact, be thus analysed. 1. We have a portion, almost wholly luminous, which went through the tube direct to the pile; 2, a portion arrested by the first glass plate; 3, a smaller portion arrested by the second glass plate; 4, we have the heat radiated by the first glass plate towards the second, and wholly absorbed by the latter; 5, we have the heat radiated by this latter against the pile. This analysis will probably enable us to understand how Professor Magnus obtained an absorption of only  $2\frac{1}{2}$  per cent. with the blackened tube, and as much as 14.75 per cent. with the unblackened one. With the latter, the source, and the plate of glass nearest the source, send a copious flux down the tube to the plate at the opposite end; the oblique rays are in great part reflected by the interior surface, and thus reach the plate adjacent to the pile. With the blackened tube this oblique radiation is entirely cut off, the rays incident on the interior surface being absorbed. Thus the plate of glass adjacent to the pile must be much more intensely heated with the unblackened tube than with the blackened one. The difference in the amount of heat received by the pile-end plate in the respective cases is rendered very manifest by the experiments of Professor Magnus himself, for he finds that with the same source, twenty-six times the amount of heat transmitted by the coated tube is transmitted by the uncoated one. What, therefore, Professor Magnus ascribes to a change of quality by reflexion, would, if I am correct, be due to the higher heating in the case of the naked tube, and consequent greater chilling by the cold air, of the plate of glass close to the pile. To this must be added the effect produced by cooling the distant end of the tube itself, to which heat has been communicated from the first glass plate by the process of conduction, and the cooling of which comes most into play when the tube is uncovered.

The difference between Professor Magnus and myself as regards the action of aqueous vapour admits now of easy explanation. His effect being one of convection, and not of absorption, the quantity of vapour present in his experiments—probably not more than 1 per cent. of the volume of the gas, certainly not 2 per cent.—vanished as a convecting agent, in comparison with the air.

It is hardly necessary to repeat these reflections with reference to the experiments of Dr. Franz. The taking of the chilling of his plates for absorption, has caused him to find no difference of effect when he doubled the length of his tube. With a tube 450 millimetres long, he finds precisely the same absorption as with a tube of 900. He finds the action of carbonic acid to be the same as that of air, although at atmospheric tensions the action of the former is 90 times that of the latter \*. He finds the vapour of bromine more destructive to radiant heat than nitrous acid gas, whereas the latter is beyond comparison the most destructive. The heat rendered latent by the evaporation of the

<sup>\*</sup> The sensible equality of all the transparent gases and air was regarded as evident by Dr. Franz. "It might be seen," he writes, "from the outset that no decided difference would be observed between them" (p. 342). Similarly, Professor Magnus, speaking of aqueous vapour, writes, "Although it might be foreseen with certainty that the small amount of aqueous vapour in the air could have no influence on the radiation," &c. (p. 43).

bromine of course augmented the chill, and thus magnified the effect which in reality he was measuring. In reference to heating the glass plates by the flame, made use of in his experiments, I will cite a single passage from the memoir of Dr. Franz. It refers to the vapour of iodine produced by throwing the substance on a heated surface in a vessel closed with glass plates. "The mirror," he writes, "showed a deflection of only 178. But as the glass plates through which the heat radiated had not yet assumed a temperature high enough to reduce the iodine, which had been precipitated upon them in crystals, to a state of vapour . . . . . it was necessary to wait, and allow the radiation of the lamp to continue till all the iodine was driven from the bottle \*." This shows how much the glass plates could be heated by the radiation of the lamp; this heat on a particular occasion being sufficient to dissipate the solid iodine which had coated the glass plates.

§ 14.

As a dam built across a river causes a local deepening of the stream, so our atmosphere, thrown as a dam across the terrestrial rays, produces a local heightening of the temperature at the earth's surface. This, of course, does not imply indefinite accumulation any more than the river dam does, the quantity lost by terrestrial radiation being, finally, equal to the quantity received from the sun. The chief intercepting substance is the aqueous vapour of the atmosphere †, the oxygen and nitrogen of which the great mass of the atmosphere is composed being sensibly transparent to the calorific rays. Were the atmosphere cleansed of its vapour, the temperature of space would be directly open to us; and could we under present circumstances reach an elevation where the amount of that vapour is insensible, we might determine the temperature of space by direct experiment. Colonel Stracher has written an admirable paper on the aqueous vapour of the atmosphere ‡, in which he shows that the amount of vapour diminishes much more speedily with the elevation than might be inferred from the law of Dalton.

It might be possible to reach a height where, by preserving one face of a thermoelectric pile at the temperature of the locality, the other, protected from all terrestrial radiation, turned to the zenith, would assume the temperature of space in that direction §, while the consequent galvanometric deflection would give us the means of determining the difference in temperature between the two faces of the pile. Knowing one, we should therefore be able to determine the other; knowing the temperature of the locality, we could infer from it the temperature of stellar space. Many eminent writers,

- \* "Es musste bei fortdauernder Strahlung der Lampe der Zeitpunct abgewartet werden."
- † The mildness of an island climate must be in part due to this cause. The direct tendency of the vapour is to check sudden fluctuations of temperature. Where it is absent, as at the surface of the moon, such fluctuations must be enormous. The face turned towards the sun drinks in the solar rays without let or hindrance, while the radiation of the face turned from the sun pours unchecked into space.
  - # Proceedings of the Royal Society, vol. xi. p. 182.
- § A well of cold air would be formed within the reflector, the lowest stratum of the well sharing the temperature of the face of the pile.

it is true, have supposed the upper atmospheric regions to be colder than space, the depression of temperature being due to the radiation of the aërial particles, just as a grass-blade is lowered, by its radiation, below the air which surrounds it. This notion must, I think, be abandoned; for, as far as experiment goes, it leads us to conclude that air, and particularly air in the higher atmospheric regions, behaves as a vacuum both as regards radiation and absorption.

