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C MEMOIRS

THE LAWS
OF
RADIATION AND ABSORPTION

EDITED BY
D. B. BRACE, Ph.D.

Phys. dept

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SCIENTIFIC MEMOIRS

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XV

THE LAWS OF RADIATION AND ABSORPTION

THE LAWS
OF
RADIATION AND ABSORPTION

MEMOIRS BY PRÉVOST, STEWART, KIRCHHOFF,
AND KIRCHHOFF AND BUNSEN.

TRANSLATED AND EDITED BY

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Radiation and Absorption.

W. P. I



PREFACE.

THE attempt of Prévost to explain the experiments of Pictet, of the apparent concentration of *cold* at the focus of a mirror, without attributing the quality of radiation to *cold*, as assumed by Pictet, lead him to the enunciation of the very important principle which he called the *movable equilibrium* of *heat*, now designated as the *theory of exchanges*. Prévost, who was a disciple of le Sage, and who had issued, with many additions, his memoirs, assumed, in addition to a corpuscular fluid caloric, a free corpuscular radiant caloric, the equal interchange of which between neighboring free spaces, constituted heat equilibrium. Any interference with this equilibrium will be reestablished by the inequalities of the exchanges. On this principle he was able to explain the apparent concentration of *cold* and also to show the inadmissibility of *cold* as an agent susceptible of radiation. He was careful, however, to fortify his principle by showing that the same results would follow on the then distrusted hypothesis of undulatory exchanges, which has been adopted by his successors. Later experimenters, particularly Leslie and De la Provastaye and Desains, confirmed the theory and also showed in many instances quantitative relations between radiation and absorption. But the most important advance was made by Balfour Stewart in establishing, not only a quantitative relation, but also a qualitative or selective one. By the introduction of his ingenious idea of an impervious radiating inclosure he demonstrated the equality between the emissive and the absorptive power of any wave length. We owe to Kirchhoff, however, the first rigorous proof of the celebrated law (usually designated on the Continent as Kirchhoff's law) of the emission and absorption of light and heat, and the application of the same by both Kirchhoff and Bunsen to Spectrum Analysis. The radiation of solids and liquids and gases follows the law exactly when the conditions upon which he founded it are rigorously fulfilled, namely, the complete transformation from one to the other of

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radiant energy and their intrinsic heat. We now know that most radiations from gases are not exclusively thermal, but that the substances, cited by Kirchhoff and Bunsen, also give off so called chemical and electrical and fluorescent radiations which Kirchhoff excluded in the proof of his law. In fact none of the gases giving line spectra at temperatures heretofore used do so by simple thermal radiation, but essentially by luminescent actions (chemical, electrical, and photogenic), so that we cannot, in general, apply the law of Kirchhoff of the proportionality between radiation and absorption to either terrestrial or celestial substances. In these cases the principle of resonance usually holds, since in luminescence the radiation of line spectra is accompanied by selective absorption of the same spectral lines, so that the law may be used qualitatively, which is in fact the way Kirchhoff and Bunsen actually attempted to confirm it. The formulation of the complete law for radiations of a *black body* is only given in part by Kirchhoff. The formula of Wien, and more particularly the most recent one of Planck, deduced on theoretical grounds, approximates closely the latest observations on a black body at different temperatures and over different wave lengths.

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MEMOIR ON THE EQUILIBRIUM OF HEAT.

BY

PIERRE PRÉVOST.

Journal de Physique, vol. 38, pp. 314–322. Paris, 1791.

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MEMOIR ON THE EQUILIBRIUM OF HEAT.

BY PIERRE PRÉVOST.

I PROPOSE to analyse and fix with precision the sense of the word *equilibrium* applied to such a fluid as heat. This idea is not exactly defined in the theories which leave questions relative to the nature of this element undecided. If there is any doubt that heat is material, if there is no explanation concerning the contiguity or the noncontiguity of molecules of heat, concerning their mobility or their immobility, the kind of motion, vibratory or translatory, which is attributed to them, it is impossible to arrive at exact and complete ideas of their equilibrium. It results from this that every phenomenon which depends, not upon any equilibrium whatever but upon a specific kind of equilibrium, remains entirely unexplained. And as the imagination determines to some extent, notwithstanding, that which reason wishes to leave undetermined, the true causes are lost sight of, and vain hypotheses are arbitrarily preferred because they are suitable in certain respects and favorable to first appearances.

I will not waste time in discussing the different natures assigned to heat by various physicists. The true constitution of this fluid is connected with the theory of discrete fluids, now known, although it has not been published by its author. For its development and proof I refer to what M. DeLuc has said of it both in his "*Idées sur la météorologie*" and in his *letters* published successively in this Journal: also what I have said of it myself in my essay upon *l'origine des forces magnetiques*. Assuming then the principles of this theory, I shall merely recall them, and use them to establish true ideas on the equilibrium of heat.

I shall afterwards make the application of this theory of the equilibrium of heat to a very remarkable phenomenon which I consider inexplicable without it. This is the phenomenon of the *reflection of cold*. It has been observed by M. Pictet, who

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has described it in detail in his *essai sur le feu*. This learned scientist, with whom I have old and valued bonds of friendship, does not at all disapprove of the discussion which I am undertaking although it tends to indicate some inadequacy in the explanation which he, himself, has given to this phenomenon.

It will be seen elsewhere by what I shall say of it, that a complete explanation, such as the theory of M. le Sage furnished, does not enter into the plan which M. Pictet has proposed. I will discuss this phenomenon then, very freely. I shall show that it explains itself without any effort, by the true theory of discrete fluids. I shall also prove that it is not explained at all by the imperfect theories to which physicists commonly limit themselves. I shall close this memoir with two remarks which have some connection with this subject, without being directly related to it.

I.

THEORY OF THE EQUILIBRIUM OF HEAT.

Heat is a discrete fluid. Its elasticity consists in its expansive force. And this is the effect of the movement of its particles. This movement is caused by the impulse of a much more subtile fluid whose effect upon its particles is determined to a certain extent by their form. It is so swift that when heat is freed its translation from one place to another appears instantaneous. It is also sensibly rectilinear, so that perfectly free heat partakes, as far as the movement of its particles is concerned, of all the properties of light, at least so far as our senses can determine in the limited experiments which have thus far been performed.

A discrete fluid whose particles radiate like those of light, may be confined by barriers, but may not be confined by another radiant fluid nor, in consequence, by itself. For it is necessary to conceive of all these fluids as very rare, as having many more void intervals than full ones in the space which they occupy. Light does not stop the passage of light. If this solar emanation is so dense that two luminous currents cannot cross each other without being interrupted, the innumerable crossings and reflections which they experience will destroy entirely its rectilinear direction, and light will lose to our eyes

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all its properties which depend upon this direction. What is true of this fluid is true of all radiant fluids. Radiant heat passes through heat, which upon the earth is present in all places, and since it produces no sensible perturbation, it is necessary that these particles should be separated by intervals great relatively to their diameters. It is certain that free radiant heat is a very rare fluid, the particles of which almost never collide with one another and do not disturb sensibly their mutual movements.

In conforming to physical hypotheses, one says ordinarily that heat is coercible by itself : that two contiguous portions of heat have a mutual relation when their temperatures are equal (or as M. Volta has said, when their *tensions* are the same). These expressions are exact, only in so far as they define an appearance. In reality the heat of any portion cannot arrest that of another. These two heats give each other mutually free passage. It would then be wrong for one to conclude from these expressions that two portions of contiguous heat restrain each other mutually, as two bent springs stayed against one another, or as two masses of hair which repel each other by their elasticity.

But in what does the equilibrium of these two portions of contiguous heat consist? In order to answer this question clearly, I will suppose the two portions to be enclosed in an empty space, terminated on all sides by impenetrable walls. One may represent two cubes applied by one of their faces, forming in consequence a rectangular parallelopiped perfectly hollow, of which the six faces are of the same matter, absolutely solid and without pores. The two portions which I consider are, in this example, the two applied cubes. The heat occupying the interior of this space moves freely there, and assuredly one can see no reason why it should pass with less facility across the boundary of the two portions than across every other section of this space. There are then continual exchanges from one portion to another, and one can affirm (in consideration of the number of particles and their continual motion) that at each observable instant the state and quantity of the heat in each portion are constant. There is then no ceasing of the different particles, which are found at any one

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place, but their number and their mean distance in each portion are constant. Concerning their speed, as it is in the same free fluid (consider the constant nature of the cause which produces and renews it continually), it is clear that it does not change : and I shall leave it out of the question, since at the present moment I consider only free radiant heat.

At all times that both portions of the space are found in the circumstances which I have just described, the heat between them is in a state of *equilibrium*. This signifies that the phenomena which manifest their existence remain the same : that if these phenomena change in the same manner and in the same quantity in the two portions, the equilibrium in question will not be disturbed. This would occur if one should remove from the total space, which we are considering, a certain aliquot part of all the heat found there, or indeed if this aliquot part should be added. The identity of the phenomena which implies the equilibrium of heat between these two portions of space is a relative identity, which, as one can see, may exist whatever may be the difference or the absolute inequality.

Let us now suppose that into one of the two portions of space (which I will represent constantly by the two adjoining cubes) one passes suddenly some new heat ; for example, one tenth of all that which is contained in this portion. This heat, instantly placed in motion, spreads immediately throughout all the space where it can penetrate freely. Thus the exchanges between the two portions would be unequal. One would send to the other eleven particles, while the latter would return only ten. This state causes a *rupture* of the equilibrium between the two portions.

By reason of the unequal exchanges one may conceive that the equality would be reëstablished. Thus the rupture of the equilibrium restores very quickly the equilibrium between two portions of free heat.¹

¹ Suppose that the densities of the heat in our two cubes are as the numbers 1 and 2 (i. e., that one is twice as hot as the other) : suppose further that in one second there passes from the one cube to the other a number of igneous particles which on the whole are as 1 to 10 (so that during this short time there is exchanged one tenth of all the heat).

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Absolute equilibrium of free heat is the state of this fluid in a portion of space which receives as much as it allows to escape it. definit

Relative equilibrium of free heat is the state of this fluid in two portions of space which receive from each other equal quantities of heat, and which are, moreover, in absolute equilibrium, or experience changes precisely equal.

The heat of several portions of space at the same temperature and *near* each other is at once in the two kinds of equilibrium. If one should change the temperature of all the space at the same time, it would destroy the absolute equilibrium, but not the relative equilibrium. Should the temperature of one or of several portions be altered without affecting all, each kind of equilibrium would be destroyed. 111

If the cause which throws out or which absorbs the heat of any portion is an instantaneous cause, after the action of this cause the relative equilibrium reestablishes itself incessantly by means of unequal exchanges. And after this reestablishment the absolute equilibrium remains destroyed, that is to say, the temperature of the place is changed.

If, on the contrary, the cause is permanent, that is to say, if there is opened in any one of the portions of this space a source or a sink which gives out or which absorbs heat incessantly, relative equilibrium tends to establish itself, but does not reestablish itself entirely during the action of the cause, and absolute equilibrium is constantly destroyed.

II.

APPLICATION OF THE PRECEDING THEORY TO THE PHENOMENON OF REFLECTION OF COLD.

Let us represent two spherical concave mirrors opposite to each other on their axes, and let us suppose placed at their foci

After seven seconds the ratio of the densities of the heat in the two cubes will be as 5 to 6. After fourteen seconds, these densities will be as 28 to 29, i. e., very nearly equality : the equilibrium will appear established.

I take this result from a calculation of M. le Sage thirty years since in the case of discrete fluids different from heat.

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two bodies precisely equal and similar and of the same substance, which I will call the two *focal bodies*.

To simplify this I will suppose, (1) that all the space where the apparatus is immersed is absolutely cold and receives heat only from part of the two focal bodies, (2) that these are hot and give out radiant heat continuously, (3) that the mirrors reflect the heat but do not absorb it.

With these conditions, it is clear that the heat thrown out by either one of the two focal bodies radiates on all sides. But I shall consider only the part which strikes the mirror of which it is the focus.

This heat is reflected parallel to the axis. Striking the opposite mirror in this direction, it is reflected to the focus of this second mirror and enters as a consequence the body which occupies this focus. Similarly inversely, the heat thrown out by this latter against its mirror enters after two reflections the body which occupies the focus of the first mirror.

Let us suppose, first, the two focal bodies are at the same temperature, or each one sending out in equal intervals of time an equal quantity of radiant heat to its own mirror. The relative equilibrium of heat between the two focal bodies will not be disturbed by this operation; for each of them will receive from the other exactly what it gives up to it. Radiation will exactly compensate absorption.

Now let us change, to a greater or less degree, the temperature of one of the two focal bodies; the exchanges made between them by means of double reflection will cease to be equal: the relative equilibrium will be destroyed. It will tend then to re-establish itself, and the temperature of these two bodies will approach each other. If additional heat should be thrown upon the first body, for example, a tenth of all that which it has, the second body will make advantageous exchanges with it. For ten particles transmitted by reflection, it will receive eleven by the same means: in this way its heat will be augmented.

If one should withdraw heat from the first body, for example a tenth, the second body will make exchanges at a loss, receiving nine against ten by means of the mirror. It will be cooled.

Such is the result of the theory conforming exactly to that of the ingenious experiments of M. Pictet, in spite of all the

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conditions which I have made, since these conditions influence only the quantity of cold or of heat produced by reflection, and not the nature of these actions. It is known that this physicist has observed heat and cold equally reflected in his apparatus, which is such as I have just described. He has not hesitated to explain the reflection of cold just as that of heat in a reciprocal sense: but being limited (conformably to his representation) to explanations drawn at once from experiment, and it not being his purpose, in the important work which he has published, to treat of the constitution of discrete fluids, he has not been able to enter into the details which I have just given. It has resulted from this that the view to which he has come touching the cause of the reflection of cold, founded upon these notions of equilibrium, inapplicable to discrete fluids, is insufficient for the theory, however true as to appearances.

It is certain that when one produces cold at the focus of one of the mirrors, the heat of the thermometer placed at the opposite focus follows the course which M. Pictet traces for it. And this course is what I have just described. But what it is that causes the excess heat of the thermometer to take this course, this physicist has not shown me, because he has not been called upon to consider heat according to its natural constitution. Now if one holds to the ideas of *tension*, of *stress*, in a word, of unvariable equilibrium, he finds that the progress of the phenomenon of heat in the experiment of the reflection of cold remains absolutely inexplicable. I shall now show, (1) that in this hypothesis of unvarying equilibrium no heat ought to pass from the thermometer to its mirror, (2) that if any does pass, this heat should not converge to the focus of the other mirror.

III.

EXCLUSION OF THE INDEPENDENT EXPLANATION OF THIS THEORY.

(I) At the instant when one places a cold body, such as glass, at the focus of one of the mirrors, the heat of all the neighboring bodies passes into it. This cause acts according to the law

of the inverse square of the distance, when we suppose the bodies to be of the same nature, as we do in this instance.

The mirrors employed in the experiment of the reflection of cold were placed ten and one half feet apart. Their curvature was that of a sphere with a radius of nine inches : so that their foci were about four and one half inches from their surface, measured on the axis.

If, then, we consider only the apparatus without taking into account the supports, or the air or the surrounding and neighboring bodies, it is clear that the mirror whose focus is occupied by the glass, being twenty-eight times nearer this cold body than the other mirror, ought to send out to it seven hundred and eighty-four times as much heat in the same time.

Further, the thermometer placed at the focus of this other mirror being nearer the glass than its mirror in the ratio of 26 to 27, ought to set free more heat than a portion of the mirror equal to its bulb in the double inverse ratio (at least for the part of the mirror which lies at the origin of the axis). This ratio is that of 729 to 676, or of about 13 to 12 ; so that, through the direct influence of the glass, the thermometer loses about a thirteenth more of its heat than if it formed a part of the mirror, at the focus of which it is placed. When the cooling of the first mirror becomes sensibly equal to the second, the thermometer being less distant than the former, is also more affected by the latter in the double inverse ratio of 27 to 28 ; that is to say, in the ratio of 784 to 729, or of about 14 to 13.

Thus the thermometer is cooled more than its mirror, either directly by the glass, or indirectly by the mirror whose focus this glass occupies. Heat here then is under less *tension* than in the mirror. Consequently it cannot pass from the thermometer to the mirror, nor in consequence, radiate from there to the opposite mirror next the glass. This progress of the phenomena in a system in unvarying equilibrium is contrary to the effect which the cause should occasion. And it is still more inexplicable when we consider the supports of the apparatus and all the surrounding bodies which send heat into the glass, and constantly draw out that of the thermometer, as well as of the opposite mirror: effects independent of reflection and of the particular position of the foci.

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(II). To which it is necessary to add, in reconciling the same (which is demonstrated false in the hypothesis I have discussed), that the heat of the thermometer passes in part into its mirror; as there is carried over only what replaces that which escapes, this heat would not be reflected, but absorbed. Now, all the heat which one of the mirrors sends out to the other, aside from that by reflection to the focus, being an irregular radiation, would not converge at the focus of the other mirror. Thus the foci would not be more characteristic than two other points, taken at random between the mirrors, for repeating the experiment of reflection of cold, which is absolutely contrary to the actual observation.

It is apparent, then, that if we refuse to consider heat according to its true constitution as a discrete fluid, whose particles are in motion, and if in consequence we do not arrive at ideas which I have given of the equilibrium of radiant free heat, it is impossible to give any satisfactory explanation (compatible moreover with the principles of sound physics), of this beautiful and remarkable phenomenon of the reflection of cold. The fact is established by an excellent observer, who has very clearly recognized the progress of the phenomena of heat. The discovery of the cause is due to the author of the true theory of discrete fluids.

IV.

SUPPLEMENTARY REMARKS.

(1). Radiant heat is only a part of the heat that escapes from a hot body. Let us suppose that in the preceding experiment the two foci of the mirrors communicate by a metallic bar, terminated at both ends by these foci: if we place at one end of the extremities of this bar an exhaustless source of heat (a red-hot iron, a blast-lamp flame, the focus of a powerful lens): immediately the radiant heat, following the course indicated above, will warm the other extremity of the bar by the double reflection. At the same time the non-radiant heat, creeping gradu-

ally into the contiguous parts of the bar, will slowly heat it and will finally come to the points most distant from the source.

The air being a discrete fluid much more dense¹ than heat, arrests and intercepts the particles of the latter. But being much more rare than the metal, it allows a portion of it to pass, which produces the phenomena of radiant heat. Light, much more rare and subtle than heat, is transmitted in much greater proportion by this same air, the opacity of which is so inconsiderable that it becomes sensible only in very great masses.² The transparency or the quantity of fluid transmitted through another fluid, depends upon the rarity and the subtlety of the particles of both fluids. I do not speak here of the affinities and capacities of different bodies for heat. I speak only of the mechanical interception of this fluid by its solid parts. This interception is sufficient only to produce these two kinds of heat or of cold, *radiant* heat, and *nonradiant* heat.

Entangled, further, in the small cavities or in the interstices of solid particles, the heat may or may not recover all the velocity which properly belongs to it, according as these cavities or interstices are or are not sufficiently spacious. When it recovers only a portion of its velocity, it becomes in part insensible or *latent*. When it can recover only a very little of it or none at all, it yields to the affinities of the particles which surround it and *combines* in a thousand ways.

(2). Heat is not the only fluid of its kind. Several discrete fluids are known, radiant and nonradiant.³ We often have occasion to consider these fluids in the state of equilibrium. The determination of the true sense of this word ought then to be of much importance, independently of the theory of heat.

¹ The density which I attribute to the air in this instance, consists chiefly in the proximity of its molecules; for a discrete fluid may be composed of very dense particles, but with large spaces between them: so that it could be more permeable than heat, although more dense.

² Notice the remarks of M. de Saussure, upon the transparency of the air, in his memoirs upon light. *Académ. de Turin*, 1790.

³ In the *electrical phenomena*, there are radiations of the corresponding fluid. In *magnetic phenomena* neither of the two magnetic fluids is radiant.

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If these remarks and the preceding discussion offer any useful views, if they tend to throw light upon an important class of phenomena, if they suggest any clear ideas upon the method of motion of invisible and subtle fluids which manifest their existence by such diverse appearances: finally, if these conceptions naturally connect themselves with other theories, either already proven, or rendered probable, concerning the various effects of these subtle fluids (such as the phenomena of evaporation, of electricity and of magnetism), is it not the requital of investigating the general theory upon which all these special explanations depend? This theory (I refer to that of M. le Sage of Geneva, upon the nature of discrete fluids) merits the further attention of physicists, since it depends, itself, upon another principle, more general, which has also as a proof of its reliability, the clear and satisfactory explanation of very striking and very general phenomena, absolutely inexplicable without it.

ON RADIANT HEAT.

BY

PIERRE PRÉVOST.

Geneva, 1809.

(Selections.)

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QUESTIONS RELATIVE TO THE NATURE OF CALORIC.

CHAPTER IV. PP. 6—10.

THE word *caloric* (heat) has been originated to explain the cause of heat, with the formally expressed intention of being non-committal as to its nature.

It is desirable to leave it indefinite as to whether heat may be produced by a specific fluid, or, merely, be a movement impressed upon the molecules of a body, without the introduction of any fluid.

Many noted physicists believe there is no specific fluid to which this word *caloric* is applicable. They believe that heat is produced by internal movements of the molecules of a body. More often, however, physicists have recourse to a vibrating ether or to the air, or to some other medium propagating waves to which they attribute the phenomena of heat.

Others believe that *caloric* is a specific fluid, which penetrates the body and produces all the appearances of this kind.

Among the latter, many believe that *caloric* and light are identical. Others are of a contrary opinion.

Some look upon *caloric* as simple ; a smaller number regard it as a compound fluid. Mr. J. A. DeLuc believes that *caloric* is a kind of vapor composed of ponderable matter held in a state of suspension by light. This conception throws some light upon many phenomena and merits serious consideration. Meanwhile, pressed to arrive at the chief object which I have in view, I will refrain from all discussion as to the composition of *caloric*.

I have no desire to repeat here and weigh the general arguments stated on the one side and on the other for sustaining the various views which I have just outlined. I will limit myself to a very few remarks on this subject.

As stated below I propose to consider *caloric* as a specific fluid. I will represent the radiations of this fluid as an emission

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and never as an undulation. I believe this conception and this representation to be more conformable than any other to the nature of things and founded upon the soundest principles of general physics. But if those who believe otherwise substitute waves for an emission they may be able, perhaps, to adapt to their opinion the explanations which I give for phenomena of this class. It is no desire of mine that they should attempt it, because I am persuaded that this would be translating a language clear and natural into a language obscure and artificial. But I make this statement to make clear the kind of work which I have undertaken. I do not contest any system, I do not refute any explanation. It is my aim, in limiting myself in my subject, to explain in my own way what seems to me to admit of clear explanation, and to indicate the phenomena of which the explanation remains imperfect. If each one who has an opinion upon the theory of *caloric* will give a concise exposition of his ideas on the subject, and will show how the facts may be coördinated by means of these conceptions: physicists can see at a glance which theory is most satisfactory, or if all should be rejected.

RESUMÉ OF THE PRINCIPLES EXPOUNDED AND OF THE PRINCIPAL CONCLUSIONS WHICH HAVE BEEN DEDUCED FROM THEM.

SECTION IX. pp. 258—261.

HEAT is a discrete fluid; each element of heat follows constantly the same straight line, as long as no obstacle arrests it. Every point of a hot space is constantly traversed throughout by streams of heat.

If we admit this constitution of heat, the following conclusions are inevitable.

The first three require nothing further. The others require the assumption that heat is comparable with light in its movements of reflection and refraction.

1st. conclusion: Free heat is a radiant fluid. Or, as the surface of the body of heat becomes free, each point of the sur-

face of the body is a center to which tend, and from which are carried, in every direction, streams of heat.

2nd. conclusion: The equilibrium of heat between two neighboring free spaces consists in the equality of the exchanges.

