I.

ON THE ABSORPTION AND RADIATION OF HEAT BY GASES AND VAPOURS, AND ON THE PHYSICAL CONNEXION OF RADIATION, ABSORPTION, AND CONDUCTION.

ANALYSIS OF MEMOIR I.

THE researches embodied in the following memoir were begun in the early part of 1859; and the first notice of them is published in the 'Proceedings of the Royal Society' for the 26th of May of that year.

They arose in part from the desire to do for the gaseous form of matter what had been previously so well done by Melloni for the liquid and solid states of aggregation. They were also stimulated by the persuasion that not only the physical but the chemical, in other words the *molecular*, condition of bodies probably played a part previously unrecognised in the phenomena of radiation and absorption.

At the time here referred to, the belief was general that as regards its relation to radiant heat the gaseous form of matter was inaccessible to experiment. Of the published attempts in this direction, two only are known to me, the one by Melloni and the other by Franz. Both are referred to in the 'Introduction' to this memoir, and are there stated, I believe correctly, to have left this field of inquiry 'perfectly unbroken ground.'

The memoir naturally begins with a description of the instruments employed; the difficulty of obtaining a galvanometer-coil free from magnetic action is dwelt upon; and a simple method is proposed of testing the galvanometric purity of copper wire. It is shown that by an experiment of a moment's duration we can satisfy ourselves, before the coil is constructed, whether the wire is fit for galvanometric purposes or not.

Following the methods of observation introduced by Melloni, experiments on air and other gases were executed and recorded. They proved conclusively that to grapple with these gases far more powerful sources of heat than any previously employed would be necessary. Hence arose the problem how to employ such sources, and at the same time to maintain the needle of the galvanometer in a condition as sensitive as if no heat at all were falling upon the thermo-electric pile.

The problem is thus solved:—Two sources of heat are permitted to radiate against the two opposite faces of the pile. However powerful these opposing radiations may be, if they be only equal, they neutralise each other, and permit the needle of the galvanometer to point tranquilly to zero. Between one of these sources and the pile a wide tube is introduced, which can be exhausted or filled at pleasure with any gas. Supposing the opposing forces to be equal when the tube is empty, the introduction of any gas, capable of quenching even

an infinitesimal fraction of the heat, would give the opposite source the mastery; a deflection of the galvanometer would follow, and from the magnitude of the deflection the amount of heat quenched by the gas could be immediately deduced.

The final form of the apparatus thus sketched in outline was determined by a long course of tentative experiments. The possibilities of error were numerous, both in the arrangement of the apparatus and in the selection and purification of the substances to be examined. Experiments are recorded which show the infinitesimal action of the elementary gases and the perfectly enormous action of some of the compound gases upon radiant heat. To render these contrasting results secure; to guard against instrumental defects which might readily substitute a delusive for a real action; and to avoid impurities which, though infinitesimal when measured chemically, were found competent in the case of the feebler gases to entirely vitiate the results, some thousands of experiments were executed.

As regards instrumental arrangements, for example, it was proved that to avoid errors arising from convection, and from dynamic heating and chilling, it was absolutely necessary that the gases examined should not come into contact either with the radiating source or with the face of the thermo-electric pile. It was necessary that the heat lost by the one and received by the other should be purely *radiant heat*—a result which could never be calculated upon if contact were permitted with either the pile or the source.

One of the earliest trials with the new apparatus, in which electrolytic oxygen was employed, proved the modicum of ozone which accompanied the oxygen to exercise a far more potent action upon radiant heat than the oxygen itself. In § 19 Memoir II. this result is further developed, the constitution of ozone now generally agreed upon being deduced from these developments.

While the action of oxygen, hydrogen, nitrogen, and air, even at the full pressure of the atmosphere and subjected to the most powerful tests, proved barely measurable, amounting certainly to not more than a fraction of a unit per cent. of the incident heat; experiments on olefiant gas are recorded in which the quantities employed varied from $\frac{1}{10000}$th of an atmosphere to a whole atmosphere, and yielded throughout a perfectly measurable action. The absorption by this gas, under the pressure of an atmosphere, amounted to fully 81 per cent. of the incident radiation.

Experiments on sulphuric-ether vapour are also recorded in which the pressures employed varied from $\frac{1}{500000}$th of an atmosphere to the maximum pressure of the vapour, the quantity of vapour corresponding to the smallest of these pressures being proved capable of producing a measurable effect. Comparing equal pressures up to 5 inches of mercury, sulphuric-ether vapour was found to be more than twice as potent as olefiant gas.

The action of the following vapours at various degrees of density upon radiant heat is afterwards recorded:—Bisulphide of carbon, amylene, iodide of ethyl, iodide of methyl, iodide of amyl, chloride of amyl, benzol, methylic alcohol, formic ether, propionic ether, chloroform, and alcohol.

A curious explosive effect occurring in the cylinders of the air-pump when air is mixed with attenuated bisulphide-of-carbon vapour is referred to and explained.