#### § 15.

In his paper on the conduction of heat by gases, Professor Magnus examines the question of convection, and has adduced some striking experiments to show that the cooling of an incandescent wire in hydrogen is not due to the convection of the gas. He finds that when the wire is enclosed in a narrow tube, with only a thin film of the gas surrounding it, and where therefore currents, in the ordinary sense, are hard to be conceived of, the gas still exercises its cooling power. It had often occurred to me to make this experiment; and when I first heard of its successful performance by Professor Magnus I adopted his conclusion, that the cooling was due to conduction.

Reflection, however, caused me to change my opinion. Suppose the wire to be stretched along the axis of a wide cylinder containing hydrogen, we should have convection, in the ordinary sense, on heating the wire. Where does the heat thus dispersed ultimately go? It is manifestly given up to the sides of the cylinder. The transfer by convection is a transfer ultimately to the sides of the cylinder, and if we narrow our cylinder we simply hasten the transfer. The process of narrowing may continue till a tube like that used by Professor Magnus is the result; the convection between centre and sides will still continue, and produce the same cooling effect as before. Whether we assume conduction or convection, the tube surrounding the wire must be supposed to possess sufficient conducting power to carry the heat off, otherwise it would become incandescent itself by the accumulation of the heat.

The reasoning of Professor Magnus in connexion with this subject is of extreme ingenuity. He contends that there is no reason why stronger currents should establish themselves in hydrogen than in other gases. Currents are due to differences of density produced by the expansion of a portion of the gas by heat. Now hydrogen actually expands *less* than other gases, and hence the differential action on which the currents depend is less in this gas than in the others. Professor Magnus alludes to the friction of the particles against each other, but considers this ineffective.

This reasoning leads us to the threshold of a question which might form the subject of a long and profitable investigation. For a given difference of density, is not the mobility of hydrogen greater than that of the other gases? The experiments above recorded, where different gases were brought into direct contact with the source of heat, seem to answer this question in the affirmative. I have had no time to pursue the question regarding hydrogen; but I have made a few experiments, which show the influence of density on the mobility of a gas in a very striking manner.

Having first so purified atmospheric air as to render it sensibly neutral to radiant heat, I allowed 15 inches of it to enter the front chamber F, and there to come into contact with the source of heat. Convection of course immediately set in, and its amount was accurately measured by the quantity of heat withdrawn from the radiating surface; this quantity, expressed in the units adopted throughout this memoir, was

62.

The quantity of gas in the front chamber was now doubled, that is, it now had an atmosphere of tension; the withdrawal of heat then was expressed by the number

68

In the last experiment we had double the number of atoms loading themselves with heat and carrying it away; if their motion had been as quick as that of the atoms when half an atmosphere was used, they would have withdrawn sensibly double the amount of heat; but the fact is that half an atmosphere carried off 64, while a whole atmosphere carried off 68; hence the absolute swiftness of the atoms in the case of the denser air must be very much less than in the case of the rarer. In fact, the amount of heat withdrawn will be proportional on the one hand to the number of carrying particles, and on the other to the velocity with which they move; hence if v and v' be these velocities, we have

$$\frac{62}{68} = \frac{v}{2v'}$$
, or  $\frac{v}{v'} = \frac{62}{34}$ .

Thus, while the atoms of the rarer gas travel 62 units in a second, those of the denser gas travel only 34.

This retardation can, I think, arise from nothing else than the resistance offered by the particles of the air to the motion of their fellows. It must be borne in mind that the smallness of the increment observed on doubling the amount of gas was not due to the partial exhaustion of the source by the first quantity of gas. The heat of the source was such that the withdrawal of 64 of our units could not sensibly affect the subsequent convection.

Here, then, we see what a powerful effect density, or the internal resistance which accompanies density, has on the mobility of a gas; and there is every reason to suppose that the mobility of hydrogen is due to the comparative absence, in its case, of internal resistance. However this may be, the foregoing experiment enables us to draw some important inferences.

Storms at great heights must be greatly facilitated by the mobility of the particles of the air. In fact storms are cases of convection on a large scale, and in our front chamber we had one in miniature. With the same difference of temperature on the summit of Mont Blanc, the motion of convection would be very nearly twice as great as at the sea-level.

In the summer of 1859 I was fortunate enough to induce my friend Professor Frankland to accompany me to the summit of Mont Blanc, and to determine the comparative rates of combustion there and in the valley of Chamouni. Six candles were

purchased, burnt for an hour at Chamouni, and the loss of weight determined. The same candles were lighted for the same time on the summit of the mountain, and the consumption determined. Within the limits of error, the consumption above was equal to that below. The *light* below was immensely greater than that above, still the amount of stearine consumed in the two cases was sensibly the same. Professor Frankland surmised this to be due to the greater mobility of the rarefied air, which allowed a freer interpenetration of the flame by the oxygen \*, and the foregoing experiments show that the augmentation of mobility is just such as would account for the observed effect.

\* The influence of interpenetration is well seen in the exposed gas-jets of London, particularly in the butchers' shops on a Saturday night. A gust of wind, which carries oxygen to the centre of a flame, suddenly deprives it of light. A simple and beautiful experiment consists of passing a lighted candle swiftly to and fro through the air; the white light reduces itself to a pale-blue band. Bunsen's burner is an illustration in the same line.