3rd. conclusion: When the equilibrium is disturbed, it is reëstablished by unequal exchanges. In a medium of constant temperature, a body that is hotter or colder requires this temperature according to the law that *the periods of time being in arithmetical progression, the differences of temperature are in geometrical progression.*

4th. conclusion: In a space of uniform temperatures, if a reflecting or refracting surface is introduced it has no effect in changing the temperature of any part of this space.

5th. conclusion: In a space of unequal temperature, if there is placed a body which is either hotter or colder and if afterwards a reflecting or refracting surface be introduced, the points, upon which these surfaces direct the rays emanating from this body, will be affected by it, being heated if the body is hotter, or cooled if it is colder.

6th. conclusion: A reflecting body, having been heated or cooled internally, recovers the surrounding temperature more slowly than a nonreflector.

7th. conclusion: A reflecting body, having been heated or cooled internally will have less effect on another body placed at any distance (in heating or cooling it) than a nonreflector would under the same conditions.

All these conclusions have been verified experimentally, except that concerning the refraction of cold. This experiment remains to be made, and I am confident of the result, at least if the refraction of the heat is capable of being observed. This result is indicated in the 4th. and 5th. conclusions, which could in this way be submitted to a new test. It is hardly necessary to indicate in this place the precautions by means of which one would place himself beyond every kind of misobservation.

RADIATION AND ABSORPTION.

BIOGRAPHICAL SKETCH.

PIERRE PRÉVOST was born in Geneva, March 3, 1751, and died at the same place on the 9th of April, 1839. He was the son of a clergyman and was educated for a clerical career, but turned his attention to law and later to educational work. He became a professor of philosophy and a member of the Academy of Sciences at Berlin in 1780. Here, through his acquaintance with Lagrange, his attention was directed to science, which later he followed up with his studies on Magnetism and Heat at Geneva where he became professor of physics in 1810. He published much on different subjects, including philology, philosophy, political economy, fine arts, etc. He issued the works of le Sage, supplemented by many additions of his own. His *Du Calorique Rayonnant* appeared at Geneva in 1809 and was an exposition and extension of his theory of exchanges first advanced several years before. The original memoir and later publications appeared in the *Journal de Physique* and the *Phil. Trans.* from 1791 to 1802. His remarkable versatility is indicated in the variety of his publications. His most valuable contribution to science is undoubtedly his *Theory of Exchanges* one of the most important principles in the whole range of physical science.

AN ACCOUNT OF SOME EXPERIMENTS
ON RADIANT HEAT, INVOLVING AN
EXTENSION OF PREVOST'S THEORY
OF EXCHANGES.

BY

BALFOUR STEWART.

Transactions of the Royal Society of Edinburgh.

Vol. XXII. Part I. pp. 1—20. March, 1858.

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1. AN ACCOUNT OF SOME EXPERIMENTS ON RADIANT HEAT, INVOLVING AN EXTENSION OF PREVOST'S THEORY OF EXCHANGES.

BY BALFOUR STEWART, Esq.

COMMUNICATED BY PROFESSOR FORBES.

Read, 15th, March 1858.

Division of Subject.

1. This paper consists of two parts, the first of which is confined to describing the experiments performed; while in the second it is attempted to connect these with certain theoretical views regarding Radiant Heat.

2. The experiments were made with a fourfold object; at least for the sake of clearness, it is well to class them into four distinct groups:—

Group I. Contains those experiments in which the quantities of heat radiated from polished plates of different substances, at a given temperature, are compared with the quantity radiated from a similar surface of lamp-black, at the same temperature.

Group II. Those in which the quantities of heat radiated at the same temperature, from polished plates of the same substance, but of different thicknesses, are compared with one another.

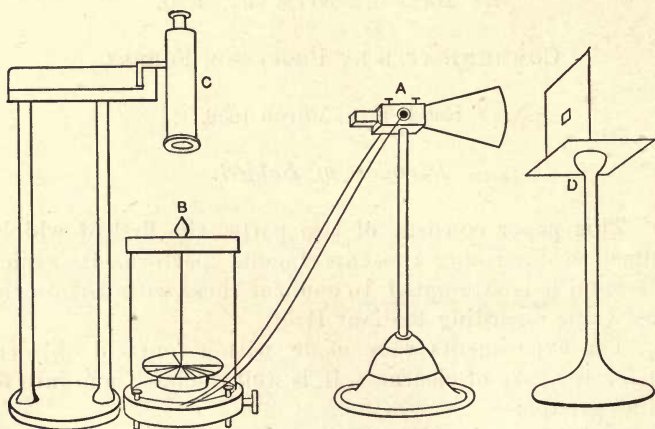
Group III. Those in which the radiations, from polished plates of different substances at any temperature, are compared with that from lampblack at the same temperature, with regard to the quality or nature of the heat radiated.

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Group IV. Those in which the same comparison is made between the radiations from polished plates of the same substance, but of different thicknesses.

Instruments used, and Method of using them.

3. I am indebted to the kindness of Professor Forbes for the use of a delicate thermo-multiplier, consisting of the sentient pile, and its attached galvanometer and telescope; as well as for much valuable information with regard to the proper method of using the apparatus.



The following arrangement was adopted for the great mass of the experiments:

A. Is the sentient pile, with a polished brass cone attached to it, for collecting the rays of heat.

B. Is the galvanometer, the position of its needle being read to $\frac{1}{10}$ th of a degree by the telescope C.

D. Is a screen placed before the mouth of the cone in which there is a small hole or diaphragm .65 inch square. The screen is covered with gilt paper, in order that, should it get slightly heated, it might radiate as little as possible.

The heated body is placed behind the diaphragm, filling up the field of view from the cone; so that every ray reaching the cone from behind the diaphragm comes from the heated body.

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In the following experiments, unless the contrary is mentioned, the distance of the diaphragm from the mouth of the cone is 2 inches.

The dimensions of the cone itself are as follows :

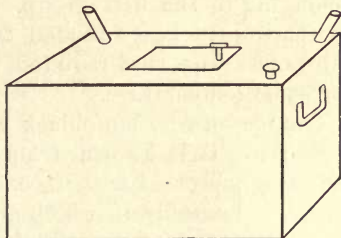
Length of axis, or distance between centre of mouth and pile, 5 inches.

Diameter of mouth or opening, 2.6 inches.

The temperature to which the heated body was raised was generally 212° , and the apparatus used for heating it was of the following construction :

It consisted of a tin vessel, having its top, bottom, and sides double (or a box within a box), and furnished on the top with a lid, also double, by means of which the body to be heated was introduced into the interior.

Water was poured into the chamber between the outer and inner boxes, and allowed to boil ; and, when the lid was shut, the temperature of the interior was found to rise very nearly to the boiling point ; a thermometer placed in the air of the chamber showing a temperature of 200° , and when lying on the bottom, a temperature of 210° . When an observation was to be made, the hot body was taken out, and that surface which lay on the bottom of the inner chamber placed behind the diaphragm, so as to radiate into the cone. In the following experiments, unless the contrary is mentioned, the body has been heated in this manner.



The first swing of the galvanometer needle was taken as representing the intensity of the heating effect : and Professor Forbes has shown, in a paper read before this Society, 2d May, 1836, that this will hold up to angles of about 20° , which is the maximum deviation used in these experiments.

Observations were always made with as little sunlight as possible ; and under these circumstances, it was ascertained that the stray heat reaching the cone was inappreciable. The needle, it was calculated, reached the limit of its swing about 12

seconds after the heated body had been taken out of the boiling-water apparatus.

Experiments were made to ascertain if the body cooled sensibly during this short period of time, and it was found that its cooling was so trifling as not to interfere in any degree with the results of these observations. In the following experiments, it is therefore assumed that the body remains at its original temperature of 210° while the observation is being made.

Four observations were generally made, and three if they agreed together exceedingly well, but never fewer. Very often the agreement was exact.

First Group of Experiments described.

4. With these remarks, I proceed to describe the experiments belonging to the first group, or those made with the view of comparing the heat radiated from polished plates of different substances with that radiated from a surface of lampblack at the same temperature.

The reason why lampblack was chosen as the standard is obvious ; for, it is known from Leslie's observations, that the radiating power of a surface is proportional to its absorbing power. Lampblack, which absorbs all the rays that fall upon it, and therefore possesses the greatest possible absorbing power, will possess also the greatest possible radiating power. The first substance compared with it was glass.

A. *Glass*.—A piece of plate glass, .3 inch thick, having paper coated with lampblack pasted on its surface next the pile, gave a deviation of 18.1. This may be taken as the radiation from lampblack.

Three plates of crown glass, each .05 inch thick, placed one behind the other, gave.....17.7.

A single piece of crown glass of the same thickness, gave.....16.5.

This difference is probably owing to the single plate cooling faster than the three plates. It may be argued that the radiation from the glass is very nearly equal to that from lampblack ; and indeed this is already well known.*

* See Leslie's "Inquiry into Nature and Propagation of Heat."

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B. Alum.—Here the boiling-water apparatus could not be used, since alum becomes calcined at a temperature much below 212° ; but a self-regulating apparatus, invented by the late Mr. Kemp, was employed instead, giving a steady temperature of 98° .

A piece of plate glass .18 inch in thickness, gave....5.0

A piece of alum of the same thickness gave.....5.0

The radiation from the alum may therefore be reckoned equal to that from glass.

C. Selenite.—At the temperature of 98° —

A piece of selenite .125 inch in thickness gave....5.1

Under the same circumstances, glass .18 inch thick
gave.....5.0

In the boiling-water apparatus,

The same piece of selenite gave.....18.0

While blackened glass gave.....18.5

The radiation from selenite may therefore be reckoned equal to that of alum or glass.

D. Mica.—A small box was constructed, having two windows of mica, the thickness of the mica in the one being .0009 inch, and of that in the other .02 inch. This box was filled with mercury (Professor Forbes having suggested the use of that metal, to keep up the temperature, while interfering very little with the radiation). The whole was then set on a glass dish in the boiling-water apparatus.

The radiation from the thin window was11.2

While that from the thick window was.....12.7

As it would have been manifestly erroneous to compare these with the radiation from the blackened glass lying in contact with the bottom of the apparatus, the thin window was removed, and the blackened paper substituted in place of it.

While the thick mica window gave.....12.7

The blackened paper gave.....13.8

In comparing the radiations from the two windows, they were observed alternately. We see, therefore, that the radiation from mica, especially thin mica, is less than from lamp-

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black in the proportion of 11.2 to 13.8, or the heat from thin mica is 80 per cent of that from lampblack.

E. *Rock Salt*.—As in the experiments with rock salt, it was desirable to obtain results of the greatest possible accuracy, the radiation from rock salt was not compared with that from blackened glass; for it was found that glass cooled more rapidly than rock salt.

The following plan was adopted :—

A piece of rock salt .18 inch thick (the temperature as in all the previous examples being about 210° , gave 3.2

A canister with water kept boiling, coated with lamp-black.....22.0

In order to estimate how much the rock salt had cooled during the observation, the following experiment was made, without any diaphragm :—

Rock salt .18 inch thick taken to the cone at once, gave.....5.1

After cooling for 15 seconds, it gave.....4.9

It will be seen from this, that were the rock salt, instead of cooling during the 12 seconds necessary for the observation, kept at the temperature of 212° , it would not have given more than 3.3, while the hot-water canister gave 22.0.

5. From these experiments, it appears that glass, alum, and selenite, at low temperatures, have an intensity of radiation very nearly equal to that from lampblack; while mica radiates somewhat less, and rock salt greatly less. This is shown by the following table :

TABLE I.

RADIATING SUBSTANCE.	TEMPERATURE.	
	212°	98°
Lampblack,.....	100	
Glass,....	98	27
Alum,.....		27
Selenite,.....	98	27
Thick mica,.....	92	
Thin mica,.....	81	
Rock salt.....	15	

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Second Group of Experiments described.

6. I now proceed to the second group of experiments, or those designed to compare together the quantities of heat radiated at the same temperature from polished plates of the same substance, but of different thicknesses.

A. *Glass*.—No direct experiment of this kind was made on glass; for although a thick plate gave a somewhat greater radiation than a thin plate, it was imagined that this was due to the unequal cooling of the two plates. Indirectly, however, we may gather that thick glass radiates somewhat more than thin glass, from the following experiment, which belongs more properly to the fourth group:

A plate of crown glass .05 inch thick, being placed before the cone as a screen, and a similar plate .05 inch thick, and 3.75 inches square, being used as the source of heat at a distance of 6 inches, and no diaphragm used, the deviation was0.95*
But when the source of heat was a similar plate .10 inch thick, the deviation became1.45

Such a difference cannot be accounted for by the unequal cooling of the plates; and it would seem to indicate that a small quantity of heat from the interior of the thick plate reached the surface; which heat, having already been sifted by its passage through glass, was easily able to pierce the screen.

In another similar experiment,

One piece of crown glass .05 inch thick, gave a deviation of.....1.1
Two plates .05 inch thick, the one behind the other, 1.55
Three such plates,.....1.9

B. and C.—No experiments of this kind were attempted with alum or selenite.

D. *Mica*.—Experiments similar to those already described, only at a distance of $2\frac{1}{2}$ inches from the cone, gave—

* Without any screen, it was calculated that the intensity of effect would have been equal to about 150° .

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For mica .0009 inch thick (average of two sets of experiments),.....	8.2
For mica, .02 inch thick (average of two sets of experiments),.....	9.3

The experiments already quoted, which were made at a shorter distance from the pile, gave—

For mica, .0009 inch thick,.....	11.2
For mica, .02 inch thick,.....	12.7

E. *Rock Salt*.—Three pieces of rock salt were used. Their dimensions were:

	1st Piece.	2nd Piece.	3rd Piece.
Length.....	1.15 inch	2.15 inches	2.5 inches
Breadth.....	1.15 “	1.4 inch	1.4 inch
Thickness....	0.18 “	0.36 “	0.77 “

For these pieces, as well as for the other substances, I am indebted to the kindness of Professor Forbes. When placed behind the diaphragm, the farthest off surface was large enough to fill up the field of view,—that is to say, all rays from the cone striking the nearest surface struck also the surface farthest off; the distance between the two surfaces being the thickness of the piece.

The following are the means of four sets of experiments :—

Radiation from 1st or thinnest piece.....	3.4
“ “ 2nd or middle piece.....	4.3
“ “ 3rd or thickest piece.....	5.3

This proves that more heat is radiated by a thick than by a thin piece of rock salt.

The following experiments were devised by Professor Forbes, to confirm the above results.

(a.) The second piece of rock salt was placed obliquely behind the diaphragm, making an angle of 20° with the prolongation of the axis of the cone. A piece of fir wood of the same dimensions was placed in the same way. The two substances being compared in this position, and also in the usual position behind

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diaphragm (viz., perpendicular to the direction of the cone's axis), the following was the result :

	Oblique.	Usual position.
Rock salt .36 inch thick,.....	4.0	4.0
Wood, same size as rock salt,	9.1	14.1

In order that this experiment may be understood, it may be well to mention, that, when the plate was placed obliquely behind the diaphragm it did not quite fill up the field of view. Hence the wood gave out less heat to the cone in this than in its ordinary position.

It appears, therefore, that the radiation from rock salt, in a direction making a small angle with the surface, bears a greater proportion to the corresponding radiation from wood than when both radiations are taken perpendicular to the surface. The reason undoubtedly is, that in the former case the rays come from a greater thickness of the substance, so that their intensity is increased.

β. The middle-sized piece of rock salt was bound tightly to the thickest piece, with a slip of tin foil between, so that the whole might cool as one piece, and thus obviate any objection that might be brought against the results, founded on the unequal cooling of the plates, owing to their thicknesses being different.

The surface of the middle-sized piece facing the pile, gave.....	6.3
That of the thickest piece, gave.....	8.1

The plates, therefore, still retain their inequality of radiation; but the amount from each was increased, owing, no doubt, to the reflection and radiation from the tin foil. The radiation from the tin foil may be estimated at 1.0, deducting which, we have 5.3 and 7.1; the increase now being due to reflection from the tin foil.

7. It thus appears, that while the difference between the radiating power of thick and thin glass is so small as not to be capable of being directly observed, there is a perceptible difference between the radiation from thick and thin mica, and a

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still more marked difference between the radiation from plates of rock salt of unequal thickness.

But (at least with the thicknesses used) the greatest radiations from mica and rock salt were still below that from lamp-black, and the radiation from rock salt greatly so.

The following table exhibits the results of the second group of experiments:

TABLE II.

SUBSTANCE.	RADIATION FROM THICK PLATE.	RADIATION FROM THIN PLATE.
Glass,.....	100	100
Mica,.....	100	89
Rock salt,.....	100	Middle } 81 thin } 64

Third Group of Experiments described.

8. I now proceed to consider the third group of experiments, or those made with the view of comparing the radiations from various polished surfaces with that from lampblack, as regards the *quality* of the heat; its quality being tested by its capability of transmission through a screen of the same material as the radiating plate.

A. *Glass*.—In an experiment already described, where a plate of crown glass .05 inch thick was used as a screen, and a similar plate of crown glass as a source of heat—

We had.....0.95
A similar plate .1 inch thick as the source of heat,
gave.....1.45
Blackened paper attached to a similar surface of plate
glass, .3 inch thick, the blackened side being next
the pile,.....1.95

Therefore heat from a thin plate of glass is less transmissible through glass than heat from blackened paper.

B. and C.—No experiment of this nature was made with alum or selenite.

D. *Mica*. —The apparatus already described gave—

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	Without screen.	With mica screen .0025 inch thick.
For window (the window, it will be borne in mind, is the radi- ating surface), .0009 inch thick..	11.2	2.5
Window .02 inch thick.....	12.7	3.2
Blackened paper attached to glass lying on the bottom of the boiling-water appara- tus, gave.....	21.0	6.3

We have therefore the proportion of heat passed by mica screen

For heat from thin mica window,.....	.223
“ “ “ thick “ “260
“ “ “ blackened paper,300

E. *Rock salt*.—The thickest piece of rock salt (thickness .77 inch) being used as a screen, and the diaphragm withdrawn, in order to give greater results; the middle sized piece of rock salt gave—

With screen.	Without screen
6.1	19.6

The same screen stopped 3 rays out of 12 for *ordinary* lamp-black heat.

This experiment is sufficient to show that rock salt is much less diathermanous for heat from rock salt than for ordinary heat. The common opinion, that rock salt is equally diathermanous for all descriptions of heat, is therefore untenable.

9. From the third group of experiments it appears, therefore, that heat emitted by glass, mica, or rock salt, is less transmissible through a screen of the same material as the heated plate, than heat from lampblack; this difference being very marked in the case of rock salt.

Fourth Group of Experiments described.

10. I now proceed to the fourth group of experiments, or those made with the view of comparing the radiations of plates of the same substance, but of different thicknesses, with regard to the quality of the heat radiated.

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A. *Glass*.—It has been already shown (Art. 8), that heat from crown glass .05 inch thick is less transmissible through glass, than that from crown glass .10 inch thick.

B. and C.—No experiments of the kind were made on alum or selenite.

D. *Mica*.—It has been already shown (Art. 8), that heat from thin mica is less transmissible through a mica screen than heat from thick mica.

E. *Rock salt*.—With a screen of rock salt .18 inch thick, the following result was obtained :

Thickest piece of rock salt, heated to 210°	
(thickness .77 inch), gave.....	2.5
Middle-sized piece of rock salt, heated to 210°	
(thickness .36 inch), gave.....	1.7
Thinnest piece of rock salt, heated to 210°	
(thickness .18 inch), gave.....	1.1
Without any screen, the same pieces gave—	
Thickest,.....	4.9
Middle-sized,.....	4.1
Thinnest,.....	3.3
Proportion of heat from thickest piece passed.....	.51
Proportion of heat from middle-sized piece passed	.41
Proportion of heat from thinnest piece passed.....	.33

A similar experiment, with a screen .29 inch thick gave—

	With screen.	Without screen.	Proportion passed.
Thickest piece...2.6	5.4		.48
Middle-sized,1.8	4.5		.40
Thinnest.....1.2	3.5		.33

It follows from this, that a screen of rock salt passes heat from thick, more easily than heat from thin rock salt.

11. From this fourth group of experiments, we learn that heat from thick plates of glass, mica, or rock salt, is more easily transmitted by screens of the same nature as the heated plate than heat from thin plates of these materials.

The following table exhibits the results of the third and fourth group of experiments :

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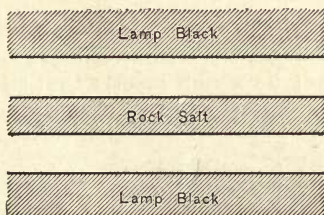
TABLE III.

SOURCE OF HEAT.	No. of Rays out of every 100 that pass through a screen of the same material as the source of Heat in 1st column, the screen being of only one thickness for each material.	No. of Rays of Lampblack Heat out of every 100 that pass through the same screen
Glass (crown $\frac{1}{20}$ th inch thick),	0.66 }	1.33
Glass (crown $\frac{1}{10}$ th inch thick),	1.0 }	
Mica (thickness .0009 inch),	22 }	30
Mica (thickness .02 inch),	26 }	
Rock salt (thickness .18 inch),	33 }	(Art. 12)
Rock salt (thickness .36 inch),	41 }	
Rock salt (thickness .77 inch),	50 }	

Results deducible from the foregoing Experiments.

12. These experiments, as well as others yet to be described, may be explained by Prévost's theory of exchanges, somewhat modified.

In the first place, it would seem to be a consequence of this theory, that radiation must take place from the interior as well as from the surfaces of bodies. For, suppose that we have two indefinitely extended surfaces of lampblack, as in the figure, and between them a plate of rock salt of a certain thickness, also indefinitely extended; and let the whole be kept at the same temperature. Then, since the temperature of the rock salt remains the same, it must radiate as much as it absorbs. But a thicker plate of rock salt, placed under the same circumstances, would absorb more of the heat radiated from the lampblack because each ray would have to pass through a greater depth of the substance of salt; hence a thick plate of rock salt must radiate more than a thin plate. We see likewise, the reason for the small radiative capacity of



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rock salt to be its small absorptive capacity. In order to prove this deduction from Prévost's theory experimentally true, the following experiment was devised:

A boiling-water canister, coated with lampblack, was put behind the diaphragm, filling up the field of view, and the three pieces of rock salt heretofore used as sources of heat, were now separately used as screens, being put before the diaphragm, so that the heat from the canister had to pass through their substance before reaching the cone. The following was the result:

	Without any screen.	Screen of Rock salt .18 inch thick.	Screen of Rock salt .36 inch thick.	Screen of Rock salt .77 inch thick.
Radiation from canister,	21.3	17.6	16.8	15.8

The difference between heat absorbed by plate,
thickness = .18 inch, and that absorbed by
plate, thickness = .36 inch,

is.....1.2 }
Another similar experiment gives.....0.9 } Mean 1.1

The difference between heat absorbed by plate,
thickness = .36 inch and that absorbed by
plate, thickness = .77 inch,

is.....1.0 }
Another similar experiment gives.....1.3 } Mean 1.1

These should nearly correspond to the differences between the radiation from the same place, under their ordinary circumstances of position (if the theory be true which asserts that the absorption of such a plate equals its radiation); accordingly we find that

The difference between heat radiated by
plate, thickness.....=.18 inch }
And that radiated by plate thickness = .36 inch, } Is 0.9
While the difference between radiation of
plate thickness.....=.36 inch }
And that of plate thickness.....=.77 inch, } Is 1.0
(Art. 6, mean of four sets of experiments.)

We see, therefore, that there is an agreement between the two sets of differences, as near as can be reasonably expected.

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13. If we now suppose a plate of glass, and not a plate of rock salt, placed between surfaces of lampblack, the plate, whether thin or thick, will allow scarcely any heat to pass through it; and, consequently, plates of different thicknesses will all absorb very nearly the same amount, that is, nearly all that enters them. In this case, therefore, the radiation (which is equal to the absorption) will be very slightly increased by an increase of thickness of the plate. Also the amount of heat radiated, being equal to the heat absorbed, will be very nearly as great as that from lampblack.