Chlorine gas is next operated on, and its action in altering the reflective power of the interior surface of the experimental tube is demonstrated. This

leads to a searching inquiry whether any of the effects observed with the vapours above mentioned could be due to a diminution of interior reflexion. Two parallel series of experiments executed with two different experimental tubes, the one polished, and the other blackened within, are recorded. In nine cases out of thirteen the order of absorption in both tubes was the same; in fact, the absorptions in the blackened tube multiplied by a certain coefficient were sensibly equal to those in the polished tube. In the case of the four remaining vapours slight deviations from the order of absorption were observed. These it was deemed unnecessary to follow up, *so conclusive was the evidence that the observed effects were really cases of absorption, and by no means to be referred to any alteration of the reflecting surface whether by chemical action or by condensation.*

The actions of other permanent gases than those already referred to are then recorded.

Experiments are next described which illustrate the action of the aqueous vapour of our atmosphere on radiant heat; and considerations follow regarding the influence of an atmosphere like ours upon the temperature of a planet. In former speculations upon this subject the density and height of the atmosphere were dwelt upon by distinguished writers; but it is here pointed out that a comparatively slight change in the variable constituents of our atmosphere, by permitting free access of solar heat to the earth, and checking the outflow of terrestrial heat towards space, would produce changes of climate as great as those which the discoveries of geology reveal.

Thus far our attention has been restricted to the *absorption* of radiant heat by gaseous matter, not only the general fact of absorption, but vast differences of absorptive power being established experimentally. We now come to a series of reciprocal experiments on the *radiation* of heat by gases, which demonstrate not only the general fact of radiation, but that the order of radiation is precisely the same as the order of absorption. As regards both radiation and absorption the elementary gases in the experiments here recorded, stand lowest; olefiant gas highest; and between these extremes stand the other compound gases without any shifting of position.

It is further shown that a film of gas, coating a polished metallic surface, may, both as regards radiation and absorption, be made to do the duty of a coat of varnish, or of lampblack, in increasing the emissive and absorptive power of the surface.

Our knowledge of this subject prior to the foregoing experiments is thus briefly summed up by Melloni. 'On ne connaît encore aucun fait qui démontre directement le pouvoir émissif des fluides élastiques purs et transparents.'—*Annales de Chimie et de Physique*, vol. xxii. p. 494.

Directly bearing upon this portion of the subject is an observation which, for a time, constituted one of the numerous perplexities besetting this inquiry in its earlier stages. A residue of vapour being in the experimental tube, air is permitted to enter; a prompt deflection follows, indicating an increase instead of a diminution of the transmission. The needle then returns, and finally, takes up a position indicating a slightly higher absorption than when the vapour-residue alone was present. On pumping out, the needle at first moves promptly, indicating a diminution instead of an increase of the transmission. After a momentary impulse in this direction, the needle returns to zero. The observation on analysis turned out to be an exceedingly interesting case of gaseous radiation

and absorption. When the air entered, the vapour was dynamically heated; it discharged its heat against the pile, and thus apparently augmented the transmission. When the tube was exhausted the vapour was chilled, and the radiation into it from the adjacent face of the pile produced for a moment the deflection due to absorption. In subsequent memoirs, under the name of Dynamic Radiation and Absorption, this subject is fully developed.

In the last section of the memoir an attempt is made to establish a physical connexion between radiation, absorption, and conduction. One of the speculative notions in this section subsequent experience has caused me to modify. Radiation and Absorption are here regarded as the acts of the molecule as a whole, whereas I now hold them to be mainly the work of the constituent atoms of the molecule. Experimental reasons for this change of conception will be given subsequently. The memoir winds up with some supplementary remarks on the thermo-electric pile and galvanometer, intended chiefly for the use of the younger student.

I.

ON THE ABSORPTION AND RADIATION OF HEAT BY GASES AND VAPOURS, AND ON THE PHYSICAL CONNEXION OF RADIATION, ABSORPTION, AND CONDUCTION.

*The Bakerian Lecture delivered before the Royal Society, February 7, 1861.**

INTRODUCTION.

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

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

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

* Received January 10. *Philosophical Transactions* for 1861; *Philosophical Magazine*, vol. xxii. p. 169.

† *La Thermochrose*, p. 136.

With a delicate apparatus of the same kind, Dr. Franz, of Berlin, found that the air contained in a tube 3 feet long absorbed 3·54 per cent. of the heat sent through it from an Argand lamp; that is to say, calling the number of rays which passed through the exhausted tube 100, the number which passed when the tube was filled with air was only 96·46.*

In the sequel it will be shown that the result obtained by Dr. Franz was due to an inadvertence in his mode of observation. These are the only experiments of this nature with which I am acquainted, and they leave the field of inquiry now before us perfectly unbroken ground.†

§ 1.

The Galvanometer and its Defects.—Magnetic Analysis of its Wire.

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

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

In consequence of this, when the needles were as perfectly astatic as I could make them they deviated as much as 30° right and left of the neutral line. To neutralise this deflection, a minute magnetic 'compensator' was made use of, by which the needle was gently drawn to zero in opposition to the magnetism of the coil.