14. There are, therefore, two peculiarities of the radiation from plates of diathermanous substances, and which are most marked for those substances which are most diathermanous.

1st, That the amount of radiation from such plates is less than that from lampblack.

2d, That the amount of radiation from such plates increases with the thickness of the plate.

The correlation between these different properties of bodies is seen from the following table:

TABLE IV.

Bodies ranked according to their Radiating Capacity (least radiating first).	Bodies ranked according to their Diathermancy (most diathermanous first).	Bodies ranked according to the proportion by which their Radiation is increased by increasing the thickness.
A stratum of heated gas (from Melloni's Experiments), Rock salt. Mica. Glass. } Selenite. } Alum. }	A stratum of gas. Rock salt. Mica. Glass. } Selenite. } Alum. }	Rock salt. Mica. Glass.

15. The reason why radiation has hitherto been supposed to be confined to the surface, or to an exceedingly small distance below the surface of a body now becomes obvious. The effect of coating a surface of polished metal with gum, for instance, is

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to increase the radiation; but, after a very small thickness of film, an additional coating is powerless to increase the radiation; the reason being, not that radiation is incapable, in all cases, of taking place except at the surface; but because such films being exceedingly impervious to heat of low temperatures, the radiation from them is very little increased by increasing their thickness.

Since, therefore, it appears that radiation takes place from the interior as well as from the surface of bodies, the question arises, are we to suppose each particle of each substance to have, at a given temperature an independent radiation of its own, equal, of course, in all directions? *A priori*, this is the most probable supposition, and it seems likewise to be conformable to experiment.

16. In an experiment already described,

A plate of crown glass .05 inch in thickness being used as a screen, the quantity of heat radiated from crown glass .05 inch thick that passed, was.....0.95
While of that radiated from crown glass, .10 inch thick there passed.....1.45

Another experiment gave—

Quantity of heat from crown glass .05 there passed..1.1
Quantity radiated from two plates of crown glass, each .05 inch thick the one placed loosely behind the other,.....1.55

From this we may infer, that the radiation from two plates of glass placed loosely behind each other is the same as the radiation from a plate of double the thickness, and, consequently, that the radiation from a particle of a substance does not diminish owing to its being placed in the interior.*

17. Let us now refer to the radiation from rock salt:

The radiation from a piece .18 inch thick, was.....3.4
That from a piece .36 inch thick, was.....4.3
That from a piece .77 inch thick, was.....5.3

* The idea of this experiment was derived from a remark of Professor Forbes, who suggested that several plates of rock salt, the one behind the other, might be advantageously substituted for a thick plate of the same material as giving the very same result.

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Now if we suppose the radiation of a particle in the interior to be as intense as that of a particle at the surface, why, it may be asked (since rock salt is extremely diathermanous), does not a piece of double thickness give nearly a double radiation and so on, the radiation increasing very nearly as the thickness?

If we still hold the doctrine of an equal and independent radiation from every particle, we are shut up to the conclusion that rock salt must be comparatively opaque to heat radiated by itself, a result which is abundantly confirmed by experiment.

Thus while the radiation from rock salt .18 inch thick, without any screen, is 3.4, with a screen of rock salt .18 inch thick it becomes 1.1.

If, therefore, we have a piece of rock salt of double the thickness, or .36 inch thick, we should expect that the radiation from it would be $= 3.4 + 1.1 = 4.5$. It is, in fact, 4.3. The difference (0.2) being within the limit of error of observation.

In rock salt, therefore, we may suppose each particle to have an independent radiation of its own, unaffected by its distance from the surface.

18. We see, therefore, that the opacity of rock salt with regard to heat radiated by itself, is a consequent of the admission, that the radiation from rock salt does not increase so rapidly as the thickness increases; and this again results from the fact, that the absorption of heat by a plate of rock salt does not increase so rapidly as the thickness increases. This, again, is due to the fact, that the first part of the plate of rock salt sifts the heat so that it is more easily transmitted by the second part; and this confirms the result arrived at by Professor Forbes, who, finding that rock salt stopped heat of lower temperature rather more readily than heat of high temperature, concluded that there are a few rays for which rock salt is opaque.*

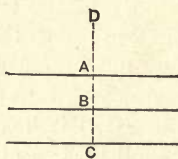
* To take a numerical example, let us suppose the heat from a single plate of rock salt to be $= 1$, then the heat from a plate four times the thickness, or (which is the same thing) the heat from four single plates, one behind another, should be nearly four times as much or $= 4$ (if we suppose the heat from each of these four plates to be readily passed by the plates between it and the pile), but the heat from the four-fold plates, instead of being four times as much, is not double of the heat

We conclude, therefore, that every body which sifts heat in its passage through its substance is more opaque with regard to heat radiated by a thin slice of its own substance, than it is with regard to ordinary heat.

19. This conclusion may be also stated thus: We have before proved (Art. 12) that the radiation of a thin slice of any substance equals its absorption; we now add that the heat radiated is the same as that absorbed, with regard to quality as well as quantity.

For this expresses the fact, that substances which sift heat are likewise opaque with respect to heat radiated by themselves. For, since the heat which they absorb is manifestly that kind of heat for which they are opaque, if the description of heat radiated is the same as that absorbed, then they also will be opaque with respect to heat radiated by themselves. Considering, therefore, the heat of any temperature to consist of heterogeneous rays, we may state the law thus: *“ The absorption of a plate equals its radiation, and that for every description of heat. ”*

20. A more rigid demonstration may be given thus: Let AB, and BC be two contiguous, equal, and similar plates in the interior of a substance of indefinite extent, kept at a uniform temperature. The accumulated radiation from the interior impinges on the upper surface of the upper plate; let us take that portion of it which falls on the particle A, in the direction DA. This ray, in passing from A to B, will have been partly absorbed by the substance between A and B, but the radiation of the upper plate being equal to its absorption (since its temperature remains the same), the ray will have been just as much recruited by the united radiation of the



from the single plate; hence, the heat from any of the interior plates of the compound plate is passed with great loss, by the plates between it and the pile. Now, since the absorption of a plate equals its radiation, the reason why the four-fold plate scarcely radiates twice so much as the single one is, that it scarcely absorbs twice as much; and this again is due to the fact, that the heat after it has passed the first plate of the four-fold plate has become sifted, and passes with little diminution of intensity through the other three plates.

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particles between A and B, as it was diminished in intensity by their absorption. It will therefore reach B with the same *intensity* it had at A. But the *quality* of the ray at B will also be the same as its *quality* at A. For, if it were different, then either a greater or less proportion would be absorbed in its passage from B to C, than was absorbed of the equally intense ray at A, in its passage between A and B. The amount of heat absorbed by the particles between B and C would therefore be different from that absorbed by the particles between A and B. But this can not be; for, on the hypothesis of an equal and independent radiation of each particle, the radiation of the particles between B and C is equal to that of the particles between A and B, and their absorption equals their radiation. Hence the radiation impinging on B, in the direction of DB, must be equal in quality as well as in quantity to that impinging upon A; and, consequently, the radiation of the particles between A and B must be equal to their absorption, as regards quality as well as quantity; that is, this equality between the radiation and absorption must hold for every individual description of heat.

21. The following experiment illustrates this law:

The quantity of heat radiated from crown glass screen,
 .05 inch thick, which passes through a crown glass
 screen .05 inch thick, = 0.95

While that from plate glass .3 inch thick, covered with
 blackened paper (the blackened paper being next the
 pile), which passes through the same screen... = 1.95

But if the surface of crown glass .05 inch thick, farthest
 from the pile, be coated with paper, the polished sur-
 face being next the pile, then the amount which passes
 the screen, = 1.85

And if three plates, the one behind the other, of crown
 glass, each .05 inch thick, be used as the source of
 heat, the surface farthest from the pile of the farthest
 off plate only being covered with paper, the amount
 of radiation which passes the screen, = 1.95

Such a plate of glass or series of plates, therefore, by having
 the farthest off surface coated with paper, gives out heat

similar to that from paper or lampblack; the reason being, that the heat from the paper on the farthest off surface is as much recruited as it is absorbed by its passage through the glass, both as regards quantity and quality; so that the radiation which falls upon the cone is virtually that from paper or lampblack.

22. There is little difficulty in explaining why heat from a thick plate of any substance should pass more readily through a screen of the same substance than that from a thin plate. The reason is, that the heat from the interior of the thick substance, having been sifted in its passage, is, therefore, now more easily able to pass through a screen of the same substance.

23. We see also why, generally speaking, bodies at the same temperature radiate the same quality of heat; let us, for instance, take a tolerably thick plate of glass, and a surface of lampblack, and compare them together. Since the plate of glass absorbs nearly all the rays that fall upon it, it will radiate nearly as much as lampblack; and since the quality of the radiated is the same as the quality of the absorbed heat, its radiated heat will very nearly have the same quality as that which is radiated by lampblack.

The influence of the Reflective and Refractive Powers of Bodies on their Radiation considered.

24. Hitherto in these investigations no account has been taken of reflection at the surfaces of the plates, because—1st, those rays only were considered which passed perpendicularly, or nearly so, through such plates; and, 2d, because the indexes of the refraction for the substances experimented on were not very high.

But for rays passing obliquely through such media, or for rays passing in any direction into substances such as metals, we must take account of reflection from the surface which will influence materially our results.

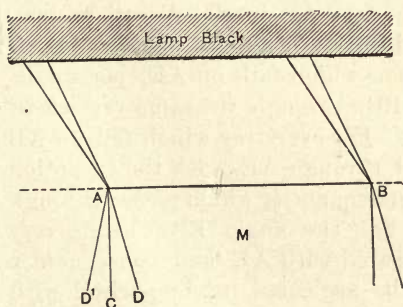
Thus, no substance is so opaque for heat as metals, but yet only a small portion of the heat falling on them is absorbed, the rest being reflected back; consequently for such bodies the radiation (which must be equal to the absorption) is very small.

It is also desirable, for another reason, to investigate the laws according to which the reflective nature of the surface of

RADIATION AND ABSORPTION.

a body influences its radiation. For the question arises, is the law of an equal and independent radiation of each particle of a body theoretically consistent with equilibrium of temperature? That is, suppose we have an irregularly-shaped inclosure walled round with a variety of substances, and each particle of each substance radiating into the inclosure, from the sides of which it is reflected many times backwards and forwards before it is finally absorbed; this being the case, will the law of equal and independent radiation, and those of reflection and refraction, so fit with one another, that every particle of the walls of the inclosure shall absorb precisely as much heat as it radiates? It will be endeavored to show that these laws are so adapted to each other; and I shall select for the proof a definite form and description of inclosure, the conclusions arrived at rendering it highly probable (if not rigidly demonstrating) that the same adaptation will hold good for every inclosure, however irregular or varied.

For these reasons, I shall now endeavor to investigate what connection the radiation of a substance has with the reflective power of its surface; and in doing so (in order to abstract entirely from the effects produced by the variable thickness of the radiating plate), I shall suppose it to be of indefinite thickness; so that all the heat which enters it is absorbed. Our consideration is, therefore, limited to the effects of *one* surface.



25. Let AB be a portion of the line of section of an indefinitely extended surface with the plane of the paper supposed perpendicular to the surface, and let this surface belong to a body (M) of indefinite thickness downwards; also let there be an indefinitely extended surface of lamp-

black parallel to this lower surface, as in the figure. Lastly, let the whole be kept at uniform temperature. In order that the body (M) may be maintained at this temperature, it is necessary that the heat which has left the surface AB, having

come from the interior of (M), in the direction contained in any very small angle CAD, shall be replaced by an equal quantity of heat entering the surface AB, to diverge into the interior through the same small angle CAD. For, by this arrangement it is clear the particles in CAD get back as much heat as they give out.

Part of the heat, no doubt, which fell on A in any direction DA, would be reflected back in the direction AD', making the same angle with the surface as AD; but this loss would be made up for by part of the heat falling upon A, in the direction D'A, being also reflected back in the direction AD.

The internal reflection at A being compensated for, if the heat that really leaves the medium be also compensated for, then as much heat will be passing at A in the direction AD as will be passing in the direction DA. It will be the same, therefore, as if the body, instead of having a surface at A, were indefinitely extended upwards from A, as well as downward; in which case, as has been already shown (Art. 20), there will be equilibrium of temperature, provided that the radiation of a particle is equal to its absorption, and that for every description of heat.

Before proceeding further with this investigation, it will be necessary to establish some preliminary propositions.

26. *1st Preliminary Proposition.*

The heat which falls on the line AB in the directions contained in the very small angle CAD, is the same which falls on AE, perpendicular, EB, through the same very small angle. For every ray which fell on AB passed through AE, with the exception of a small quantity which passed through EF; but the angle EBF being very small, EF is very small compared with AE, and consequently the heat falling on EF may be neglected in comparison with that falling on AE.

It is clear, also, that the heat falling on AB is proportional to AB, and to the size of the very small angle CAD.

The above will still hold if, instead of the substance of which AB is the surface being supposed below AB, and the rays fall-

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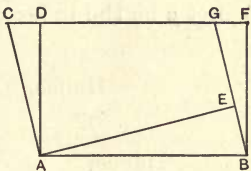
ing on it through a vacuum, we suppose a substance to be indefinitely extended upward and the rays to originate in the substance itself, and fall on its surface AB.

For, although any ray GE, which falls on E, will be partly absorbed between E and B, it will be as much recruited by the united radiation of the particles between E and B as it was absorbed; so far, indeed, as regards quality and intensity (from what has been already proved, Art. 20), we may consider such a ray to be traversing a vacuum, it being recruited just in proportion as it is absorbed.

It is evident, also, that in this case the quantity of heat falling on AB will be proportional to the size of the very small angle CAD.

27. 2d Proposition.

First case.—If AB represent a surface (the substance being below AB), and CF a surface of lamp-black indefinitely extended (as in Art. 25), from which rays fall on AB through a small angle CAD; then, if AE be drawn perpendicular to GB, the heat that falls on AB will = a const. \times AE, whatever be the value of the angle CAB.



For, since the angle CAD is exceedingly small, CD may be considered very small in comparison with CF or CG; therefore the heat which impinges on AB through the angle CAD may be taken to be that which radiates from CG in direction between CA and DA; but since the radiative power of lampblack in any direction varies as the sine of the angle which that direction makes with the surface, this will = const. \times AE. Hence, if $R \times CAD$ be the quantity of heat which falls on AB, when AB is perpendicular to GB, that which falls on it when GB makes any angle GBA with AB. will be $R \times CAD \sin GBA$.

If i denote the angle which GB makes with the perpendicular to AB, then the heat impinging on AB will be $R \cos i \times CAD$.

2d case.—If the substance be above AB, and the rays falling on AB originate in the substance, the same formula will hold, for it has been shown, in Prop. 1st, that in this case, the heat falling on AB through the small angle CAD = that which falls

on AE through the same small angle; but, since the radiation from the interior of the substance is the same in all directions (each particle radiating independently and equally in all directions), the amount falling on AE will not be affected by the angle which AE makes with the surface; hence the heat falling on AB = const. \times AE = const. \times sin GBA.

If $R' \times CAD$ = quantity which falls on AB when AB is perpendicular to GB, that which falls on it when GB makes any angle GBA with AB, will be $R' \times CAD \sin GBA$; also the expression corresponding to $R \cos i' \times CAD$ will be $R' \cos i' \times CAD$.

28. *3d Proposition.* Let a ray strike the surface of a medium, at an angle of incidence = i ; and another ray at an angle of incidence $i + \delta i$, it is required to find the difference between the two angles of refraction.

Let μ be the index of refraction, then,

$$\begin{aligned} \sin i &= \mu \sin i' \\ \text{Hence, } \delta(\sin i) &= \mu \delta(\sin i') \\ \cos i \delta i &= \mu \cos i' \delta i' \end{aligned}$$

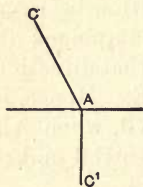
$$\begin{aligned} \text{Hence, } \delta i' &= \frac{\cos i}{\mu \cos i'} \delta i \end{aligned}$$

29. I shall also make the following supposition with regard to the laws of reflection and refraction.

1st. That if Q represent the quantity of heat falling on the surface of a medium in any direction CA, and aQ be the quantity reflected, then $(1 - a)Q$ is the quantity of heat refracted into the medium in the direction AC'. This follows from the law of the conservation of *vis viva*.

2d. That if the same heat Q originate in the medium, and strike A in the direction C'A, the quantity reflected back into the medium will be aQ , and the quantity refracted out in the direction AC will be $(1 - a)Q$.

30. These preliminary propositions being established, and suppositions made, let us suppose that heat from the surface of lampblack strikes the surface AB of the indefinitely thick medium (Fig. Art. 25) through a small angle δi (i being the angle of incidence), by Prop. 2d. the quantity of this heat will



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be $R \cos i \delta i$; while the part of it which enters the substance we shall call $(1-a) R \cos i \delta i$. These rays will diverge in the substance through an angle $\delta i' = \frac{\cos i}{\mu \cos i'} \delta i$ (Prop. 3).

But the quantity of heat that falls on AB from the interior through this angle will be

$$R' \cos i \delta i' = R' \cos i' \frac{\cos i}{\mu \cos i'} \delta i = \frac{R'}{\mu} \cos i \delta i,$$

and the portion of this which leaves the medium will be $\frac{(1-a) R' \cos i \delta i}{\mu}$

Equating this with $(1-a) R \cos i \delta i$, which enters the medium, we have $\frac{R'}{\mu} = R$ or $R' = \mu R$. With this supposition,

therefore, the law of an equal and independent radiation of each particle will give us equilibrium of temperature in the particular case under consideration. Had R' been a function of i' , it would have shown that the law of an equal independent radiation was inconsistent with equilibrium of temperature.

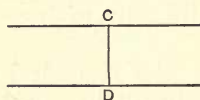
31. Only part, however, of the heat from the lampblack falling on AB entered into the medium, a portion of it $= a R \cos i \delta i$ being reflected back to the lampblack, hence the total quantity of heat radiated and reflected which leaves the surface AB through the small angle δi will be $= R \cos i \delta i$, the same as if the substance had been lampblack, the only difference being, that, in the case of lampblack, *all this heat is radiated*, whereas in other substances *only part is radiated, the remainder being reflected heat*.

32. Although we have considered only one particular case, yet this is quite sufficient to make the general principle plain. Let us suppose we have an enclosure whose walls are of any shape, or any variety of substances (all at a uniform temperature), the normal or statical condition will be, that the heat radiated and reflected together, which leaves any portion of the surface, shall be equal to the radiated heat which would have left that same portion of the surface, if it had been composed

of lampblack. And, indeed, we may see, from what has been already proved, that should such a state of things only once take place, it would always remain, there being no disposition to alter it.

Let us suppose, for instance, that the walls of this enclosure were of polished metal, then only a very small quantity of heat would be radiated ; but this heat would be bandied backwards and forwards between the surfaces, until the total amount of radiated and reflected heat together became equal to the radiation of lampblack.*

33. The equation $R' = \mu R$ must necessarily hold for every individual description of heat. We have, therefore, two laws necessary to the equilibrium of temperature—1st, That the absorption of a particle is equal to its radiation, and that for every description of heat ; 2d, That the flow of heat from the interior upon the surface of a substance of indefinite thickness, is proportional *caeteris paribus* to its index of refraction and that for every description of heat. It will, however, be borne in mind, that the former of these laws has been verified by ex-



* This will be clearly seen if we consider only those rays that are radiated perpendicular to the surface to the case of two parallel plates of polished metal of the same description radiating to one another.

For let r be the common radiation of the point C in direction CD, and of the point D in the direction DC, then since these radiations are bandied backwards and forwards in the directions CD, DC, until they are extinguished, we have the total quantity of heat falling on D in the direction CD (if ar denote the proportion of r reflected after one single reflection) expressed as follows:

$$\left. \begin{array}{l} \text{Total heat radi-} \\ \text{ated and reflected,} \\ \text{falling on D,} \end{array} \right\} = \left\{ \begin{array}{l} r + a^2r + a^4r + \text{etc.} \\ + ar + a^3r + a^5r + \text{etc.} \end{array} \right\} = \left\{ \begin{array}{l} r(1 + a + a^2 + a^3 + \text{etc.}) \\ \frac{r}{1-a} \end{array} \right. \quad (\text{since } a < 1)$$

But $1-a$ denotes the absorptive power of the metallic surface (all the heat not reflected being absorbed). Hence, since the radiative powers of bodies are proportional to their absorptive powers (Leslie's Inquiry) 1 being the absorptive power of lampblack, the perpendicular radiation

of a lampblack point will be $= \frac{r}{1-a}$ which is the very same expres-

sion we have obtained for the total heat radiated and reflected together, falling on D, in the same perpendicular direction from the metallic point C.

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periment, while the latter is only deduced from a theoretical investigation. It will also be seen, that by increasing the thickness of the radiating plate indefinitely, the radiation becomes ultimately independent of the diathermancy of the plate and is regulated only by its refractive index.

34. The connection which we have attempted to trace between the refractive and radiative power of a substance, presumes that those rays which we have been considering, have the power of forming wave lengths with the medium under consideration ; that is, of being capable of proper reflection and refraction.

It may be, however, that glass and other similar substances are so opaque, with respect to most of the rays of heat of low temperature, as to stop them almost entirely at the surface.

As such rays may, therefore, be conceived to be absorbed within the limit of physical surface of the medium, the corresponding radiation may be conceived to proceed from this physical surface. To such a case we may perhaps suppose reasoning similar to that of Fourier (as given by Professor Forbes in the *Philosophical Magazine* for Feb., 1833,) to be applicable ; the intensity of radiation being therefore proportional to the sine of the angle which the direction makes with the surface.

35. Let us now see, in conclusion, whether these investigations seem to point out any connection between internal radiation and conduction.

Now, without in the least confirming that these are identical there seem to be two points of similarity between them.

1st, Since the heat which enters metals is all absorbed at a very small depth, it follows that the flux of radiant heat from within upon the interior of metallic surface is derived from a very small depth.

Also, if we allow (what it has been endeavored to prove, Art. 30) that the flux of heat upon the interior of the surface is proportional to the index of refraction, this flux will be greatest in the case of metals which may be supposed to have a very high refractive power ; besides which, it will, as we have seen, be derived from a very small depth. The radiation of a metallic particle is therefore very great.

Now, if internal radiation be in any way connected with con-

duction, we might expect that good conducting substances should also be good internal radiators of heat, and we see they are so.

2d, The second bond of similarity is this. It seems to be a law that substances are almost invariably more diathermanous for heat of high temperature than for heat of low ; consequently, at high temperatures, the radiation of a thin plate or particle of a substance will bear a smaller proportion to the total lamp-black radiation of that temperature than at low temperatures. The internal radiations of particles of bodies would therefore diminish at high temperatures (not absolutely, but with respect to the proportion which they would bear to the total radiation of these temperatures). If the same rule holds for metals, and conduction be connected with internal radiation, we should expect that at high temperatures the conducting power of metals would be less than at low temperatures. Now this has been proved to be the case by Professor Forbes.

RESEARCHES ON RADIANT HEAT.

SECOND SERIES.

BY

BALFOUR STEWART.

Transactions of the Royal Society of Edinburgh.

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VI.—RESEARCHES ON RADIANT HEAT.

SECOND SERIES.

BY BALFOUR STEWART, M. A.

COMMUNICATED BY PROFESSOR FORBES.

(Read April 18th, 1859.)

Division of Subject.

I. The first part of this paper describes the following groups of experiments :

Group I. On the effect which roughening the surface of a body produces on its radiation.

II. On the nature of that heat which is radiated by rock salt at 212°F .

III. On the radiation of glass and mica, at high temperature.

The second, or theoretical, portion of the paper, has reference to the law which connects the radiation of a particle with its temperature and to Dulong and Petit's experiments on this subject.

There is also an addition of a later date than the rest of the paper on General Diathermancy.

Instruments used, and Method of Investigation.

2. The instruments used, and the method of using them, were much the same as described in the first series of these researches, Art. 3. Should any difference occur in the method of conducting a particular experiment, it will be mentioned when the experiment so performed comes to be described.

First group of Experiments Described.

3. This group of experiments has reference to the effect of roughening the surface of a body upon its radiation. This was

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suggested to the writer by Professor Forbes. The first substance tried was rock salt.

A. *Rock salt*.—It was found that roughening the surface by means of emery paper, until it became quite dim, had little or no effect in increasing the radiation, as will be seen from the following statement embodying the mean result of three sets of experiments.*

The pieces used were the middle piece (thickness = .36 inch) and the thickest piece (thickness = .77 inch), described in first series, Art. 6. These pieces were placed at a distance of about four inches from the mouth of the polished brass cone, and in order to increase the effect, no diaphragm was used. They were heated in the boiling-water apparatus already described. With this arrangement

The thick piece gave, when polished, a deviation of $.21^{\circ}.1$
when roughened, 21.8

The middle piece gave, when polished, a deviation of $.13.6$
when roughened, 13.5

4. The next point was to ascertain if roughening had any effect upon the *quality* of heat radiated.

The following table will show that it does not alter the quality of the heat sensibly; its quality being tested by its capacity of penetrating a screen of rock salt.

TABLE I.

SOURCE OF HEAT.	Percentage of whole Heat which penetrates a Rock Salt Screen thickness .29 inch.
Rock salt, .77 inch thick,	
polished,.....	49
roughened,.....	51
Rock salt, .36 inch thick,	
polished,.....	42
roughened,.....	43

* In the experiments with roughened surfaces, only one of the surfaces of the substance was roughened, the other being left polished. In *radiation* experiments, therefore, the roughened surface was placed next the pile; while in *transmission* experiments it was placed furthest from the pile.

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The trifling difference between polished and roughened salt in this table may fairly be attributed to error of experiment. We may therefore conclude, that roughening by emery paper neither alters the quantity nor the quality of the heat radiated by rock salt.

5. Again, the transmissive power of rock salt for lampblack heat of the temperature 212° , is not sensibly altered by roughening the surface. This will be seen from the following statement :

The percentage of Lampblack
heat transmitted was

With Screen of Rock salt, thick-	
ness .36 inch, polished,.....	77
With Screen of Rock salt, thick-	
ness .36 inch, roughened,.....	77

This result naturally follows from the previous one, for it has been shown (First Series, Art. 19) that the absorption of a plate equals its radiation and since roughening its surface does not influence the radiation it ought not to influence the absorption.

6. B. *Glass*.—It is already known that roughening the surface of a plate of glass does not sensibly increase its radiation. It is only necessary, therefore, to ascertain whether roughening the surface of a radiating plate of glass alters the capacity of its heat for penetrating a screen of glass. Accordingly, a plate of crown glass .05 inch thick, 3.75 inches square being placed before the cone as a screen, and a similar plate roughened, heated in the boiling-water apparatus, being used as the source of heat, and no diaphragm used,

The deviation was.....	$1^{\circ}.0$
When the source of heat was a similar plate, .10 inch	
thick, the deviation became,.....	1.5
And lastly, when the source of heat was a plate	
covered with lampblack, the deviation was,....	1.9

With the same sources of heat, only the glass polished instead of being roughened, these numbers were $0^{\circ}.95$, $1^{\circ}.45$, $1^{\circ}.95$. From the correspondence between these two sets of results, we may infer that the quality of the heat radiated by glass (at least in so far as transmission through a plate of glass

can test it) is not altered by roughening the surface of the glass.

7. And from all these experiments, we may infer (what has indeed been already remarked by Professor Forbes), that although roughening its surface with sand or emery paper renders a body dim for light yet it still remains specular for heat rays, which, possessing a greater wave length than those of light, are less liable than the latter to be influenced by scratches or furrows.

Second Group of Experiments Described.

8. The second group of experiments has reference to the nature of the heat which is radiated by rock salt at 212° . Its quality being tested by transmission through

- a. A screen of mica.
- β . One of mica split by heat.
- γ . One of glass.

9. a. *Mica Screen*.—By the mean of three sets of experiments, a mica screen (thickness = .003 inch nearly) passed about 31 per cent of ordinary lampblack heat, while it only passed 18 per cent of rock salt heat. Or if we call the proportion of black heat passed by the mica 100, that of rock salt heat will be 58.

10. β . *Split Mica Screen*.—Two sets of experiments agreed in giving twenty per cent as the proportions of lampblack heat of 212° , transmitted through a screen of mica split by heat, while the proportion of rock salt heat transmitted by the same screen was only $15\frac{1}{4}$ per cent. These numbers are to one another as 100 to 76.

11. γ . *Glass Screen*.—In order to avoid secondary radiation from the screen, which, in this case, absorbs nearly all the heat, two screens of microscopic glass were used, the one behind the other, with an interval between.

Moreover, as in this case, the proportion of heat transmitted is exceedingly small, the following arrangement was adopted to make it measurable.

The experiment consisted of four parts,

1st. The effect of rock salt heat upon the pile without a screen was observed by the ordinary galvanometer.

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2d. The effect of lampblack heat, also without a screen, was observed by the same galvanometer.

3d. The wires of the pile were then transferred to a more sensitive galvanometer, and the effect of lampblack heat observed, the glass screen being interposed.

4th. The sensitive galvanometer and glass screen being retained, the effect of rock salt heat was lastly observed.

By this method of experimenting, it was merely the relation between the diathermancy of the screen for lampblack heat and for rock salt heat that was measured; its absolute diathermancy for either of these heats not being determined. Two sets of experiments, conducted in this manner, gave the following result:

By the first set, calling the proportion of the whole lampblack heat which passed the screen 100, that of the rock salt heat which passed the same screen was 54. And by the second set, these numbers were 100 to 60.

12. As in these experiments with a glass screen the proportion of heat passed is very small, great numerical accuracy cannot be looked for and the results obtained are valuable rather as determining the direction and character of a fact, than as measuring the extent to which it holds.

13. It is already well known that rays of great refrangibility or small wave length pass through glass and mica more readily than those of an opposite character. The difficulty with which rock salt heat penetrates these substances as compared with ordinary heat might therefore lead us to infer that the wave length of this heat is greater than that of ordinary lampblack heat.

14. If, therefore, the heat radiated by rock salt is of great wave length since (First Series, Art. 19) the quality of the heat radiated is the same as that of the heat absorbed, it follows that the heat most absorbed by rock salt must be heat of great wave length; and this derives confirmation from a fact noticed by Professor Forbes, viz., that rock salt passes a somewhat greater proportion of heat of high temperature than of that of low; heat of high temperature possessing a less average wave length.

15. If we look now to the relative transmission of the two

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descriptions of heat through mica split by heat, we see that the facility of transmission is yet in favor of ordinary heat, but not so strikingly as with a screen of common mica. This will be seen from the following table :

TABLE II.

NATURE OF SOURCE.	Transmission of Ordinary Heat, at 212° F.	Transmission of Rock salt Heat at 212° F.
Mica.....	100	58
Mica split by heat.....	100	76

Compare this with the following table deduced from the results given by Professor Forbes, in the Fourth Series of his Researches, Art. 9.

TABLE III.

NATURE OF SCREEN.	Transmission of Heat from Blackened Brass at 700° F.	Transmission of Black Heat at 212° F.
Mica .015 inch thick,.....	100	52
Mica split by heat,.....	100	64

From a comparison of these two tables, it will be seen that, as tested by the two substances, mica and mica split by heat, rock salt heat at 212° F bears to ordinary heat of that temperature a relation similar to that which ordinary heat at 212° F bears to heat at 700° F; that is to say, that just as heat of 212° F has a greater wave length than heat of 700° F, so rock salt heat at 212° F has a greater wave length than ordinary heat at that temperature. And the *surface stoppage* produced by splitting the mica, telling most powerfully upon heat of high temperature, or small wave length, while the *stoppage* by *substance* is in the opposite direction, we see how the one effect tends, to a certain extent, to neutralize the other, rendering the proportions of different kinds of heat passed by split mica more nearly alike than those passed by ordinary mica.

16. All these experiments concur in showing that heat from rock salt possesses very great wave length, and probably heat from a thin plate of this substance, at a low temperature, may

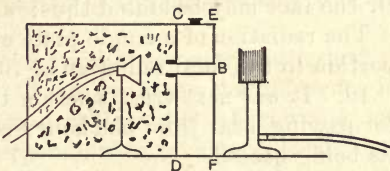
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be found to possess a greater average wave length than any other description of heat which can be exhibited.

Third Group of Experiments Described.

17. I now proceed to describe the third group of experiments, or those on the radiation of glass and mica at high temperatures.

A. Glass.—For the experiments on glass, the following apparatus was used: The pile was placed within a box, and surrounded with cotton wadding. The orifice through which radiant heat was admitted into the box consisted of a brass tube AB, blackened in the inside. The diameter of this tube was $\frac{1}{2}$ inch, its length 3 inches, and during the greater part of its length it passed through water, contained in the chamber CEFD. The side of the box (CAD) next the pile was lined with tin foil. Owing to the small divergence of the rays of heat which had to pass through the narrow tube, the cone might be placed several inches to the left of A without sensibly weakening the effect, and, on the other hand, the source of heat might be placed some distance to the right of D without ceasing to fill up the field of view. By this means, the distance between the pile and the source of heat being considerable, no currents of heated air from the latter would be able to reach the former; and as the tube AB was blackened in the inside, and passed through water, reflection and secondary radiation would both be avoided. By means of a lid fitting on the tube at A the aperture might be diminished at pleasure. The pile was connected with a very sensitive galvanometer.



When glass at a high temperature was the source of heat, a very small aperture was sufficient, and thus the advantage was gained of having the whole field covered with glass, all at a high temperature, which could not have been the case had the aperture been large.

Slips of glass about $\frac{3}{4}$ inch broad were used, and were set vertically, just touching a gas flame from a Bunsen's burner. When two slips—one behind the other—were used, the one

just touched that portion of the flame next the pile, and the other that portion furthest from it. A cross section of the arrangement is shown on page 59.

A single slip of glass about .1 inch thick thus heated gave a deviation of $16^{\circ}.5$, while two slips, the one behind the other, gave $18^{\circ}.5$. When the slips were .05 inch thick these numbers were $29^{\circ}.1$ and $36^{\circ}.3$.

18. From these experiments we may conclude, that at a high temperature, 700° or 800° F, the radiation from two plates of glass, one behind the other, is sensibly greater than that from one—a result which does not hold for glass at 212° . Or the fact may be stated thus:

The radiation of a single plate of glass bears a smaller proportion to the total radiation of 700° than at 212° .

19. It was next tried whether the capacity of a glass screen for passing heat from blackened copper at 700° was altered by its being heated.

In order to ascertain this, blackened copper at 700° F was placed behind a slip of glass, and the amount of heat from the copper which passed the glass was observed.

Firstly, When the glass was cold.

Secondly, When it was heated to between 700° and 800° F.

20. As in these experiments the considerably fluctuating temperature of the source of heat causes a somewhat large difference between successive observation, and renders necessary a great number in order to arrive at a correct result, it was thought desirable, instead of using momentary deviations, to employ permanent ones. This was done with complete success; the application of the heated copper, or its removal, causing an unmistakable alteration of the position of the needle.

21. The experiment was then varied in the following manner: The needle was kept permanently deviated by the heated glass, and the momentary swing due to the application or withdrawal of the heated copper was noticed, and was compared with that occasioned by the hot copper when the glass was cold and the needle at zero.

22. These experiments, which are not, perhaps, individually susceptible of very great exactness, agreed, however, in rendering it probable that glass, owing to its being heated up to

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about 700° F. does not change its diathermancy for heat of 700° F.

23. B. *Mica*.—The experiments on mica were made with the ordinary galvanometer. A piece of mica, thickness about .008 of an inch, being used as a screen, and a diaphragm, .65 of an inch square, at the distance of three inches from the mouth of the pile, being employed, the mean of two sets of experiments made the proportion of black heat of 200° F passed by the mica to be 13 per cent. Placing an additional diaphragm of the same size $3\frac{1}{2}$ inches beyond the first, and using as a source the temperature of 400° F, the mean of two sets of experiments made the proportion of heat passed by the mica screen to be 21 per cent.

In order to test whether the apparently greater diathermancy of the screen for heat of 400° F was owing to the difference in the nature of the heat, or to the heat at 400° F striking the screen more nearly at a perpendicular incidence, and thus experiencing less reflection as well as passing through a smaller thickness of mica, an experiment was made on heat at 200° F, with the arrangement and distance used for heat of 400° F, which seemed to show that this difference of distance does not affect sensibly the proportion transmitted. We may therefore conclude that the difference in proportions transmitted is owing to a difference of quality in the two descriptions of heat.

24. A cast-iron box was next constructed having this same plate of mica inserted as a window, so that, while one side of the box consisted merely of a moderately thin plate of cast-iron, the other, except round the edges, was composed of mica. The cast-iron side was then blackened, and the box filled with mercury. A thermometer inserted in the box measures the temperature. At 200° F, with the usual diaphragm three inches from the mouth of the pile, the proportion between the radiation of the blackened side and the mica window was, by the mean of three sets of experiments, as 100 to 87.8, while at 400° F, with the usual arrangement of two diaphragms, the same proportion was 100 : 84.1.

25. Let us endeavor to discuss these results. The radiation from the mica window consists of three portions :

a. The proper radiation of the mica plate.

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β. That portion of the radiation of the mercury which has been able to penetrate the mica plate.

γ. That portion of the radiation of the mica which, striking upon the mercury, is reflected back by it and has penetrated the mica plate.

Now, supposing there was no mercury behind the mica, and that mica between 200° and 400° does not alter its diathermancy as a screen in any respect, let us inquire what ought to have been the result obtained. Then, since the radiation of a thin plate equals its absorption (First Series, Art. 19), and since the absorption of this mica plate was 8 per cent less at 400° than at 200° (Art. 23), its proportional radiation ought to be 8 per cent less at 400° than at 200° .

26. But the effect of the mercury behind the mica manifestly tends to diminish this difference. For we know that the mica (Art. 23) passes 8 per cent more of lampblack heat at 400° than at 200° ; it will therefore no doubt pass a greater proportion of the heat from the mercury behind at 400° than at 200° . But we have reason to think that the radiation of mercury is nearly $\frac{1}{4}$ of that of lampblack.* Consequently we may suppose that owing to this action of the mercury, the proportional radiation of the mica window at 400° is increased about $\frac{1}{4}$ of 8, that is, 2 per cent. This reduces therefore the difference from 8 to 6 per cent.

27. But the mercury acts in another manner also in the same direction. Had mercury been a perfect reflector, its presence behind the mica would have been equivalent to doubling the thickness of the plate; for it would have sent the whole radiation of the mica that fell upon it back through the mica. But the difference between the proportional radiation at 200° and at 400° is less for a thick plate of mica than for a thin one (indeed, when the plate is indefinitely thick, this difference vanishes, and the proportional radiation is the same at all temperatures); this action of the mercury, therefore, would tend still further to diminish the already diminished difference of

* Provostaye and Desains estimated the proportion of heat reflected by mercury to be 77 per cent. The radiation, being complementary to this, may be reckoned to be 23 per cent nearly.

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6 per cent. The amount of this action cannot be far from 2 per cent, * in which case the 6 per cent would be reduced to 4 per cent; now 3.7, or, in round numbers, 4 per cent is the observed difference between the proportional radiation of the mica window at the temperatures 200° and 400° .

28. We see thus that the behavior of the mica as a screen, compared with its behavior as a radiator, agrees very well with the supposition which we made in Art. 25; viz., the mica between the temperatures of 200° and 400° does not alter its diathermancy in any respect; a result similar to that which we have already deduced for glass (Art. 22) between somewhat wider limits.

29. Experiments with the same object in view, but of a more direct description, were made upon mica, similar to those already described as having been made upon glass, that is, it was endeavored to ascertain whether hot mica passed as much heat from hot copper as cold mica; but in these experiments the fluctuation was very considerable, probably owing to the small body of the mica. Nevertheless, they confirmed the results above obtained; viz., that mica does not change its diathermancy in any respect owing to its being heated.

30. We may therefore conclude that this property (at least within moderate limits) is common both to glass and to mica, and indeed, *a priori*, there appears no good reason why the mere heating of a substance should change its diathermancy. It is the theoretical importance of this property that has induced me to take pains to verify experimentally and its importance will be seen from some of the consequences which follow its establishment, which I shall now proceed to discuss.

* It would have been better to have tested, by means of a direct experiment, to what extent the difference between the proportional absorption and radiation of mica at 200° F and at 400° F would have been diminished by doubling the thickness of the plate; but unfortunately the plate of mica was so much cut up by being used as a window, as to be unfit for being formed into a double screen.

We see, however, from Art. 37, that while the difference between the proportional radiation of a plate of glass (thickness 1mm) at 100° C and and 390° C is 9 per cent, the same difference for a plate of double the thickness is only 7 per cent, or 2 per cent less. We may, therefore, without much risk of error, adopt this difference of 2 per cent for mica under experiment.

On the Law which Connects the Radiation of a Body with its Temperature.

31. The experiments of Dulong and Petit upon the cooling of two thermometers, one naked, and the other covered with silver, seemed to show that the proportion between the radiations of these two substances was the same at the different temperatures of experiment.

Now I have endeavored to prove in these researches—1st, That the radiation of a thin plate at any temperature equals its absorption of black heat of that temperature. 2nd, That the diathermancy of glass and mica (and probably of other substances) is not altered by heating the substances. Again, it is well known that substances are generally more diathermanous for heat of high, than for heat of low temperature; it follows that the radiation of a thin plate of a substance at a high temperature should bear a less proportion to the total radiation of that temperature than at a low temperature.

32. While, therefore, it is likely that the radiation of a silvered thermometer (silver leaf being quite opaque for all heat) will bear a constant relation to that of a blackened thermometer at all temperatures, we should expect that for a naked thermometer, just as for the mica window, the radiation should bear a somewhat less proportion to the total radiation at a high temperature than at a low. We should therefore expect the radiation of the naked thermometer to increase somewhat less rapidly with the temperature than that of the silvered thermometer. Dulong and Petit, nevertheless, found the rate of increase to be the same for both.

33. Now, in the first place, since glass is exceedingly opaque for heat even of 300°C (the highest temperature experimented on), the difference we are in search of (analogous to the difference of four per cent in the mica window) would be exceedingly small. But, in the second place, Dulong and Petit had two thermometers, one of which, containing about three pounds of mercury, was used for high, and the other and smaller one for low temperatures. This latter circumstance will complicate or even vitiate their experiments so far as regards this peculiar difference we are treating of.

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34. Although, for these reasons, attaching little importance to Dulong's and Petit's observations, so far as varying diathermancy is concerned, yet it may be well to state that they show, on the whole, a very small difference in the direction which would indicate a superior diathermancy of the glass at a high temperature.

35. Assuming it proved that the proportional radiation of a thin plate is less at a high than at a low temperature, I shall now endeavor to show that this difference increases as we diminish the thickness of the plate. To prove this, it is only necessary to exhibit the following table, given by Melloni :

TABLE IV.

NUMBER OF RAYS OUT OF 100 PASSED.				
Thickness of Glass Screen.	Locatelli Lamp.	Incandes- cent Platinum.	Black Copper at 390° C.	Blackened Copper at 100° C.
mm				
0.07	77	57	34	12
.5	54	37	12	1
1.0	46	31	9	0
2	41	25	7	0
4	37	20	5	0
6	35	18	4	0
8	33.5	17	3.4	0

36. We have already seen that glass does not change its properties with regard to heat, by being raised to the temperature of 390° C ; it is perhaps, however, too much to conclude, that when heated to the temperature of a Locatelli lamp, its properties would remain unchanged. At all events, in order to make use of the whole of the above table, we may suppose the properties of the glass to remain the same throughout, especially as the results we shall deduce from the supposition will be of the same nature as if we had only extended it to glass at 390° C.

37. Presuming, therefore, that the diathermancy of glass does not alter through its being heated, and allowing 4 per cent as the proportion of the heat striking it reflected from the first surface of a glass screen, and supposing also the same proportion of the heat which is able to reach the second surface to be

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reflected from it, we may, on the principle that the proportional radiation of a plate equals its proportional absorption, construct the following table :

TABLE V.

PROPORTIONAL RADIATION OF GLASS PLATES AT DIFFERENT TEMPERATURES, (RADIATION OF LAMPBLACK = 100).				
Thickness of plate.	Temp. of Locatelli Lamp.	Temp. of Incandescent Platinum.	390° C.	100° C.
mm				
0.07	16	37	61	84
.5	40	58	84	95
1.0	48	64	87	96
2	53	70	89	96
4	58	75	91	.96
6	60	77	92	96
8	61.5	78	92.6	96

38. Let us call the proportional radiation of the glass plate at 100° C unity, and we derive the following table.

TABLE VI.

PROPORTIONAL RADIATION OF GLASS PLATES AT DIFFERENT TEMPERATURES, THEIR RESPECTIVE PROPORTIONAL RADIATIONS AT 100 C. BEING RECKONED UNITY.				
Thickness of Plate.	100° C.	390° C.	Temp. of Incandescent Platinum.	Temp. of Locatelli Lamp.
mm				
0.07	1	.72	.44	.19
.5	1	.88	.61	.42
1.0	1	.91	.66	.50
2	1	.93	.73	.55
4	1	.95	.78	.60
6	1	.96	.80	.62
8	1	.965	.81	.64

39. We see thus that the radiation of thick plates of glass increases most rapidly, and that of thin plates least rapidly, as the temperature increases, and we may suppose, that if we could procure a plate of glass of sufficient tenuity, we might (without heating the plate at all), by finding its absorption for heat of

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different temperatures find its radiation at those temperatures, which (if the plate were thin enough) would give us the law of radiation of a glass particle. This law would not increase nearly so fast with increasing temperatures as Dulong and Petit's law; it may even be that the radiation of glass particles is proportional to its absolute temperature.

40. But all substances (with the exception of black mica and black glass, whose peculiarity may perhaps be otherwise explained) have the same properties as glass with regard to heat; that is, they are more diathermanous for heat of high than for heat of low temperatures. The radiation of thin plates or particles of all substances will therefore increase less rapidly with temperature than that of black surfaces. It may therefore be, that the same law of radiation is common to very thin plates or particles of all bodies; this law (whatever it be) giving in all cases, a less rapid increase of radiation with temperature than is indicated by Dulong and Petit's law. Had, however, the diathermancy of thin plates of different substances in some cases diminished and in others increased for heat of high temperature, the law of radiation of a particle could not have been the same for all bodies.

The generality of this law of increased diathermancy of all bodies for heat of high temperatures seems, therefore, to me, to argue in favor of the universality of the unknown law of particle radiation which depends upon the former.

41. What, then, does Dulong and Petit's law express? The answer is, it expresses the law of radiation of indefinitely thick plates, and we have shown that it increases faster than the law of radiation of a material particle.

To facilitate the comprehension of this subject as much as possible, I have put it in the following shape. Suppose we have two substances opposite one another, the one having the temperature of 0° , and the other of 100° , the latter will of course lose heat to the former—let us call its velocity 100. Suppose, now, that (the first surface still retaining its temperature of 0°) the second has acquired the temperature of 400° ; then we should naturally expect the velocity of cooling to be denoted by 400; but by Dulong and Petit's law, it is much greater. The reason of the increase may be thus explained.

At the temperature of 100° we may suppose that only the exterior row of particles of the body supplied the radiation, the heat from the interior particles being all stopped by the exterior ones as the substance is very opaque for heat of 100° ; while at 400° we may imagine that part of the heat from the exterior particles is allowed to pass, thereby swelling up the total radiation to that which it is by Dulong and Petit's law.