But the instrument suffered much in point of delicacy from this arrangement, and accurate quantitative determinations

* Pogg. *Ann.* vol. xciv. p. 342.

† No doubt many experimenters had attempted to establish the action of air upon radiant heat; otherwise the conviction could not have become universal that no such action was discoverable.

with it were unattainable. I therefore sought to replace the Berlin coil by a less magnetic one. Mr. Becker first supplied me with a coil which reduced the lateral deflection from 30° to 3°.

But even this small residue was a source of great annoyance, and for a time I almost despaired of obtaining pure copper wire. I knew that Professor Magnus had succeeded in obtaining it for his galvanometer, but the labour of doing so was immense. He first fused, and had drawn into wire, copper obtained from a galvano-plastic manufactory, but found, after the completion of his coil, its magnetic condition intolerable. 'I have therefore,' he says, 'specially purified my copper in the following manner: A solution of sulphate of copper was saturated with ammonia, until the precipitated oxide was again dissolved. The precipitated oxide of iron was removed by filtration, and, as copper is not easily precipitated electrolytically from an ammoniacal solution, the fluid was evaporated to dryness, and all the ammonia thus drawn off. The sulphate of copper thus purified was dissolved in water and precipitated by the Voltaic current. As it was found impossible to separate the copper in an adherent mass, it was necessary to fuse it. Unhappily a very brittle metal is thus obtained, which cannot be drawn into wires. The metal had to be fused eight times in succession before it was rendered fit for this purpose. This process,' continues Magnus, 'of purifying copper is very troublesome and very costly. Without doubt it would be possible to obtain silver quite as free from magnetism as this wire, and by an easy calculation it might be proved that it would cost considerably less than an equal weight of copper prepared in the foregoing way.' *

* Pogg. *Ann.* vol. lxxxiii. p. 489.

Melloni gives the following account of the formidable nuisance of a magnetic coil: 'Les systèmes astatiques très-sensibles appliqués comme nous venons de l'indiquer aux hélices d'un fil ordinaire de cuivre ou d'argent, présentent presque toujours le fait curieux de ne pouvoir s'arrêter au zéro du cadran; c'est-à-dire que, généralement, les systèmes astatiques doués d'une grande sensibilité ne peuvent s'arrêter dans le plan vertical qui divise l'hélice en deux portions égales, parallèlement à la direction des spires. Lorsqu'on cherche à les amener dans ce plan, en tournant doucement l'hélice vers leur position d'équilibre, on les voit s'écarter aussitôt, à droite ou à gauche, et, après quelques oscillations, se fixer stablement dans une position d'équilibre plus ou moins éloignée du zéro. On mesure aisément cet arc de déviation moyennant un cercle gradué que l'on fixe à la partie supérieure de l'hélice après y avoir pratiqué une ouver-

While pondering over the means of avoiding so formidable a task, the thought occurred to me that a magnet furnished an immediate and perfect test as to the quality of the wire. Pure copper is *diamagnetic*; hence its repulsion or attraction by the magnet would at once declare its fitness or unfitness for the purpose in view.

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

I then removed the silk covering from the latter and tested the naked wire. *It was repelled.* The whole annoyance in its case was thus fastened on the green silk; some iron compound had been used in the dyeing of it, and to this the deviation of the needle from zero was manifestly due.

I had the green coating removed and the wire overspun with silk, clean hands being used in the process. A perfect galvanometer is the result. The needle, when released from the action of the current, returns accurately to zero, and is perfectly free from all magnetic action on the part of the coil. In fact, while we have been devising agate plates and other elaborate methods to get rid of the impurities of our galvanometer coils, the means of doing so by magnetic analysis are at hand. Diamagnetic copper wires are readily found. Out of eleven specimens, four of which were furnished by Mr. Becker, and seven taken at random from our laboratory, nine were found diamagnetic and only two paramagnetic.

Perhaps the only defect of those noble instruments with which

ture longitudinale dans le sens du zéro et de la division des spires. La déviation est égale des deux côtés; elle peut aller jusqu'à 10 ou 12 degrés et même davantage, si, en opérant sur un système astatique d'une grande perfection, *on donne une certaine largeur à la fente qui sert à introduire dans l'hélice l'aiguille inférieure du système.* Le phénomène dérive donc du partage du fil en deux masses égales, qui ont chacune un centre d'attraction, vers lequel tendent les pôles des aiguilles aimantées. Ainsi le cuivre, dont ces fils sont ordinairement composés, tout en n'étant pas un métal magnétique par lui-même, opère sur les aiguilles aimantées comme s'il contenait des parcelles de fer. C'est, en effet, le cas du cuivre de commerce; et l'on en devine facilement le motif, lorsqu'on réfléchit à l'imperfection des procédés de raffinage et au contact des outils employés dans les transformations successives du cuivre en rosettes, en verges et en fils. Et il ne faut pas s'imaginer que le fil ordinaire d'argent soit en de meilleures conditions; car l'argent, qui se trouve presque toujours en présence du fer pendant les opérations nécessaires à son extraction, ne se convertit en fil qu'à l'aide du marteau et des filières d'acier.'