42. We have thus ascertained—1st, That Dulong and Petit's law is not the law of radiation of a material particle; and, 2d, That this law increases less rapidly with the temperature than Dulong and Petit's law. But now the question arises, can any method be indicated of ascertaining, experimentally the law of radiation of a material particle? Now, by continually diminishing the thickness of the plate whose radiation at different temperatures we are ascertaining, we certainly approach nearer and nearer to the desired law, and, by using the method indicated in Art. 37, we may avoid heating this plate at all and thus overcome one source of experimental difficulty. Yet the thinnest plate we can procure of a substance such as glass or mica acts, to all intents, as an indefinitely thick substance for a great many of the rays of heat—that is, it stops them all. The change, therefore, of the unknown law of particle radiation into Dulong and Petit's law will to a great extent, have taken place even within this very thin plate; so that, in order to reach the desired law or even approximate to it, we should have to use much thinner plates than we could possibly procure; and, even without the necessity of heating the films, the experimental difficulty and labor of such an investigation would be very great.

On the other hand, we may suppose that, since a thin film stops so much heat, a portion may be stopped in the physical surface of the body, and the absorption might thus influence the law of reflection of heat from the surface. The amount of this influence depending on the absorptive nature of the particles, we might be able to measure the absorption, and, consequently, the radiation of the physical surface, that is, of a very thin plate. But, in the first place, the difficulties of such an investigation would be even greater than in the previ-

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ous case ; and, in the second place, the true law of reflection is not yet finally settled.

I am therefore induced to think that it is nearly hopeless to attempt to ascertain the true law of radiation of a material particle, at least by any method of experimenting depending upon the use of thin plates, or on the change which absorption may be presumed to cause in the amount of heat reflected from the surface of a body.

Edinburgh, March 22, 1859.

On General Diathermancy (added 15th June).

43. Circumstances having occurred which may interfere in the meantime with my further experiments on heat, I annex to this paper an account of some experiments made since the day of reading. These were proposed with the view of ascertaining whether diathermancy is confined to rock salt or whether bodies partake of this property. If the latter be the case, the reason why we have not hitherto ascertained it to be so is evidently the difficulty of obtaining crystals of many bodies sufficiently large to operate upon ; and if we wish to prove these diathermanous we must do so in a way that does not render necessary the use of large crystals.

44. Now, a body that is transparent for light, forms, when pounded, a white powder or one that reflects a great deal of light. It will be granted that the reason of this is because we have not only the reflection from the outer surfaces of the crystals, but also from many interior surfaces. Now the same remark is applicable to heat. A body that is diathermanous or transparent for heat should, as a powder, be white for heat, or, in other words, reflect it. But (First Series, Art. 31) the reflection *plus* the radiation of the body at any temperature equals the lampblack radiation at that temperature. Hence a powdered diathermanous substance ought to radiate less than lampblack. Accordingly, different substances having been pounded into a fine crystalline powder, made into a paste with water, spread on the two sides of parallelopipedons of wood, dried and one of the sides, when dry, rubbed over with lampblack, the following result was obtained :

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TABLE VII.

RADIATION AT 212°		
NAME OF SUBSTANCE.	WHITE SIDE.	BLACK SIDE.
Table salt.....	83.1	100
White sugar.....	98.7	100
Alum.....	100.0	100
Sulphate of potash.....	88.1	100
Nitrate of potash.....	86.7	100

45. Thus we see that table salt being white for heat, the radiation of the white side is less than that of the black side; and further, white sugar and alum being both nearly black for heat, the radiation of the one side is nearly equal to that of the other. We see, moreover, that sulphate of potash and nitrate of potash, especially the latter, are white for heat, although not quite so much so as table salt. May we not therefore presume that these substances are diathermanous? There is, moreover, the following method of confirming the testimony in favor of the diathermancy of these substances as derived from this experiment.

46. Table salt being white for heat, part of the reflected heat will be composed of rays which have been reflected from the internal surfaces of crystals. Such rays have therefore been sifted, having left behind that description of heat which passes with difficulty through rock salt and also (Art. 9) through mica. The whole reflected heat from a surface of table salt should therefore be of a nature which passes more easily through mica than ordinary heat, and (First Series, Arts. 31 and 33) since the sum of the reflected and the radiated heat is equal both in quantity and quality to that from lampblack, it follows that the radiated heat from table salt (and probably from other substances white for heat) should, in order to make up the average quality, have a somewhat greater difficulty in passing through mica than ordinary lampblack heat. Accordingly, it was found that the diathermancy of a mica screen for heat from table salt was less than that for ordinary lampblack heat in the proportion of 92 to 100, while it was less for heat from pounded sulphate of potash in the proportion of 93 to 100, thus confirming the analogy between

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rock salt and sulphate of potash. No such difference was observed for heat from sugar.

47. We see also from the above table that the radiation and therefore the absorption of table salt is 83.1 per cent, leaving 16.9 per cent for the reflected heat. Now Melloni found that chalk absorbed 56.6 per cent, and consequently reflected 43.4 per cent, of heat from a Locatelli lamp; and if we suppose table salt to be at least as white as chalk for heat of that temperature, we must conclude that table salt is less white for heat of 212° , than for heat from a Locatelli lamp, following in this respect the same law as chalk, which, from being nearly black for heat at 212° , becomes comparatively white for heat from a Locatelli lamp. There is also little doubt that table salt reflects more than 16.9 per cent of the light that falls upon it. Hence we may conclude generally that powders even of diathermanous bodies are less white for heat of low temperature than for heat of high temperature and for light.

48. It would also seem, that, although comparing one powder with another, there is no relation between apparent whiteness and whiteness for heat, since it was found that very white surfaces of pounded sugar and alum (the particles compressed, not made into a paste with water) reflected little or no heat; yet, comparing powdered surfaces of the same diathermanous body together, there seems to be some relation between their apparent whiteness and their whiteness for heat, insufficient pounding, or any circumstance which diminishes the apparent whiteness, diminishing also its whiteness for heat.

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BIOGRAPHICAL SKETCH.

BALFOUR STEWART was born Nov. 1, 1828 at Edinburgh. He studied at the Universities of St. Andrews and Edinburgh, and later entered upon commercial life. His particular taste for physical science soon developed itself, however, and we have in 1858 a couple of his earliest papers. He became associated with Kelland and Forbes at this time and in 1858 contributed his most important work on the extension of Prévost's Theory of Exchanges in radiation. With the elaborate (at that time) facilities at his command he was able to demonstrate the equality of the radiating and absorbing power of every substance. For this and other work he was awarded the Rumford Medal some years later. In 1859 he was appointed director of the Kew Observatory, where for eleven years he directed the important studies and investigations carried on there. During this period he was seriously injured in an accident from which he never recovered. In 1870 he was appointed to the chair of Physics in Owens College, Manchester, which he occupied until his death Dec. 19, 1887. During this time he issued his well-known texts in Physics. His "*Conservation of Energy*," "*The Unseen Universe*" (in conjunction with Tait), his experiments on the viscosity of ether, etc., all illustrate the comprehensiveness of his mind and the originality of his genius.

ON THE RELATION BETWEEN THE
EMISSIVE AND THE ABSORPTIVE
POWER OF BODIES FOR
HEAT AND LIGHT.

BY

G. R. KIRCHHOFF.

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us Viva - living struggle (Latin)

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ON THE RELATION BETWEEN THE EMISSIVE AND THE ABSORPTIVE POWER OF BODIES FOR HEAT AND LIGHT.¹

§ 1

HEAT rays have the same nature as light rays ; these constitute a special class of the former. The invisible heat rays are distinguished from light rays only by the period of vibration or the wave length. All heat rays follow the same laws in their propagation, which are known for light rays. A luminous body in space sends out light rays that are independent of the bodies on which they fall ; similarly all heat rays which a body sends out are independent of the bodies which form its environment.

Of the heat rays that are sent out to a body by its surroundings a part are absorbed, the others are sent on in directions which are varied by reflection and refraction. The rays refracted and reflected by it pass off along with those sent out by it, without any mutual disturbance taking place.

Through the radiations which a body sends out, the quantity of heat which it contains will, according to the law, sustain a loss which is equivalent to the *vis viva* of those rays and, through the heat rays which it absorbs, a gain which is equivalent to the *vis viva* of the absorbed rays. But in certain cases an exception to this rule may occur, in that the absorption and the radiation produce other changes in the body, as for example in bodies which are chemically changed by light, and light absorbing media which lose their power of shining

¹ Investigations on the solar spectrum and the spectra of the chemical elements, 2d. Edition, Berlin, Ferd. Dummler's publishing house 1862.

through the radiation of the light which they have absorbed. Such cases should be excluded on the assumption that *neither by means of the rays which it radiates or absorbs, nor by means of other influences to which it is exposed, does the body possess the power to undergo a change, if its temperature is kept constant by the addition or the subtraction of heat.* Under these conditions, according to the law of equivalence of heat and work, the amount of heat which must be transferred to a body in a given time to prevent cooling, which would occur in consequence of its radiation, is equivalent to the *vis viva* of the emitted rays ; and the amount of heat which must be withdrawn in order to counterbalance the heating from absorption of radiations, is equivalent to the *vis viva* of the absorbed rays.

Let a body which satisfies these conditions be surrounded by an enclosure, having the same temperature, through which no heat rays can penetrate, whose temperature is kept constant and which satisfies the same conditions. The body sends out heat rays and is encountered by such heat rays, which, in part, proceed from the enclosure, in part, are thrown back to the same by reflection from it, absorbing a part of them. Its temperature must thus remain the same, unless heat is withdrawn from it or communicated to it as follows on the principle from which Carnot's law results. For this reason, the *vis viva* of the rays, which it sends out in a certain time, must equal the *vis viva* of the rays which it absorbs in the same time.

The proof which rests upon this conclusion requires the accurate investigation of the rays that travel back and forth between the body and the enclosure. This investigation will be much simplified if we imagine the enclosure to be composed, wholly or in great part, of bodies which, for infinitely small thickness, completely absorb all rays which fall upon them.

I will call such bodies *perfectly black*, or more briefly *black*. A *black body*, in this sense of the word, must have the same refractive index as the medium in which the radiation takes place ; then there will be no reflection at its surface, and all incident rays will be wholly absorbed. Thick iodine vapour in contact with air, or pitch in contact with glass, may be treated as black bodies, approximately, but not iodine vapour in contact with glass or pitch in contact with air. Next, the radia-

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tion in empty space will be investigated ; the *black bodies* referred to must therefore have a refracted index which differs only infinitely little from 1.

The assumption that such *black bodies* are conceivable forms an important aid in the proof which will be presented here. Further, it will be assumed that perfectly diathermanous bodies are conceivable, that is, such which will absorb none of the incident heat rays of whatever nature these may be, and finally, that a perfect mirror is conceivable, i.e., a body which reflects completely all heat rays. A perfect mirror, like every diathermanous body, can itself send out no rays ; for if it did (confined in an enclosure of like temperature) it would warm this enclosure more and more and cool itself more and more.

§ 2.

DEFINITIONS.

Before a body *C*, Figure 1, imagine two screens, S_1 and S_2 placed in which are two openings 1 and 2, whose dimensions are infinitely small with respect to their distance apart, and each of which has a center.

Through these openings passes a pencil of rays sent out by the body *C*. Of this pencil of rays, let us consider the part, whose wave length lies between λ and $\lambda + \delta\lambda$, and let this be divided into two polarized components, whose planes of polarization are the planes *a* and *b* perpendicular to each other, passing through the axis of the ray pencil.

Let $E\delta\lambda$ be the intensity of the component polarized in *a*, or, what is the same thing, the increase, which the *vis viva* of the ether beyond the screen S_2 experiences through this component in the unit of time. The quantity *E* is called the *emissive power* of the body *C*.

Conversely, upon the body *C* there falls through the openings 2 and 1 a pencil of rays having the wave length λ , polarized in the plane *a*; of this, the body absorbs a part while it reflects or transmits the remainder ; let the ratio of the inten-

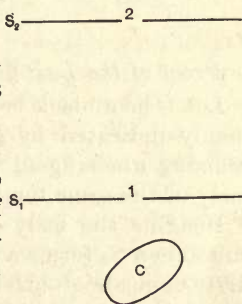


FIG. 1.

sity of the absorbed rays to the incident rays be A and let this be called the *absorptive power* of the body C . The quantities E and A depend upon the nature of the condition of the body C , besides also upon the form and position of the openings 1 and 2, the wave length λ and the direction of the plane a .

§ 3.

Under these conditions the following law holds : *The ratio between the emissive and the absorptive power is the same for all bodies at the same temperature.*

This law will be proven, first, for the case where only black bodies are compared with each other, that is, those whose absorptive power $= 1$; i. e., it will be shown that the radiating power of all black bodies is the same at the same temperature.

The proof of this special law is similar to that of the general law, but simpler ; it will therefore facilitate the understanding of the latter. Moreover, conclusions which are drawn from the special law will be used in the proof of the common law.

§ 4.

Proof of the Law § 3 for black bodies.

Let C be a black body ; let its emissive power, which is commonly indicated by E , be called e ; it will be proven that e remains unchanged, when C is replaced by any other black body of the same temperature.

Imagine the body C enclosed in a black covering, of which the screen S_1 forms a part, let the second screen S_2 , like the first, be made of black substance and let both be united with each other on all sides by black walls, as shown in Figure 2. Suppose the opening 2 to be closed at first by a black surface, which I will call surface 2. The whole system must have the same temperature and the covering be maintained at a constant temperature throughout. According to the statements made in Figure 2, § 1, the *vis viva* of the rays which the body C sends out in the given time, must then equal the *vis viva* of the rays, which it absorbs in the same time ; in other words : the sum of the intensities of the rays which it sends out must equal the sum of the intensities of the rays which strike it, since according to

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supposition it completely absorbs the latter. Now suppose the surface 2 removed, and the opening closed by a portion of a perfectly reflecting spherical surface, placed directly back of it and having its center at the middle point of the opening 1. Equilibrium of temperature will then exist. There must also be equality between the intensity of the rays which the body *C* sends out, and of those incident upon it. Since the body *C* now sends out the same rays as in the cases previously considered, it follows that the intensities of the rays incident upon *C* are the same in both cases. By the removal of surface 2 the rays are withdrawn from *C* which pass through opening 1; therefore the concave mirror placed at opening 2 throws just the same rays back to *C* which this sends out itself through the openings 1 and 2, for the concave mirror forms from opening 1 an image which coincides with itself.¹

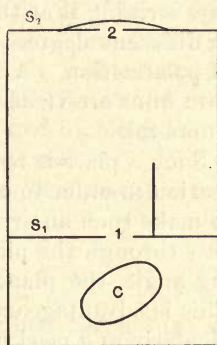


FIG. 2.

The law given would therefore be proved if all rays of the two pencils compared have the wave length λ and are polarized in the plane α . Both pencils of rays, however, are made up of different components and form the equality of the intensity of the whole pencil. We may not directly infer the equality of the intensity of corresponding parts.

The necessary completion of the proof may easily be given when a plate is supposed to exist, having the property of transmitting undiminished rays whose wave length lies between λ and $\lambda + d\lambda$ and whose plane of polarization is parallel to the plane α ; but which completely reflects rays of other wave

¹ The diffraction of the rays at the edges of opening 2 may be neglected, since the openings 1 and 2 may be assumed infinitely small with respect to their distance and yet infinitely great with respect to the wave length, that is, so great, that the defraction may be inappreciable.

From this it follows that the intensity of the pencil of rays, which the body *C* sends out through openings 1 and 2, equals the intensity of the pencil of rays which the black surface 2 sends out through the opening 1. Since this intensity is independent of the form and further character of the black body *C*, so, likewise, is the former.

lengths or of an opposite polarization. If we should imagine the arrangement shown in Figure 2 modified by bringing such a plate before opening 1, then we may immediately arrive at the law to be proved by the treatment employed in respect to this figure.

The assumption that such a plate is possible is in no wise justified. On the contrary, a plate is possible which, of the rays striking it at the same angle, transmits and reflects them in different degrees according to their wave length and plane of polarization. A plate, which is so thin that the colors of thin films are visible and which is placed obliquely in the path, shows this.

Such a plate is required for the investigation under consideration in order to compare them. Besides this, it is necessary to make such an arrangement that both pencils of rays do not pass through the plate, but are reflected from it at the polarizing angle, the plane of reflection coinciding with the plane a . This is advantageous in as much as the rays polarized perpendicularly to a need not be considered. Further, the plate must be made of a perfectly diathermanous medium, it will then absorb no rays and send out none.

§ 5.

In the arrangement described in Figure 2 imagine a plate of

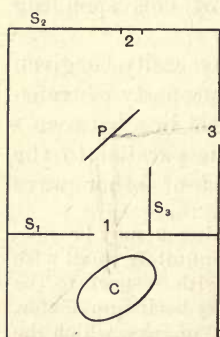


FIG. 3.

the kind described and designated as P , brought between the openings 1 and 2 (Fig. 3). Let it be so placed that the pencil of rays passing through the openings 1 and 2 is incident at the polarizing angle and the plane of incidence is the plane a . Let the wall which unites the screens S_1 and S_2 be so shaped that the image, which the plate P casts from the opening 2 lies within it; in the place and of the form of this image imagine an opening which I will call opening 3. Let opening 2 be closed by a black surface of the temperature of the whole

system, and let opening 3 be closed in the first place by a similar surface, and in the second place by a perfect concave

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mirror having its center where the plate P forms the image of the middle of opening 1. In both cases the equilibrium of temperature is maintained; through consideration given in the preceding paragraph, it follows therefore that the sum of the intensities of the rays, which the body C is deprived of through the removal of surface 3 equals the sum of the intensities of the rays which are brought to it through the agency of the concave mirror. Let a black screen S_3 (of the temperature of the whole system) be so placed that none of the rays which surface 3 sends out are directly incident upon opening 1. The first sum, then, is the intensity of the rays which proceed from surface 3, and are reflected by plate P and pass through opening 1; they will be designated by Q . The second sum is made up of two parts; one component comes from C and is :

$$= \int_0^{\infty} d\lambda e r^2$$

where r represents a quantity dependent upon the nature of the plate P and the wave length λ ; the second part consists of rays which have come from a portion of the black wall which unites the screen S_1 and S_2 , have passed through the plate P and been reflected from the concave mirror, and then from the plate P ; this part will be designated as R . It is unnecessary to examine further the value of R ; it suffices to notice that R , as well as Q , is independent of the nature of C . Between the magnitudes introduced there exists the equation :

$$\int_0^{\infty} d\lambda e^{\frac{1}{2}} r^2 + R = Q$$

If we now imagine the body C replaced by another black body of the same temperature, letting e' indicate for this what e has represented for the other, there exists the equation

$$\int_0^{\infty} d\lambda e' r^2 + R = Q$$

From this it follows that

$$\int_0^{\infty} d\lambda (e - e') r^2 = 0$$

Let us now assume that the index of refraction of the plate P

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differs but little from unity. From the theory of the colors of thin plates it follows then that we can place

$$r = \rho \sin^2 \frac{p}{\lambda}$$

where p represents a quantity proportional to the thickness of the plate P , independent of λ , and a quantity independent of this thickness. From this follows the deduced equation :

$$\int_0^\infty d\lambda (e-e') \rho^2 \sin^4 \frac{p}{\lambda} = 0$$

Since this equation must hold for every thickness of the plate P , and hence for every value of p , it follows that for every value λ we may conclude that

$$e-e' = 0$$

To prove this, substitute in that equation for $\sin^4 \frac{p}{\lambda}$:

$$\frac{1}{8}(\cos 4 \frac{p}{\lambda} - 4 \cos 2 \frac{p}{\lambda} + 3)$$

and differentiate twice with respect to p : we then have

$$\int_0^\infty d\lambda \frac{(e-e') \rho^2}{\lambda^2} (\cos 4 \frac{p}{\lambda} - \cos 2 \frac{p}{\lambda}) = 0$$

In place of λ let us introduce a new quantity into the equation; where

$$\frac{2}{\lambda} = a$$

and set

$$(e-e') \rho^2 = f(a)$$

we thus obtain

$$\int_0^\infty da f(a) (\cos 2 p a - \cos p a) = 0$$

If we consider that when $\phi(a)$ represents any arbitrary function of a

$$\int_0^\infty da \phi(a) \cos 2 p a = \frac{1}{2} \int_0^\infty da \phi\left(\frac{a}{2}\right) \cos p a$$

from which we may conclude that if we substitute $\frac{a}{2}$ for a , we may therefore write

$$\int_0^\infty da [f\left(\frac{a}{2}\right) - 2f(a)] \cos p a = 0$$

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Multiply this equation by $dp \cos xp$, where x represents an arbitrary quantity, and integrate it from $p = 0$ to $p = \infty$. According to Fourier's formula which is expressed by the equation

$$\int_0^\infty dp \cos px \int_0^\infty da \phi(a) \cos pa = \frac{\pi}{2} \phi(x)$$

we have

$$f\left(\frac{x}{2}\right) = 2f(x) \text{ or } f\left(\frac{a}{2}\right) = 2f(a)$$

From this it follows that $f(a)$ either vanishes for all values of a , or becomes infinitely great when a approaches zero. When a approaches zero λ becomes infinite. If we remember the meaning of $f(a)$ and consider that ρ is a proper fraction, and that neither e nor e' can become infinite when λ increases to infinity, then it is evident that the second case cannot exist and therefore, that for all values of λ , $e = e'$.

In a similar way we may treat the case when C is not a black body but is an arbitrary one. We shall not assume for the same that it is homogeneous; partly on its surface, partly in its interior will the rays therefore, which are incident upon it from the black envelope, experience the most manifold modifications. On these grounds, there must be, as a preliminary to the proposed proof, a study made of the radiation which takes place between black surfaces of the same temperature, for arbitrary bodies. To this investigation, which depends upon the formula just proved, the following paragraphs are devoted.

§ 6.

MUTUAL RADIATIONS OF BLACK SURFACES.

If the pencil of rays which the body C sends out through openings 1 and 2 should be partly linearly polarized, the plane of polarization of the polarized portion must rotate when C is rotated around the axis of the pencil. Such a rotation must therefore change the value of e . Since, according to the equation proved, such a change cannot take place, the pencil of rays can have no linearly polarized portion. It can be proved also, that it can have no circularly polarized part. But the proof for this will not be given here.

We will also grant, without this, that black bodies are con-

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ceivable in whose structure there is no reason why they should send out in any direction more right handed circularly polarized rays than left handed circularly polarized rays.

Of this character will the black bodies, concerned in the further treatment, be assumed; they send out in all directions unpolarized rays.

§ 7.

The quantity represented by e depends, aside from the temperature and wave length, on the form and the relative position of the openings 1 and 2. If w_1, w_2 represent the projections of the openings upon planes perpendicular to the axis of the pencil, and if s is called the distance of the openings, then

$$e = I \frac{w_1 w_2}{s^2}$$

where I is a function of the wave length of the temperature only.

§ 8.

Since the form of a body C is arbitrary, a surface may be substituted, which exactly fills opening 1 and which I will call surface 1; the screen S_1 may then be imagined removed. Further the screen S_2 may be considered removed if the pencils of rays which e covers, is defined as that which falls from surface 1 upon surface 2, which the opening 2 exactly fills.

§ 9.

A consequence of the last equation, which immediately follows and which will later be used, is that the value e remains unchanged if we imagine the openings 1 and 2 interchanged.

§ 10.

We will now establish a law which may be treated as a generalization of the law presented in the last paragraph.

Between the two black surfaces of the same temperature 1 and 2, is placed a body which may refract, reflect, or absorb in any way the rays which one sends to the other. Several pencils of rays may pass from surface 1 to surface 2; choose one of these, and consider the part of the one at 1 whose wave length lies between λ and $\lambda + d\lambda$, and divide this into two components

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whose planes of polarization are the planes of a_1 and b_1 which are perpendicular to each other (otherwise arbitrary). Let the part of the first component which enters 2 be divided into two components whose planes of polarization are the planes a_2 and b_2 perpendicular to each other (otherwise arbitrary). Let the intensity of the component polarized in a_2 be $Kd\lambda$. Of the pencil of rays which passes over the same path as the preceding one, from 2 to 1, let us consider the part at 2 whose wave length lies between λ and $\lambda + d\lambda$, and divide this into two components polarized in a_2 and b_2 . Divide the portion, which reaches 1 from the first component, into two parts whose planes of polarization are a_1 and b_1 . Let the intensity of the components polarized in a_1 be $K'd'\lambda$. Then

$$K = K'.$$

The proof of this law will be made upon the assumption that the rays under consideration undergo no weakening in their path, and also upon the assumption that refraction and reflection occur without loss, that there is no absorption and that the rays, coming from 1, polarized in a_1 , reach 2 polarized in a_2 , and *vice versa*.

Through the middle point of 1 pass a plane perpendicular to the axis of the pencil of rays, either incident or emergent at this point, and imagine in this a right-angled coördinate system, whose origin is that middle point. Let $x_1 y_1$ be coördinates of any point in the plane, Figure 4. At the distance of unity from this plane, imagine a second, parallel to it, and in this, a coördinate system whose axes are parallel to each of those, and whose origin lies in the axis of the pencil of rays. Let $x_3 y_3$ be coördinates of any point in this plane. In a similar manner pass through the middle point of 2, a plane perpendicular to the axis of the bundle of rays, incident or emergent at this point, and introduce in this, a rectangular system of coördinates whose origin is the middle point mentioned. Let $x_2 y_2$ be coördinates of a point in this plane. Finally, at a distance of unity from this plane and parallel to it imagine a fourth, and in it a system of coördinates whose axes are parallel to the axis of x_2, y_2 and whose origin lies in

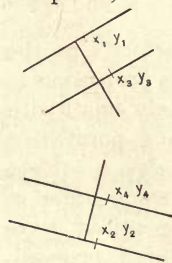


FIG. 4.

the axis of the pencil of rays. Let x_4, y_4 be coördinates of any point in this fourth plane.

From an arbitrary point let a ray pass to any other point (x_2, y_2) ; let T be the time required to pass from one point to the other; we will suppose it to be a known function of x_1, y_1, x_2, y_2 . If the points (x_3, y_3) and (x_4, y_4) lie in the path of the ray referred to, (and if for the sake of brevity the velocity of the ray *in vacuo* be taken as unity) the time which the ray requires to pass from (x_3, y_3) to (x_4, y_4) will be

$$= T - \sqrt{1 + (x_1 - x_3)^2 + (y_1 - y_3)^2} \\ - \sqrt{1 + (x_2 - x_4)^2 + (y_2 - y_4)^2}$$

Assuming the points $(x_3, y_3), (x_4, y_4)$ given, and the points $(x_1, y_1), (x_2, y_2)$ required, we could find these from the condition that the above expression is a minimum. If we assume that the eight coördinates $x_1, y_1, x_2, y_2, x_3, y_3, x_4, y_4$ are infinitely small, the following equations express the condition that the four points $(x_1, y_1), (x_2, y_2), (x_3, y_3), (x_4, y_4)$ lie in one ray :

$$x_3 = x_1 - \frac{\partial T}{\partial x_1}, x_4 = x_2 - \frac{\partial T}{\partial x_2}, \\ y_3 = y_1 - \frac{\partial T}{\partial y_1}, y_4 = y_2 - \frac{\partial T}{\partial y_2}$$

Now let (x_1, y_1) be a point in the projection of surface 1 on the plane x_1, y_1 and let dx_1, dy_1 be an element of this projection in which the point x_1, y_1 lies and which is infinitely small with respect to the surfaces 1 and 2. Let (x_3, y_3) be a point in a ray proceeding from (x_1, y_1) to surface 2, dx_3, dy_3 , a surface element in which the point (x_3, y_3) lies, of the same order as dx_1, dy_1 . The intensity of the rays of the required wave length and of the given plane of polarization, which, proceeding from dx_1, dy_1 , pass through dx_3, dy_3 , is then according to § 7 ;

$$d\lambda \ I \ dx_1 \ dy_1 \ dx_3 \ dy_3.$$

According to the supposition, this amount of rays reaches surface 2 undiminished and forms an element of a quantity designated by $Kd\lambda$. K is the definite integral

$$I \int \int \int \int dx_1 dy_1 dx_3 dy_3.$$

The integration here with respect to x_3, y_3 is to be taken over those values which these quantities have according to the above equations, while x_1 and y_1 remain constant and x_2, y_2 have all the values which correspond to the projections of surface 2 upon the plane x_2, y_2 . The integration with respect to x_1, y_1 is then to be taken over the projection of surface 1. The double integral

$$\int \int dx_3 dy_3 \text{ so limited,}$$

is, however,

$$= \int \int \left(\frac{\partial x_3}{\partial x_2} \frac{\partial y_3}{\partial y_2} - \frac{\partial x_3}{\partial y_2} \frac{\partial y_3}{\partial x_2} \right) dx_2 dy_2$$

or from the equations for x_3, y_3

$$= \int \int \left(\frac{\partial^2 T}{\partial x_1 \partial x_2} \frac{\partial^2 T}{\partial y_1 \partial y_2} - \frac{\partial^2 T}{\partial x_1 \partial y_2} \frac{\partial^2 T}{\partial x_2 \partial y_1} \right) dx_2 dy_2,$$

where the integration is taken over the projections of surface 2
Whence

$$K = I \int \int \int \int \left(\frac{\partial^2 T}{\partial x_1 \partial x_2} \frac{\partial^2 T}{\partial y_1 \partial y_2} - \frac{\partial^2 T}{\partial x_1 \partial y_2} \frac{\partial^2 T}{\partial x_2 \partial y_1} \right) dx_1 dy_1 dx_2 dy_2$$

where the integration is taken over the projections of surfaces 1 and 2.

If the magnitude of a K' be treated in the same way, remembering that a ray requires the same time to pass over a path between two points in either direction, the same expression will be found for K' as for K . Thus, the enunciated law is proved, subject to the limiting conditions under which it will next be proved. This limitation may, however, be immediately disposed of by an observation made by Helmholtz in his "Physiological Optics," p. 169. Helmholtz says here (with somewhat different notation): "A light ray passes from point 1 to point 2 after any number of refractions, reflections, etc. Through 1 suppose two arbitrary planes a_1 and b_1 passed in the direction of the ray perpendicular to each other, in which its vibrations are supposed to be resolved. Two similar planes, a_2 and b_2 are also passed through the ray at 2. Then the following

may be proved: If a quantity i of light polarized in the plane a_1 proceeds from 1 in the direction of the ray mentioned and of this, the quantity k of light polarized in the plane a_1 reaches 2, so will *vice versa* the quantity k of light polarized in a_2 reach point 1 if the quantity i of light polarized in a_2 proceed from point 2." ¹

Applying this law, and representing by γ the value of the ratio $\frac{k}{i}$ for the two rays which pass in either direction between the points (x_1, y_1) and (x_2, y_2) , then an expression is obtained for K as well as for K' which differs from that formed only in that now γ appears as a factor under the integral sign.

The equality of K and K' exists accordingly when γ has a different value for the rays into which one of the pencils compared may be divided; for example, it is unaffected if a part of the pencil is intercepted by a screen.

§ 11.

Of the same pencils which were compared in the preceding paragraphs, the following law also holds: of the pencil passing from 1 to 2, consider the part at 2 whose wave lengths lie between λ and $\lambda + d\lambda$ and resolve this into two components polarized in a_2 and b_2 ; let the intensity of the first component be $Hd\lambda$. Of the pencil which passes from 2 to 1, consider at 2 the portion whose wave lengths lie between λ and $\lambda + d\lambda$, and resolved this into two components polarized in a_2 and b_2 . Let the portion of the first component reaching point 1 be $H'd\lambda$.

Then $H = H'$. The proof of this law is the following; K and K' are to have the same meaning as in the preceding paragraph; let L and L' be the quantities which arise from K and K' when plane a_1 is interchanged with plane b_1 .

¹ The law of Helmholtz, as he himself noted, does not hold good when the plane of polarization of a ray undergoes any rotation, such as magnetic force produces according to Faraday's discovery; therefore, in the following considerations magnetic force must not be considered as present. Helmholtz limited his law also by supposition that light undergoes no change of refrangibility such as occurs in fluorescence; this limitation is unnecessary in the application of the law, if rays of only a given wave length are regarded.

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Then $L = L'$, similarly $K = K'$, further $H = K + L$, because rays polarized perpendicularly to each other do not interfere, when they are brought back to a common plane of polarization in case they are a part of an unpolarized ray; and according to § 6 the surface 1 sends out unpolarized rays.

Finally $H' = K + L'$, because two rays, whose planes of polarization are perpendicular to each other, do not interfere. From these equations it follows that $H = H'$.

§ 12.

Let Fig. 2 have the same meaning as in § 4, only let the body C be not a black body but an arbitrary one. Let opening 2 be *closed* by surface 2. This surface sends out a pencil of rays through opening 1 to the body C , which is partly absorbed by this body, and partly scattered in different directions by reflection and refraction. Of this pencil consider the part between 1 and 2 whose wave lengths lie between λ and $\lambda + d\lambda$ and resolve this into two components polarized in plane a and the plane perpendicular to this. Let that part of the first component which escapes absorption by C , and hence strikes the black covering in which the body C is inclosed, be $M'd\lambda$. A certain portion of the rays which a part of the covering sends out to the body C , fall upon surface 2 through opening 1; thus by means of the body C a pencil of rays is produced which passes through opening 1 to the surface 2. Of this, consider the part whose wave lengths lie between λ and $\lambda + d\lambda$ and divide it into two components polarized in plane a and the plane perpendicular to it. Let the intensity of the first components be $Md\lambda$.

Then $M = M'$. The truth of this law follows from the proposition from the preceding paragraph, if we apply this to all pencils of rays, which surface 2 and all the elements of the black cover surrounding the body C interchange with each other by means of the body C , and then form the sum of the equations so obtained.

§ 13.

Proof of the proposition § 3 for any body.

Let the arrangement shown in Fig. 3 and described in § 5 be

taken, only let the body C no longer be a black body, but arbitrary. In both cases described there, the equilibrium of heat subsists; then the *vis viva* which is drawn out from the body C by the removal of the black surface 3, must therefore be equal to the *vis viva* which is supplied to this by the presence of the concave mirror. The symbols used in § 5 will be used here with the same meaning. The letters E and A will have the meaning given them in § 2.

If surface 3 is removed, then the rays are withdrawn from the body C which this surface sends to it; the intensity of the part of these rays which it absorbed is $= \int_0^\infty d\lambda \epsilon r A$.

Now the rays must be examined which are transmitted to the body by the presence of the concave mirror. All these rays must be reflected from the concave mirror to plate P and from this to opening 1, and these must pass in the same direction as if they came from opening 2. Before they strike the concave mirror, they have either experienced a reflection from it or not. In the first case they can only be sent back again to the concave mirror by means of the body C over the path which is the reverse of that already described. It must next be premised that the body C has such a position that, of the rays which pass to it through 2 and 1, only an infinitely small part will be reflected back again through opening 1 to opening 2. Then, of the rays in question, only an infinitely small fraction have suffered multiple reflection at the concave mirror, and it is sufficient to consider those which are reflected only once at the mirror. Of these, a part proceed from the body C , the rest from the black covering. The first part has experienced a double reflection at plate P ; the *vis viva* which the body C absorbs from it is

$$= \int_0^\infty d\lambda E r^2 A.$$

The second part which proceeds from the black enclosure may again be considered as consisting of two parts; one which passes to the concave mirror without the mediation of the body C , and a second, by means of it. Each arises from rays which proceed from black partition opposite the concave mirror, and have passed through the plate P , have been reflected from the concave mirror to the plate P and from this to opening 1.

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Without examining from which part of the black wall these rays have proceeded, their intensity may be found by the law established in § 11.

By the application of this, the intensity of those rays which were absorbed by the body C is shown to be

$$= \int_0^{\infty} d\lambda r (1-r) A.$$

Finally in order to find the intensity of the rays which proceed from the black covering by means of the body C to the concave mirror, and pass back from this to the body C and are here absorbed, let N designate the quantity which the quantity indicated by M in § 12 becomes in consequence of plate P being brought into its place and the surface 3 removed; the intensity

is then $= \int_0^{\infty} d\lambda N r^2 A.$

The difference between M and N arises only from the variation which the rays, falling upon the body C from the black covering through opening 1, undergo by the introduction of plate P and the removal of surface 3. Suppose the plate P brought into its position, without removing surface 3, then M can undergo no change, since all the pencils of rays, which go to the opening 1 remain unchanged; the pencil proceeding from surface 2, for example, suffers a loss through reflection at plate P which will be exactly replaced by the reflection of the rays going out from the surface 3. The difference $M-N$ is therefore only produced by the removal of surface 3 and is also equal to the part of M which arises from the rays sent out by surface 3 to opening 1 by means of plate P . According to the supposition made in these paragraphs concerning the position of the body C , $M-N$ is infinitely small in comparison with the intensity of the rays of equal wave length which surface 3 sends to opening 1 by means of plate P , as well as infinitely small in comparison with the intensity of rays of equal wave length and polarized in the plane a , which surface 2 sends to opening 1 by the absence of the plate P , and therefore finite and also infinitely small with respect to the quantity represented by M' in § 12 (assuming that $1-A$ is not infinitely small). Since, however, as already pointed in the places cited, $M' = M$, we may also place

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$$N = M = M'.$$

But according to the definition given of M'

$$M' = e (1-A) \text{ and therefore}$$

$$\int_0^\infty d\lambda N r^2 A = \int_0^\infty d\lambda e (1-A) r^2 A.$$

The proposition presented at the beginning of this paragraph would then be expressed by the equation :

$$\int_0^\infty d\lambda e r A = \int_0^\infty d\lambda E r^2 A + \int_0^\infty d\lambda e r (1-r) A + \int_0^\infty d\lambda e (1-A) r^2 A,$$

or by the equation $\int_0^\infty d\lambda (E - Ae) A r^2 = 0.$

By the same treatment employed in § 5 with reference to a similar equation, we may conclude that for every value of λ

$$\frac{E}{A} = e,$$

or substituting for e its value in § 7.

$$\frac{E}{A} = I \frac{w_1 w_2}{s^2}.$$

Thus, the law § 3 is proved under the assumption that, of the pencil which falls from surface 2 through the opening 1 upon the body C , no finite part is reflected by this back to the surface 2 ; further, that the law holds without this limitation, if we consider that when the condition is not fulfilled, it is only necessary to turn the body C infinitely little in order to satisfy it, and that by such a rotation the quantities E and A undergo only and infinitely small change.

§ 14.

A Generalization of the Law § 3.

The discussions given assume that the space in which the radiation occurs is a vacuum. But the same treatment also obtains when this space is filled with any perfectly diathermanous medium ; only the function I will then be different than in the former case. The symbol I may then be retained for a vacuum and I' may be called the corresponding function of temperature and wave length for a certain diathermanous medium ; if n is the index of refraction of the same for the

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temperature and wave length to which I and I' refer, then a simple relation exists between I', I , and n ; the same follows from the law already demonstrated as will be here shown.

Imagine a layer of a diathermanous medium bounded by two parallel planes, and with one side in contact with the black surface F . Let the thickness of the layer = 1. For this body, the

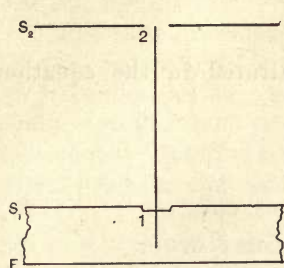


FIG. 5.

absorptive power of A , and the emissive power E , in relation to a certain pencil of rays will be investigated. The opening 1 and 2 which determine the form of the pencil will be in screens S_1 and S_2 , of which the first covers the surface of the layer hitherto supposed to be free, and the second is parallel to it; let the line joining the middle points of the open-

ings be perpendicular to the screens. Of any pencil of rays of a definite wave length and direction of polarization, which passes from the opening 2 to the opening 1, a fraction will be reflected at the latter which may be designated by ρ ; the rest passes to the surface F and is here completely absorbed; therefore

$$A = 1 - \rho.$$

To find E , represent by x, y ; x_1, y_1 ; and x_2, y_2 the coördinates of a point of the surface F , the opening 1, and the opening 2, reckoned from those points which are found in the axis of the pencil. If these points lie in a ray, then if s again represents the distance of the two openings,

$$n \left(1 + \frac{(x_1 - x)^2}{2} + \frac{(y_1 - y)^2}{2} \right) + \left(s + \frac{(x_2 - x_1)^2}{2s} + \frac{(y_2 - y_1)^2}{2s} \right)$$

must be a minimum with respect to x_1 and y_1 : i. e.,

$$x = x_1 - \frac{x_2 - x_1}{ns}, \quad y = y_1 - \frac{y_2 - y_1}{ns}$$

if w_1 and w_2 are the surfaces of the two openings, we find by a treatment, which is given in a more general form in § 10, the intensity of the rays (polarized in a and of wave lengths between λ and $\lambda + d\lambda$) which, falling from F upon opening 1, in part, pass to opening 2,

$$= I \, d\lambda \, w_1 \, w_2 \left(\frac{\partial x}{\partial x_2} \frac{\partial y}{\partial y_2} \frac{\partial x}{\partial y_2} \frac{\partial y}{\partial x_2} \right),$$

that is

$$= \frac{I \, d\lambda \, w_1 \, w_2}{n^2 \, s^2}$$

Of these rays the fraction $1-\rho$ goes through the opening 1 and arrives at the opening 2.

$$\text{Thus } E = (1-\rho) \frac{I \, w_1 \, w_2}{n^2 \, s^2}$$

If these values of E and A are substituted in the equation

$$\frac{E}{A} = \frac{I \, w_1 \, w_2}{s^2}$$

then

$$I = n^2 \, I.$$

§ 15.

Some Results of the Law § 3.

When any given body—a platinum wire for instance—is gradually heated, it emits, up to a certain temperature, only rays whose wave lengths are greater than that of the visible rays. At a certain temperature, rays of the wave length of the extreme red begin to be visible; as the temperature rises higher and higher, rays of a shorter and shorter wave length are added, so that for every temperature, rays of a corresponding wave length come into existence, while the intensity of the rays of greater wave lengths increase. If the law proven be applied to this case, it will be seen that the function I for any wave length vanishes for all temperature below that of a certain temperature, depending on the wave length for higher temperatures increases with the same. From this it follows, when the same law is applied to other bodies, that all bodies, whose temperature is gradually raised, begin to send out rays of the same wave length at the same temperature, and begin to glow with red rays at the same temperature, and at a higher common temperature, yellow, and so on. The intensity of rays of a certain wave length which different bodies send out at the same temperatures may, however, be very different; it is proportional to the absorptive powers of bodies for rays of that particular wave length. At the same temperature accordingly metal glows more brightly than glass, and this more brightly than a gas. A body that remains perfectly transparent at the

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highest temperature would never become incandescent. Into a ring of platinum wire of about 5mm diameter, I introduced some phosphate of soda and heated it in the nonluminous flame of the Bunsen burner. The salt melted and formed a fluid lens and remained perfectly clear; but it emitted no light, while the platinum ring in contact with it radiated the most brilliant light.

Draper¹ has drawn the conclusion from investigations that all solid bodies begin to glow at the same temperature. From his researches he has, however, noted that certain bodies like chalk, marble, fluor spar glow at a lower temperature than they should according to this law; he called this luminosity *phosphorescence*, and said it clearly differed from glowing, by the color. But whatever name may be given to this luminosity, it is in contradiction with law, § 3, and a body which shows it must therefore not satisfy the assumptions which were made in the proof of the law, that, at a constant temperature, it must remain unchanged; phosphorescence is not purely an effect of heat, and is not exclusively determined by the temperature, but is produced by changes in the body; if these changes—whether they are chemical or of another nature—have ceased then the phosphorescence must vanish.

§ 16.

From the law, § 3, it follows that a body, which absorbs more rays from one plane of polarization than from another, sends out in the same ratio more rays from the first plane of polarization than from the second. Consequently, as is known to happen, a glowing opaque body having a smooth surface sends out light in directions oblique to this surface which is partially polarized perpendicularly to the plane passing through the ray and the normal to the surface; of the incident rays, which are polarized perpendicularly to the plane of incidence, the body reflects less, but also absorbs more than it does of rays whose plane of polarization is the plane of incidence. According to this law the state of polarization of the rays sent out may easily be given if the law of the reflection of the incident rays is known.

¹ Phil. Mag. XXX. p. 345; Berl. Ber. 1847.

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A tourmaline plate, cut parallel to the optic axis, absorbs, at ordinary temperatures, more of the rays which strike it normally, if the plane of polarization of these is parallel to the axis than when it is perpendicular to it. Assuming that the tourmaline plate retains this property when it is at a glowing heat, it must give out rays in a direction normal to it, which are partially polarized in the plane passing through the optic axis and which is the plane perpendicular to that which is called the plane of polarization of the tourmaline. I have proved this striking deduction from theory by experiment and it confirmed the same. The tourmaline plates employed withstood a considerable temperature, glowing for a long time in the flame of the Bunsen burner without undergoing any permanent change; only after cooling did they appear dull at the edges. The property of polarizing transmitted light was retained even at an incandescence, although in a considerable less degree than at a lower temperature. This appeared on observing, through a double refracting prism, a platinum wire made incandescent in the flame and placed behind a tourmaline plate. The two images of the platinum wire were of unequal brightness, although the difference was much less than when the tourmaline plate was outside of the flame. The double refracting prism was then given the position in which the difference of the intensities of the two images was a maximum; suppose the upper image were the brighter; then, after removal of the platinum wire the two images of the tourmaline plate were compared. The upper image was not strikingly, but, unmistakably, darker than the other; both images appeared exactly like to two similar incandescent bodies, of which the upper had a less temperature than the lower one.

§17.

Still another result of the law established may, in conclusion, be admitted here. When a space is surrounded by bodies of the same temperature, and no rays can penetrate through these bodies, every pencil in the interior of the space is so constituted, with respect to its quality and intensity, as if it proceeded from a perfectly black body of the same temperature, and is therefore independent of the nature and form of the

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bodies, and only determined by the temperature. The truth of this statement is evident if we consider that a pencil of rays, which has the same form but the reverse direction to that chosen, is completely absorbed by the infinite number of reflections which it successively experiences at the assumed bodies. In the interior of an opaque glowing hollow body of given temperature there is, consequently, always the same brightness whatever its nature may be in other respects.

BIOGRAPHICAL SKETCH.

GUSTAV ROBERT KIRCHHOFF, the son of Counselor-at-law Kirchhoff, was born March 12, 1824, at Königsberg. He took his degree of doctor of philosophy at the University in 1847. The following year he became private-docent at the University of Berlin. He early showed those rare mathematical faculties which later distinguished him. As early as his eighteenth year he decided upon physics as the branch to which he should devote his life's work. By 1845 he had investigated electric currents, and established the two so-called Kirchhoff's laws for current conduction. Other important papers on electricity followed in rapid order. In 1854 he was called to Breslau, where he became associated with Bunsen. He went to Heidelberg in 1854 where Bunsen had preceded him. Here in his prime he wrought and sought for twenty years, and in connection with Bunsen achieved some of the most important discoveries in the history of physical science. In 1875 he accepted, after twice declining an invitation to the University, a call to the chair of theoretical physics at Berlin where he became associated with his former colleague von Helmholtz. Here he delivered for eleven years (with serious interruption in the last two years) his famous courses of lectures on theoretical physics. It is during this period that we find the most brilliant aggregation at Berlin of scholars in the faculty of mathematics and physics during the century. His contributions extend over optics, heat, fluid, motion, electricity, elasticity, etc., and all bear the imprint of the great genius he was. He died unexpectedly Oct. 17, 1887, after many months of disability. His papers and lectures have been collected and edited and now form one of the enduring monuments in physical science.

CHEMICAL ANALYSIS BY SPECTRAL
OBSERVATIONS.

BY

G. KIRCHHOFF AND R. BUNSEN.

Poggendorf's Annalen, Band 110, 1860 ; *Gesammelte Abhandlungen von G. Kirchhoff*. pp. 598-625, 1882.

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CHEMICAL ANALYSIS BY SPECTRAL OBSERVATIONS.¹

It is well known that many substances have the property when they are brought into a flame of producing in the spectrum certain bright lines. We can found on these lines a method of qualitative analysis which greatly enlarges the field of chemical reactions and leads to the solution of problems unsolved heretofore. We shall confine ourselves here only to the extension of the method to the detection of the metals of the alkalis and the alkali earth and to the illustration of their value in a series of examples.

The lines referred to show themselves the more plainly, the higher the temperature and the weaker the natural illuminating power of the flame. The gas lamp² described by one of us gives a flame of very high temperature and very small luminosity; this is consequently especially adapted to investigations on those substances characterized by bright lines.

In Figure 1 the spectra are represented which the flames referred to give when the salts, as pure as possible, of potassium, sodium, lithium, strontium, calcium, and barium are vaporized in it. The solar spectrum is annexed in order to facilitate the comparison.

The potassium compound used for the investigation was obtained by heating chlorate of potassium which had been six to eight times recrystallized beforehand.

The chloride of sodium was obtained by combining pure carbonate of sodium and hydrochloric acid and purifying the same by repeated crystallization.

The lithium salt was purified by precipitating fourteen times with carbonate of ammonium.

For the production of the calcium salt a specimen of marble

¹ Kirchhoff and R. Bunsen, Pogg. Ann. Vol. 110. 1860.

² Bunsen, Pogg. Ann. Vol. 100 p. 85.

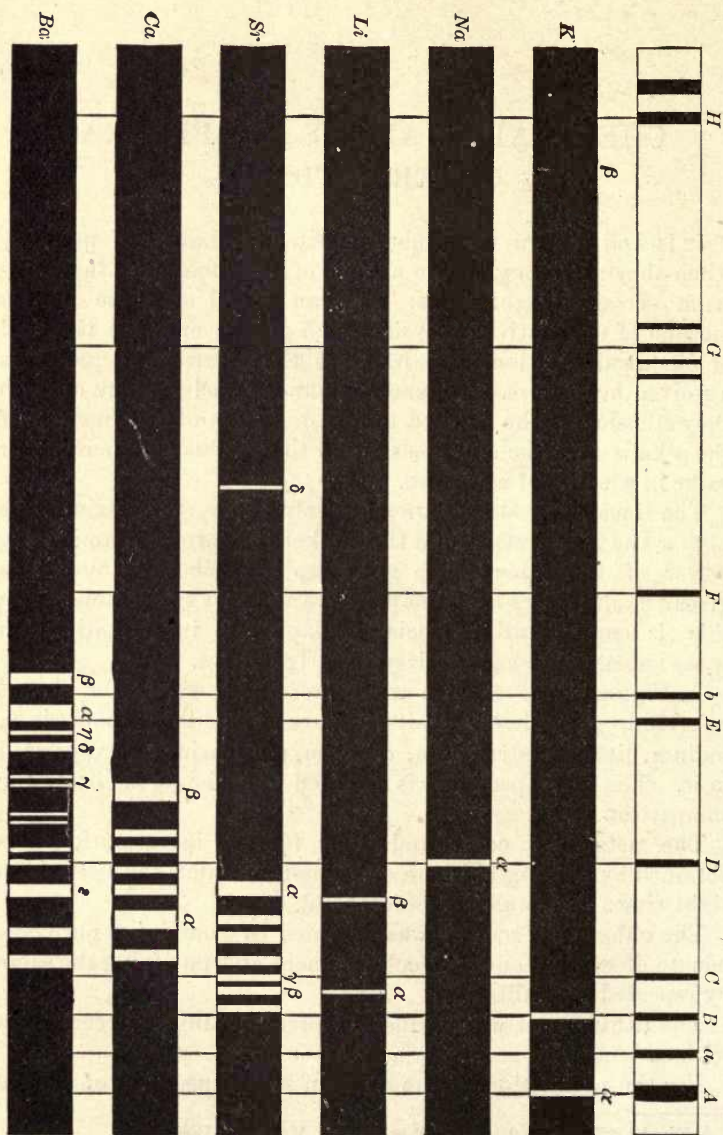


FIGURE 1.

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as pure as possible, and dissolved in hydrochloric acid, was used. From this solution the carbonate of calcium was thrown down by a fractional precipitation with carbonate of ammonium in two portions, of which only the latter, precipitated in calcium nitrate, was used. The calcium salt thus obtained we dissolved several times in absolute alcohol and converted it finally into the chloride by evaporating the alcohol and by precipitation with carbonate of ammonium in hydrochloric acid.

In order to obtain the pure chloride of barium we extracted it from the commercial salt by pulverizing and boiling repeatedly in nearly absolute alcohol. The residue thus extracted and freed from alcohol was dissolved in water and thrown down by fractional precipitation in two portions, only the second being dissolved in hydrochloric acid, and the barium chloride thus obtained being further purified by repeated crystallizations.

In order to obtain chloride of strontium, as pure as possible, the commercial salt was crystallized out from alcohol, and fractionally precipitated in two portions with carbonate of ammonium, the second part being dissolved in nitric acid and the nitrate freed from the last traces of calcium by pulverizing and boiling with alcohol. From the product thus purified the chloride of strontium was obtained finally by precipitating with carbonate of ammonium and dissolving the precipitate in hydrochloric acid. All these purifications were made in platinum vessels as far as it was possible.

Figure 2 represents the apparatus which we have used

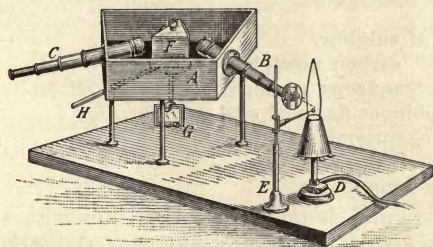


FIG. 2.

mainly in the observation of the spectra. *A* is a box blackened on the inside the bottom of which has the form of a trapezium and rests on three feet; the two inclined sides of the same form an angle with one another of about 58° and carry the

two small telescopes *B* and *C*. The ocular of the first is removed and replaced by a plate in which is a slit formed of two brass cheeks which are placed at the focus of the objective. The

lamp *D* is so placed before the slit that the mantle of the frame is intersected by the axis of the tube *B*. Somewhat beneath the point where the axis meets the mantle the end of a very fine platinum wire bent into a small hook and carried by the holder *E* passes into the same; on this hook is melted a globule of the chloride previously dried. Between the objective of the telescopes *B* and *C* is placed a hollow prism *F* with a reflecting angle of 60° and filled with carbon disulphide. The prism rests on a brass plate which can be rotated on a vertical axis. This axis carries on its lower end the mirror *G* and above it the arm *H* which serves as the handle to rotate the prism and the mirror. A small telescope is adjusted before the mirror which gives an image of a horizontal scale placed at a short distance. By rotating the prism we can cause to pass before the vertical thread of the telescope *C* the entire spectrum of the flame and bring every portion of the spectrum into coincidence with this thread. To every reading made on the scale there corresponds a particular portion of the spectrum. If the spectrum is very weak the cross hair of the telescope *C* is illuminated by means of a lens which throws some of the rays from a lamp through a small opening which is placed laterally in the ocular of the telescope *C*.

The spectra in Fig. 1. obtained by means of the pure chloride above mentioned we have compared with those which we obtained if we introduce the bromides, iodides, hydrated oxides, sulphates, and carbonates of the several metals into the following flames:—

into the flame of sulphur,
 “ “ “ “ carbon disulphide,
 “ “ “ “ aqueous alcohol,
 “ “ non-luminous flame of coal gas,
 “ “ flame of carbonic oxide,
 “ “ “ “ hydrogen and
 “ “ oxyhydrogen flame.

From these comprehensive and lengthy investigations whose details we may be permitted to omit, it appears that the difference in the combinations in which the metals were used, the multiplicity of the chemical processes in the several flames, and the enormous differences of temperatures of the latter *exert no influence on the position of the spectral lines corresponding to the individual metals.*

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How considerable the differences of temperature mentioned are, is shown by the following treatment.

We may arrive at an approximation of temperature of a flame by means of the equation $t = \frac{\sum gw}{\sum ps}$, in which t is the temperature of the flame sought, g the weight of the substance burning in oxygen, w the heat of combustion of the same, p the weight and s the specific heat of one of the products of combustion.

If we take as the heat of combustion

of sulphur.....	as 2240° C
“ carbon disulphide.....	3400
“ hydrogen.....	34462
“ marsh gas.....	13063
“ elayle.....	11640
“ ditetryle.....	11529
“ carbonic oxide.....	2403

and place according to Regnault the specific heat at constant pressure

for sulphurous acid.....	=0.1553
“ carbonic acid.....	=0.2164
“ nitrogen.....	=0.2440
“ aqueous vapor	=0.4750

we find accordingly the temperature

of the sulphur flame.....	1820° C
“ “ bisulphide of carbon flame....	2195
“ “ coal gas flame ¹	2350
“ “ carbonic oxide flame ²	3042
“ “ hydrogen flame in air ³	3259
“ “ oxyhydrogen flame ⁴	8061.

It appears that the same metal compound gives in one of these flames a spectrum as much more intense as the temperature is higher. Of the compounds of these metals, those give the greatest intensity in a flame which have the greatest volatility.

In order to obtain a further proof that each of the severally mentioned metals always give the same bright lines in the spectrum, we have compared the spectra referred to with those

¹ Liebig's Ann. Vol. CXI. p. 258.

² Gasometric Methods by R. Bunsen, p. 254.

³ Ibid.

⁴ Ibid.

which an electric spark produces which passes between electrodes made from these metals.

Small pieces of potassium, sodium, lithium, strontium, and calcium were fastened on a fine platinum wire and so melted in pairs within glass tubes that they were separated by a distance of 1 to 2mm from one another the wires piercing the sides of the tubes. Each of these tubes was placed before the slit of the spectroscope; by means of a Ruhmkorff's induction apparatus, we caused electric sparks to pass between the metal pieces mentioned and compared the spectrum of the same with the spectrum of a gas flame in which the chloride of the corresponding metal was brought. The flame was placed behind the glass tube. When the Ruhmkorff apparatus was thrown alternately in and out of action it was easy to be convinced, without any accurate measurement, that, in the brilliant spectrum of the spark, the bright lines of the spectrum of the flame were present undisplaced. In addition to these there appeared other bright lines in the spark spectrum a part of which must be attributed to the presence of foreign metals in the electrodes, others to nitrogen which filled the tubes after the oxygen had partly oxidized the electrodes.¹

It appears, accordingly, beyond a question that the bright lines of the spectra indicated may be considered as certain proof of the presence of the metal in consideration. They can serve as reactions by means of which this material may be detected more certainly, and quickly and in smaller quantities than by any other analytical method.

The spectra, represented, refer to the case when the slit is wide enough so that only the most prominent of the dark lines of the solar spectrum are visible, the magnifying power of the observing telescope being small (about four-fold) and the intensity of the light moderate. These conditions seem to us

¹ In one investigation with strontium electrodes we used a tube filled with hydrogen instead of nitrogen, and the stream of sparks was transformed very soon into an arc, while the sides of the tube were covered with a gray precipitate. On opening the tube under rock-oil it appeared that the hydrogen had vanished and a vacuum existed. The gas appears, therefore, at the enormous temperature of the electric spark, to have dissociated the strontium oxide which had not been completely removed from the surface of the metal.

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most advantageous when it is necessary to carry out a chemical analysis by spectral observations. The appearance of the spectrum may under other conditions be quite different. If the purity of the spectrum is increased, many of the lines appearing as single, resolve themselves into several, the sodium line, for example, into two; if the intensity is increased new lines appear in many of the spectra shown and the relation of the brightness of the old ones becomes different. In general the brightness of a darker line increases with greater luminosity more rapidly than the brighter ones, but not so much that the former exceed these. A clear example of this is given by the two lithium lines. We have observed only one exception to this rule, namely, with the line $Ba\eta$, which, with low luminosity, is barely visible while $Ba\gamma$ appears very distinct, and, with greater luminosity, much brighter than the former. This fact appears of importance, and we shall make a further study of the same.

We will now consider more closely the characteristics of the several spectra, the knowledge of which is of importance from a practical standpoint, and indicate the advantage which the chemical analytical method founded upon it furnishes.

SODIUM.

Of all the spectral reactions that of sodium is the most sensitive. The yellow line $Na\alpha$, the only one which is shown in the sodium spectrum coincides with Fraunhofer's line D and is characterized by its peculiarly sharp boundary and its extraordinary brilliancy. If the temperature of the flame is very high and the quantity of the substance used very great, traces of a continuous spectrum are seen in the immediate neighborhood of the line. Lines of other substances, in themselves very weak, lying near it appear still weak and will, therefore, often first be visible after the sodium reaction has begun to disappear.

In the oxygen, chlorine, iodine and bromine compounds in sulphuric acid and carbonic acid the reaction is most evident. But it is present also in the silicates, borates, phosphates and other non-volatile salts.

Swan¹ has already called attention to the minuteness of the

¹ Pogg. Ann. Vol. C, p. 311.

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quantity of common salt which can produce the sodium line clearly.

The following investigation shows that chemistry produces no single reaction which in the remotest degree can compare in sensitiveness with this analytical spectral determination of sodium. We detonized in one corner of the experiment room which contained about 60 cubic meters of air and as far as possible from our apparatus three milligrams of chlorate of sodium with milk sugar while the non-luminous flame was observed before the slit. After some minutes, the flame, becoming gradually colored pale yellow, gave a strong sodium line, which, after ten minutes, again completely vanished. From the weight of the detonized salt and the air contained in the room it is easy to calculate that in a unit weight of the latter not a $\frac{1}{20000000}$ th part of sodium smoke could have been suspended. As the reaction can be readily observed in a second, and as, in this time, according to the rate of flow and the composition of the gases in the flame, only about 50 ccm or 0.0647 grams of air which contained less than $\frac{1}{20000000}$ th of sodium salt, reach the state of incandescence in the flame, it follows that the eye is capable of detecting less than $\frac{1}{30000000}$ th of a milligram of sodium salt with the greatest distinctness. With such a sensibility of the reaction it is evident that only rarely is a sodium reaction not visible in glowing atmospheric air. The earth is covered over more than two-thirds of its surface with a solution of chloride of sodium, which, by the waves breaking into foam, is transformed continually into spray; the particles of sea-water, which reach the atmosphere in this way, evaporate and leave behind them motes of salt which vary in magnitude, but, as it appears, are rarely absent from the atmosphere, and, perhaps, serve to supply the small organisms the salt which the larger plants and animals secure from the ground. The presence in the air of salt, easily shown by spectral analysis, is yet of interest from another standpoint. If, as we yet can scarcely doubt, there are catalytic influences which are the cause of the miasmatic spread of disease, it is possible that an antiseptic substance, such as salt, even in vanishingly small quantities, may indeed not be without definite influence upon such processes in the air. From daily and long continued

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spectrum observation it would be easy to learn whether the variation in the intensity of the spectral line $Na\alpha$, produced by the sodium combination in the air, is related in any degree to the appearance and the spread of endemic diseases.

In the exceedingly delicate sodium reaction may also be sought the reason why all bodies exposed to the air show the sodium line after a time when heated in the flame, and why it is possible with only a few compounds to eliminate the last trace of the sodium line $Na\alpha$ by crystallizing it out ten or more times from water which has come in contact with platinum vessels only. A hair wire of platinum, which has been freed, by heating, from every trace of sodium, shows the reaction most vividly again, if it is exposed some hours to the air. Dust which settles in the room from the air shows it in the same degree, so that, for example, the slapping of a dusty book is quite sufficient to produce at a distance of several spaces the most brilliant flashes of the $Na\alpha$ line.

LITHIUM.

The incandescent vapors of the lithium compound give two sharply defined lines, one a very weak yellow $Li\beta$ and a red brilliant line $Li\alpha$. In certainty and delicacy this reaction exceeds all those known heretofore in analytical chemistry. It approximates in sensibility that of the sodium reaction perhaps because the eye is more sensitive for yellow rays than for red. On detonizing nine milligrams of carbonate of lithium with a large excess of milk sugar and potassium chlorate in the room which contained about 60 cubic meters of air, the line became quite evident. The eye can therefore in this way, as a calculation similar to the one made above will show, perceive less than $\frac{1}{1000000}$ th of a milligram of carbonate of lithium with the greatest distinctness. 0.05 grams of the same salt, detonized in the way already mentioned, made it possible to observe the $Li\alpha$ line in the air of the same room during more than an hour.

The oxygen, chlorine, iodine and bromine compounds are most suitable for observing lithium. But the carbonate, sulphate, and even phosphate are almost as well suited for this purpose. Minerals containing lithium, as triphyllin, triphan, petalit, lepidolith, need only to be held in the flame in order

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to give the line *Lia* with an intense lustre. In this way it is possible to show the presence of lithium in many feld-spars, for example in orthoclase from Baveno. The line is seen only momentarily immediately after the insertion of the specimen in the flame. Thus mica from Altenberg and Penig indicates the presence of lithium while on the contrary mica from Miask, Ashaffenburg, Modum, Bengal, Pennsylvania, etc., is free from lithium. When in naturally deposited silicates only a vanishingly small quantity of lithium is present, it escapes immediate observation. The test in such cases is then best made in the following way: we digest and evaporate a small quantity of the substance for examination with hydrofluoric acid or fluoride of ammonium, moisten the remainder with sulphuric acid, and dissolve the dry mass with absolute alcohol. The alcoholic solution is then evaporated to dryness, again dissolved with alcohol, and the fluid, thus obtained, evaporated in as shallow a dish as possible. The product which remains can be easily scraped together by means of an erasing knife and brought into the flame on platinum wire. $\frac{1}{10}$ th of a milligram of the same is usually quite sufficient for the experiment. Other compounds than the silicates, in which we may wish to detect the least traces of lithium, may be transformed into sulphates by evaporation with sulphuric acid or in any other way and then treated as above.

By means of these experiments, the unanticipated conclusion is readily drawn that lithium belongs to those substances which are most widely distributed in nature. This is easily shown by means of 40 cubic centimeters of sea-water which was collected in the Atlantic ocean in latitude $41^{\circ} 41'$ and longitude $39^{\circ} 14'$. Ashes of Fucoids (kelp) which was driven on to the Scottish coast from the Gulf Stream contained appreciable traces of it. All orthoclase and quartz from the granite of the Oldenwald which we have tested show a lithium content. A very pure drinking water from a spring on the western granitic declivity of the Neckar valley in Schlierbach near Heidelberg contained lithium, while the spring rising in the red sandstone which supplies the water pipes of this chemical laboratory was free from it. Mineral water, in a litre of which lithium can scarcely be detected by the ordinary analytical methods, shows

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the *Li a* line frequently if we put a drop of the same into the flame on a platinum wire.¹ All the ashes of woods in the Oldenwald which grow on granite soil, as well as Russian and other commercial potashes examined by us, contain lithium. Neither, even, in the ashes of tobacco, vine leaves, vine-wood and grapes,² as well as in the ashes of crops which were cultivated in the Rhine plain near Waghausel, Deidesheim and Heidelberg on non-granitic earth, was lithium lacking, nor in the milk of the animals which were fed upon these crops.³

It will be scarcely necessary to remark that a mixture of volatile sodium and lithium salts shows, along with the reaction of sodium, that of lithium with a scarcely less preceptible sharpness and distinctness. The red line of the last appears still quite distinct when a small bead containing the $\frac{1}{10000}$ th part of lithium salts is introduced into the flame, where the eye, unaided, perceives in the same, nothing more than yellow light of sodium without any indication of red coloration. On account of the greater volatility of lithium salts, the sodium reaction lasts somewhat longer. When, therefore, it is desired to detect very small traces of lithium along with sodium, the bead for testing must be introduced into the flame whilst we are observing through the telescope. We then often observe the lithium line only for a few moments during the first products of volatilization.

In the production of lithium compounds on a commercial scale spectrum analysis is a means of inestimable value in the selection of the raw material used and the determination of an efficient method of manufacture. Thus for example, it is only necessary to evaporate a drop of the different mother-liquors in

¹ When it is required to introduce a liquid into the flame we bend in the end of a horse-hair platinum wire, a ring of suitable diameter and hammer the same flat. If we let a drop of the fluid fall into the ring thus formed a sufficient quantity for the investigation remains hanging within.

² Lithium is concentrated so much in the mother-liquors in the manufacture of tartaric acid that we can obtain considerable quantities from them.

³ Dr. Folwarczny has even been able to show with the lithium line *Li a* the lithium compounds in the ash of human blood and of muscular tissue.

the flame and observe through the telescope, in order to show at once, that, in many of these saline residues, a rich and hitherto overlooked lithium source exists. Thus in the process of preparation, we can follow any loss of lithium in the associated products and wastes by means of the spectral reaction, and thus easily seek more efficient methods of production than those heretofore used.¹

POTASSIUM.

The volatile potassium compounds produce in the flame a very extended continuous spectrum which only show two characteristic lines; the first K_{α} , in the outermost red bordering on the ultra red rays falls exactly on the dark line A of the solar spectrum; the second K_{β} far in the violet toward the other end of the spectrum, corresponds likewise to a Fraunhofer's line. A very weak line, coinciding with the Fraunhofer's line B , which, however, is only visible with an intense flame, is less characteristic. The blue line is somewhat weak but is almost as well suited for detecting potassium as the red line. The position of both lines, in the neighborhood of the limits of the rays perceptible by the eye, renders the reaction somewhat less sensitive.

In the air of our room it became first visible when we burned about one gram of chlorate of potassium mixed with milk sugar. We can, therefore, make clear to the eye in this way about $\frac{1}{1000}$ th of a milligram of chlorate of potassium.

Potassium hydrate and all compounds of potassium with volatile acids, show the reaction without exception. Potassium silicate and similar non-volatile salts, on the contrary, produce it only when the potassium is present in large quantities. With small amounts, the test bead may be melted together with some carbonate of sodium in order to make the characteristic lines visible. The presence of the sodium does not prevent the reaction and hardly affects the sensibility. Ortho-

¹ We obtained by such an approved method from two jars of mineral water (about four litres) a mother-water, which gave on evaporation with sulphuric acid a residue of 1.2 K, half an ounce of carbonate of lithium of the purity of the commercial, whose cost would be about 140 fl. per pound. A great number of other mother-waters which we examined showed a like wealth in lithium compounds.

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clase, sanidine, and adularia may easily be distinguished in this way from albite, oligoclase, Labradorite, and anorthite. In order to detect traces of potassium, vanishingly small, we need to heat to a feeble incandescence the silicate, with a large excess of fluoride of ammonium, in a platinum crucible and introduce the residue into the flame on a platinum wire. In this way we find that almost every silicate contains potassium. The lithium salts disturb the reaction but little. Thus, for example, it is only necessary to hold the ash end of a cigar in the flame before the slit, in order to produce at once very distinctly the yellow line of the sodium and the two red ones of potassium and lithium, the last metal being scarcely ever absent in tobacco ash.

STRONTIUM.

The spectra of the alkali earths are not so simple as those of the alkalis. That of strontium is characterized, particularly, by the absence of green bands. Eight lines of the same are quite remarkable namely six red, one orange and one blue. The orange line *Sr a* which appears close to the sodium line toward the red, the two red lines *Sr β*, *Sr γ* and finally the blue line *Sr δ* are the most important in their position and intensity. In order to test the sensibility of the reaction we heated quickly in a platinum dish, over a large flame, an aqueous solution of chloride of strontium of known concentration until the water was evaporated and the dish began to glow. The salt then began to decrepitate into microscopic particles which were thrown into the air in the form of white smoke. A weighing of the salt residue in the dish showed that in this way 0.077 grams of chloride of strontium had passed out into the 77,000 grams' weight of air of the room in form of a fine dust. After the air of the room had been thoroughly mixed, by means of an open umbrella moved rapidly about, the characteristic lines of the strontium spectrum were very beautifully outlined. We can according to this experiment estimate the amount of chloride of strontium perceptible at $\frac{1}{1000000}$ th of a milligram.

The chlorine and the other haloid compounds of strontium give the most distinct reaction. Strontium hydrate and carbonate of strontium show them much more feebly; the sulphate

still less distinctly; the compounds, with the non-volatile acids, the weakest or not at all. We must therefore introduce into the flame, first, the bead for testing by itself, and then again, after previously moistening with hydrochloric acid. If we assume sulphuric acid in the bead, we must hold it some moments in the reducing part of the flame before moistening with hydrochloric acid, in order to transform the sulphate into the sulphide which is decomposed by hydrochloric acid. To detect strontium in compounds of silicic, phosphoric, boracic or other non-volatile acids we proceed best in the following manner: for fusing with carbonate of sodium a conical spiral of platinum wire is used instead of a platinum crucible. The same is made white hot in the flame and dipped into dry fine pulverized carbonate of sodium which, when possible, contains enough water so that the necessary quantity of the salt remains hanging to the same on the first immersion. Fusion can be effected in this spiral much quicker than in the platinum crucible, since the mass of the platinum heated is small and the salt to be fused comes into immediate contact with the flame. If we transform the fine pulverized substance to be tested into the glowing fluid soda by means of a small platinum spatula, and maintain it in a glowing state for a few minutes, we need only to knock the spiral, inverted with its vertex upward, on the edge of the lamp stand in order to obtain the contents of the same in the form of a large solidified bead. We then cover the bead with a sheet of writing paper and press it by means of an elastic knife blade, which we also use after removing the paper, in order to reduce the mass still farther to the finest powder. This is collected on the edge of a plate slightly tilted and carefully covered with hot water which is allowed to flow backwards and forwards over the substance, heaped up by gentle tipping of the plate and finally, the fluid, remaining over the sediment, is decanted. It is easy, by repeated heating of the plate, to draw off the soluble salt after several repetitions of this process without stirring up the sediment and losing an appreciable amount of the same. If instead of water we use a common salt solution, the operation may be conducted more quickly and certainly. The residue contains the strontium as carbonate, of which a few tenths of a

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milligram, moistened with a little hydrochloric acid on a platinum wire, give a brilliant reaction. In this way, without platinum crucible, mortar, evaporating dish, and without funnel and filter, it is possible to carry out, in a few minutes, all the necessary operations of fusing, powdering, digesting and washing.

The reaction of potassium and sodium is not affected by the presence of strontium. The lithium reaction takes place along with the three mentioned with perfect distinctness, if the quantity of lithium is not too small with respect to that of the strontium. The lithium line *Li a* then appears as a narrow intensely red and sharply defined band upon the weaker red background of the broad strontium band *Sr β* .

CALCIUM.

The spectrum of calcium can be immediately distinguished at the first observation from the four spectra already considered in that a very characteristic and intense line *Ca β* is present in the green. Also a second not less characteristic feature is the very brilliant orange line *Ca a* which lies considerably farther toward the red end of the spectrum than the sodium line *Na a* and the orange line of strontium *Sr a*. By burning a mixture of calcium chloride, chlorate of potassium and milk sugar we obtain a smoke whose reaction is approximately of the same sensibility as that of the fumes from the chloride of strontium under the same conditions. It follows from an examination made in this way that $\frac{1}{100000}$ of a milligram of calcium chloride can be detected easily and with absolute certainty. Only the calcium compounds, volatilized in the flame, show this reaction, and the more volatile they are the more distinct it is. Chloride of calcium, iodide of calcium, and bromide of calcium are best in this respect. Sulphate of calcium gives a spectrum only after it has become basic but then very brilliantly and long continued. In the same way the reaction of the carbonate becomes distinct after the acid has been driven off.

Compounds of calcium with non-volatile acids remain indifferent in the flame, but if they are attacked by hydrochloric acid, the reaction may be easily obtained in the following way:

we introduce a few milligrams, or perhaps only a few tenths of a milligram, of the finely pulverized substance on the flat platinum ring, somewhat moistened, into the less heated portion of the flame until the powder is frittered without being melted. If we allow a drop of hydrochloric acid to fall on the ring the greater part of it will remain hanging. If we pass this drop before the slit of the spectroscope into the hottest part of the flame it volatilizes without boiling on account of its spheroidal condition. If during the volatilizing of the drop we look into the telescope there appears at the instant when the last portion of the fluid has been evaporated a brilliant calcium spectrum which flashes out but for a moment with a small amount, but continues a longer or a shorter time with considerable quantities of metal.

Only in silicates which are attacked by hydrochloric acid can the calcium be found in this way; in silicates which are not attacked by hydrochloric acid the test is best obtained in the following way:—a few milligrams of the substance to be tested are pulverized as fine as possible and placed on a flat platinum crucible cover with about a gram of half-dissolved fluoride of ammonium and the cover held in the flame until it volatilizes the fluoride of ammonium. We moisten the salt residue remaining on the cover with one to two drops of sulphuric acid, and drive off the excess of the same by gently heating over the flame. If the residue of the sulphates now remaining on the cover be scraped together with the finger-nail or a spatula and about a milligram of the same be introduced into the flame by means of a wire, we obtain, if *K*, *Na* and *Li* are present, the characteristic reaction of these three bodies simultaneous or successively. If calcium and strontium be also present their spectra usually first appear after *K*, *Na* and *Li* have been vaporized. The reaction of these metals fails with weak contents of calcium and strontium; we obtain it, however, immediately if we introduce the wire for a few moments into the reducing part of the flame, moisten it with hydrochloric acid, and bring it again into the flame.

All these tests, as the heating of it alone, or with hydrochloric acid, the treatment with ammonium fluoride alone, or with sulphuric and hydrochloric acid, provide the mineralogist

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and still more the geologist with a series of highly simple tests for determining many substances occurring in nature even in the smallest particle, such, for example, as the minerals so similar to one another, consisting of double silicates, containing lime, with a certainty which is scarcely attainable with an abundant supply of material by means of an extended and protracted analysis. Some examples will illustrate this best.

1. A drop of sea-water evaporated on a platinum wire showed a strong sodium reaction, and after volatilizing the chloride of sodium a weak calcium reaction which, by moistening the wire with hydrochloric acid, became for a moment very brilliant. If we treat a few decigrams of the residue of sea-water, in the way described for lithium, with sulphuric acid and alcohol we easily obtain the reaction of potassium and lithium. The presence of strontium in sea-water can be observed best in the boiler crusts of steamships. The filtered hydrochloric acid solution of the same leaves, on evaporation and solution in the smallest quantity of alcohol, a dull yellow coloring from the basic iron salt which is deposited after some days and collected on a filter and washed with alcohol. The filter burnt on a fine platinum wire gives, along with the calcium line, a complete and bright strontium spectrum.

2. Mineral waters often show at once the potassium, sodium, lithium, calcium, and strontium reactions. For example, if we introduce a drop of Durkheim or Krauznach mineral water into the flame we obtained the lines $Na\alpha$, $Li\alpha$, $Ca\alpha$, and $Ca\beta$. If we use instead of the mineral water a drop of the mother liquid the same lines appear with great brilliancy. In proportion as the chloride of sodium and lithium are volatilized and the chloride of calcium has become more basic, the characteristic lines of the strontium spectrum gradually develop themselves and, becoming brighter, finally are seen in all their extent. We obtain here also, by a mere glance at a single drop vaporized in the flame, the complete analysis of the mixture of five substances in a few moments.

3. The ash of a cigar moistened with some HCl and held in the flame gives the lines $Na\alpha$, $K\alpha$, $Li\alpha$, $Ca\alpha$, $Ca\beta$.

4. Potash glass of a combustion tube gave, both with and without hydrochloric acid, $Na\alpha$ and $K\alpha$, and treated with

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fluoride of ammonium and sulphuric acid $Ca\alpha$, $Ca\beta$ and traces of $Li\alpha$.

5. Orthoclase from Baveno gives either alone or with hydrochloric acid only $Na\alpha$ with traces of $K\alpha$ and $Li\alpha$; with fluoride of ammonium and sulphuric acid the intense line $Na\alpha$, $K\alpha$ and somewhat less distant $Li\alpha$. After volatilizing the constituents thus observed the bead introduced, into the flame with HCl , gives only a scarcely distinguishable flash of the lines $Ca\alpha$ and $Ca\beta$. The residue remaining on the platinum wire after this test showed, when moistened with cobalt solution and heated, the characteristic color of alumina. If we employ the well-known reaction of silicic acid also it follows from this examination, made in a few minutes, that the orthoclase from Baveno contains silicic, alumina, potash with traces of soda, lime and lithia whilst every trace of baryta and strontia fail.

6. Adularia from the Gotthard conducted itself quite similar to the orthoclase from Baveno only that the lithium reaction failed entirely and the calcium reaction nearly so.

7. Labradorite from St. Paul gives, by itself, only the sodium line $Na\alpha$ and not the calcium spectrum. But the sample moistened with hydrochloric acid gives the calcium lines $Ca\alpha$ and $Ca\beta$ very brilliantly. With the test by means of fluoride of ammonium we still obtain a weak potassium reaction and very faint traces of lithium.

8. Labradorite from the Diorite of Corsica comported itself similarly only that the traces of the lithium reaction were wanting.

9. Mosanderite from Brevig and Tscheffkinite from the Ilmen mountains gave by itself only the sodium reaction, but the calcium line $Ca\alpha$ and $Ca\beta$ when treated with hydrochloric acid.

10. Melinophane from Lamoe gave by itself only $Na\alpha$ but with hydrochloric acid $Ca\alpha$, $Ca\beta$ and $Li\alpha$.

11. Scheelite and Sphene gave, on treatment with hydrochloric acid, the very brilliant calcium reaction.

12. If small quantities of strontium are present with calcium we employ the line $Sr\delta$ most advantageously to detect the former. By means of the same it is easy to detect a small content of strontium in very many sedimentary limestones. $Na\alpha$, $Li\alpha$ $K\alpha$ particularly $Li\alpha$ are shown immediately on heating the

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limestone in the flame. Those minerals, converted into calcium chloride by hydrochloric acid and introduced into the flame in this form, give the same lines and besides frequently the line *Sr δ* quite distinctly. But this appears only for a short time and most distinctly whilst it is being developed in the course of the volatilization in the flame and shortly before the fading out of the calcium spectrum.

In this way the lines *Na α*, *Li α*, *K α*, *Ca α*, *Ca β*, *Sr δ* were found in the following limestones:—

Silurian limestone¹ from Kugelbad near Prague,
Shell limestone from Rohrbach near Heidelberg,
Lias limestone from Malsch in Baden,
Chalk from England.

The following limestones showed the lines *Na α*, *Li α*, *K α*, *Ca α*, *Ca β*, without the blue strontium line:—

Marble from the granite of Auerbach,²
Devonian limestone from Gerolstein in the Eifel,
Carboniferous limestone from Planitz in Saxony,
Dolomite from Nordhausen in the Hartz,
Jura limestones from the Streitberg in Franconia.

We now see from these few experiments that extended and careful spectral analysis of the lithium, potassium, sodium, and strontium content of various limestone formations are of the greatest geological interest with respect to their order of formation and their local disposition and may possibly lead to unexpected conclusions on the nature of the earlier ocean and sea basins in which the formation of these minerals took place.

BARIUM.

The spectrum of barium is the most complicated of the spectra of the alkalis and alkaline earths. It is distinguished at the first glance from those heretofore examined by

¹ The lithium line could not be detected with certainty in this class of minerals, the line *Sr δ* on the contrary was very strong.

² By means of the experiment with alcohol above described enough nitrate of strontium was obtained from twenty grams of marble to produce a bright and complete spectrum of strontium. Whether the remaining limestones treated in this way show a strontium content we have not investigated.

the green lines $Ba\alpha$ and $Ba\beta$, which exceed all the others in brilliancy, appearing first and disappearing last in weak reactions. $Ba\gamma$ is less distinct but is still always to be treated as a characteristic line. The relatively great extension of its spectrum is the reason why the spectral reaction of the barium compounds is somewhat less delicate than those of the substances heretofore examined. 0.3 grams of chlorate of barium burned in our room with milk sugar gave, after the air had been thoroughly mixed by moving an open umbrella, the line $Ba\alpha$ most distinctly, for a long time. We may therefore conclude from a calculation made similar to that for sodium, that the reaction will show, with perfect distinctness, not less than $\frac{1}{10000}$ th of a milligram.

Chloride, bromide, iodide, and fluoride of barium, the hydrated oxide, the sulphate, and the carbonate, give the reaction most markedly and can therefore be determined by immediate heating in the flame.

Silicates decomposable by hydrochloric acid containing barium give the reaction, if, as indicated in the case of lime, they are introduced into the flame with a drop of hydrochloric acid. Thus, for example, barytharmotome treated in this way gives the line $Ca\alpha$ $Ca\beta$ along with the lines $Ba\alpha$, $Ba\beta$.

Compounds of barium with non-volatile acids, which are indifferent with or without hydrochloric acid in the flame, we may fuse best, in the way given for strontium, with carbonate of sodium and then test the carbonate of barium thus obtained. If in such compounds Ca , Ba and Sr occur together in very unequal amounts, we dissolve in a drop of sulphuric acid the carbonates obtained by fusion and extract the salt with alcohol from the evaporated residue. The residue then contains only barium and strontium both of which may be easily detected if they do not occur in too unequal quantities. When it is desired to test for the smallest traces of Sr or Ba , we transform the residue, by heating with sal ammoniac, into chlorides, from which the chloride of strontium can be easily extracted in a sufficiently concentrated state for detection by means of alcohol. If neither of the substances to be tested is present in very small quantities all such methods of separation are quite unnecessary, as the following experiment shows:—a mixture of sodium, potassium,

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lithium, calcium, strontium, and barium chlorides which contained $\frac{1}{10}$ th of a milligram of each of these six substances at the most, was introduced into the flame and observed. At first the brilliant sodium line $Na\alpha$ appeared on the background of a weak continuous spectrum. As soon as this began to fade away, the sharply defined brilliant red line of lithium $Li\alpha$ appeared and on the same side of the sodium line, still farther away, the faint potassium line $K\alpha$ whilst the barium lines $Ba\alpha$ and $Ba\beta$ appeared very distinctly in their characteristic position and peculiar shade. Whilst the compounds of potassium, lithium, and barium were slowly volatilized their lines faded away, or vanished again gradually in succession until, after a few minutes, the lines $Ca\alpha$ $Ca\beta$ and $Sr\alpha$ $Sr\beta$ $Sr\gamma$ $Sr\delta$ became visible out of the less and less prominent lines of strontium, as from a dissolving view, in all their characteristic form, shade and position, and then faded away and entirely vanished after a very long time.

The absence of any one or more of these components could be instantly detected, in the observation, by the absence of the corresponding lines.

For those who have become familiar with the individual spectra by repeated observation, an accurate measurement of the individual lines is unnecessary; their color, their relative position, their characteristic definition and shade, the gradation in their brilliancy, are criterions which are quite sufficient for definite recognition even for the inexperienced. These characteristics may be compared with the distinguishing features which the various precipitates present in their outward appearance, which we use as a reaction test. Just as the character of a precipitate determines whether it be gelatinous, pulverulent, flocculent, granular or crystalline, so also the spectral lines indicate their characteristics in the sharpness of their edges, in the shading off uniformly or irregularly on one or both sides, or in their broader or narrower appearance, as the case may be. And just as we use only those precipitates in analysis which can be produced by the greatest possible dilution, so we also use in spectrum analysis for this purpose only those lines which require for their production the smallest amount of the

substance and only a moderately high temperature. In such characteristics therefore the two methods are quite similar. On the contrary spectrum analysis furnishes, in the color phenomena used in the reaction, a property which gives it unlimited advantage over every other method of analysis. Most of the precipitates which are used for the detection of substances are white and only a few colored. Further the tint of the latter is not very constant and considerably differentiated according to the greater or less condensed state of the precipitate. Often the smallest mixture of a foreign substance is sufficient to obliterate completely a characteristic color. Small differences of color of the precipitate can therefore be no longer used as a chemical test. In spectrum analysis, on the contrary, the colored bands remain undisturbed by such foreign influences and are undisturbed by the presence of other bodies. The positions which they have in the spectrum determine a chemical characteristic which is of as unalterable and fundamental a nature as the atomic weight of the substance, and therefore, permits us to determine it with an almost astronomical exactness. What, however, gives to the spectral analytical method a peculiar importance, is the fact that it almost infinitely exceeds the limits to which chemical analysis of matter has heretofore reached. It predicts for us the most valuable conclusions on the distribution and arrangement of geological substances in their formation. Already the few investigations, which this memoir contains, lead to the unexpected conclusion that not only potassium and sodium but also lithium and strontium must be counted among the substances of the earth most widely scattered, though only in minute quantities.

Spectrum analysis will also play a not less important part in the discoveries of elements not yet detected. For if there are substances which are so sparsely scattered in nature that the methods of analysis heretofore used in observing and separating them fail, we may hope to detect and determine many of them, by the simple examination of their spectra in flames, which would escape the ordinary method of chemical analysis. That there are actually such elements heretofore unknown we have already had an opportunity of showing. We believe that we shall be able yet to declare with absolute certainty, supported

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by the unquestioned results of spectral analytical methods that besides potassium, sodium and lithium, there is still a fourth metal belonging to the alkali group which will give quite as characteristic a spectrum as lithium—a metal which shows, with our spectral apparatus, only two lines, a weak blue line, which almost coincides with the strontium line $Sr\delta$ and another blue line, which lies only a little farther toward the violet end of the spectrum, rivaling in intensity and distinctness the lithium line.

On the one hand spectrum analysis offers, as we believe we have already shown, a means of wonderful simplicity for detecting the slightest traces of certain elements in terrestrial substances, and on the other, it opens up to chemical investigation a field heretofore completely closed, which extends far beyond the limit of the earth even to our solar system itself. Since, by the analytical method under discussion, it is sufficient simply to see the gas in an incandescent state in order to make an analysis, it at once follows that the same is also applicable to the atmosphere of the sun and the brighter fixed stars. A modification with respect to the light which the nucleus of these heavenly bodies radiate must be introduced here. In a memoir “On the Relation between the Emission and the Absorption of Bodies for Heat and Light”¹ one of us has proven, by theoretical considerations, that the spectrum of an incandescent gas is *reversed*, that is, that the bright lines are transformed into dark ones when a source of light of sufficient intensity, which gives a continuous spectrum, is placed behind the same. From this we may conclude that the sun’s spectrum, with its dark lines, is nothing else than the reversal of the spectrum which the atmosphere of the sun itself would show. Hence the chemical analysis of the sun’s atmosphere requires only the examination of those substances which, when brought into a flame, produce bright lines which coincide with the dark lines of the solar spectrum.

In the article mentioned, the following examples are given as experimental proof of the theoretically deduced law referred to:

¹ Kirchhoff, Pogg. Ann. Vol. CIX p. 275. See previous memoir.

The bright red line in the spectrum of a flame in which a bead of chloride of lithium is introduced is changed into a black line when we allow full sunlight to pass through the flame.

If we substitute for the bead of lithium one of sodium chloride, the dark double line *D* (which coincides with the bright sodium line) shows itself in the sun's spectrum with unusual brilliancy.

The dark double line *D* appears in the spectrum of the Drummond's light if we pass its rays through the flame of aqueous alcohol, into which we have introduced chloride of sodium.¹

It will not be without interest to obtain still further confirmations of this remarkable theoretical law. We may arrive at this by the investigation which will now be described.

We made a thick platinum wire incandescent in a flame and by means of an electric current brought it nearly to its melting point. The wire gave a brilliant spectrum without any trace of bright or dark lines. If a flame of very aqueous alcohol in which common salt was dissolved were introduced between the wire and the slit of the apparatus, the dark line *D* showed itself with great distinctness.

We can produce the dark line *D* in the spectrum of a platinum wire which has been made incandescent by a flame if we merely hold before it a test tube into which some sodium amalgam has been introduced, and then heat it to boiling. This investigation is important, on this account, in that it shows that far

¹ In the March number of the Philosophical Magazine for 1860 Stokes calls attention to the fact that Foucault had made already an observation in 1849 which is similar to that mentioned above. In the examination of the electric arc between two carbon points he observed (1, Institut 1849, p. 45) that in the spectrum the same bright lines were present in the position of the double line *D* of the solar spectrum, and that the dark line *D* of the arc is intensified, or produced, if we allow the rays of the sun or one of the incandescent points to pass through it and then resolve them in the spectrum. The observation mentioned in the text gives the explanation of this interesting phenomena already observed by Foucault eleven years before and shows that the same is not influenced by the peculiarity of the electric light, which is still, from many points of view, so enigmatical, but arises from a sodium compound which is contained in the carbon and is transformed by the current into incandescent gas.

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below the point of incandescence of sodium vapor, its absorbent effect is exercised exactly in the same parts of the spectrum as with the highest temperatures which we are able to produce and at which that of the solar atmosphere exists.

We have been able to reverse the bright lines of the spectra of *K*, *Sr*, *Ca*, *Ba* by the employment of sunlight and mixtures of the chlorates of these metals with milk sugar. Before the slit of the apparatus a small iron trough is placed; into this the mixture was introduced, and the full sunlight passed along the trough to the slit and the mixture ignited on one side by an incandescent wire. The telescope was set with the intersection of its cross hairs, which were mounted at an acute angle with one another, on the bright line of the flame spectrum, the reversal of which was to be tested; the observer concentrated his attention on this point in order to judge whether at the moment of ignition a dark line was visible, passing through the intersection of the cross hairs. In this way it was quite easy with the proper proportion of the mixture, to be burnt, to establish the reversal of the lines *Ba_α* and *Ba_β* and the line *K_β*. The last of these coincided with one of the most distinct lines of the solar system, although not indicated by Fraunhofer; this line appeared much more distinctly at the moment of ignition of the potash salt than otherwise. In order to observe the reversal of the bright lines of the strontium spectrum in the way described, the chlorate of strontium must be dried in the most careful manner; a slight trace of moisture causes the sun's rays to be weakened and produces the positive spectrum of strontium on account of the flame becoming filled with salt particles which have been spattered about by the ignition.

We have limited ourselves in this memoir to the investigation of the spectra of the metals of the alkalis and alkaline earths, and these only in so far as was necessary for the analysis of terrestrial matter. We reserve for ourselves the further extension of these investigations which are desirable in connection with the analysis of terrestrial substances and the analysis of the atmospheres of the stars.

Heidelberg, April, 1860.

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BIOGRAPHICAL SKETCH.

ROBERT WILHELM BUNSEN was born in Göttingen March 15, 1811. He received his doctor's degree in 1830 and became private-docent in 1833 in that University. In 1836 he became Professor of Chemistry in the Polytechnic School at Cassel and in 1838 accepted a similar position in the University of Marburg. In 1851 he went to Breslau and the following year to Heidelberg, where he remained until his death. Both as a teacher and as an investigator, he was one of the most eminent of his generation, making many important contributions to both Physics and Chemistry. His spectroscope, photometer, calorimeter, gas burner, filter pump, battery, etc., on the one hand, and his early contributions to organic chemistry, the methods of gas analysis, photochemical action, etc., on the other, illustrate the versatility of his genius. His work in connection with his colleague, Kirchhoff, resulted in one of the most brilliant achievements of the century,—the application of the spectroscope to the analysis of terrestrial substances,—which revealed at once several new elements and showed the common constitution of all bodies in the stellar system. His final contribution was made in 1887 after an illustrious scientific career of nearly sixty years. During his last years he was a familiar figure on the streets of Heidelberg, in which city he died Aug. 15, 1899.

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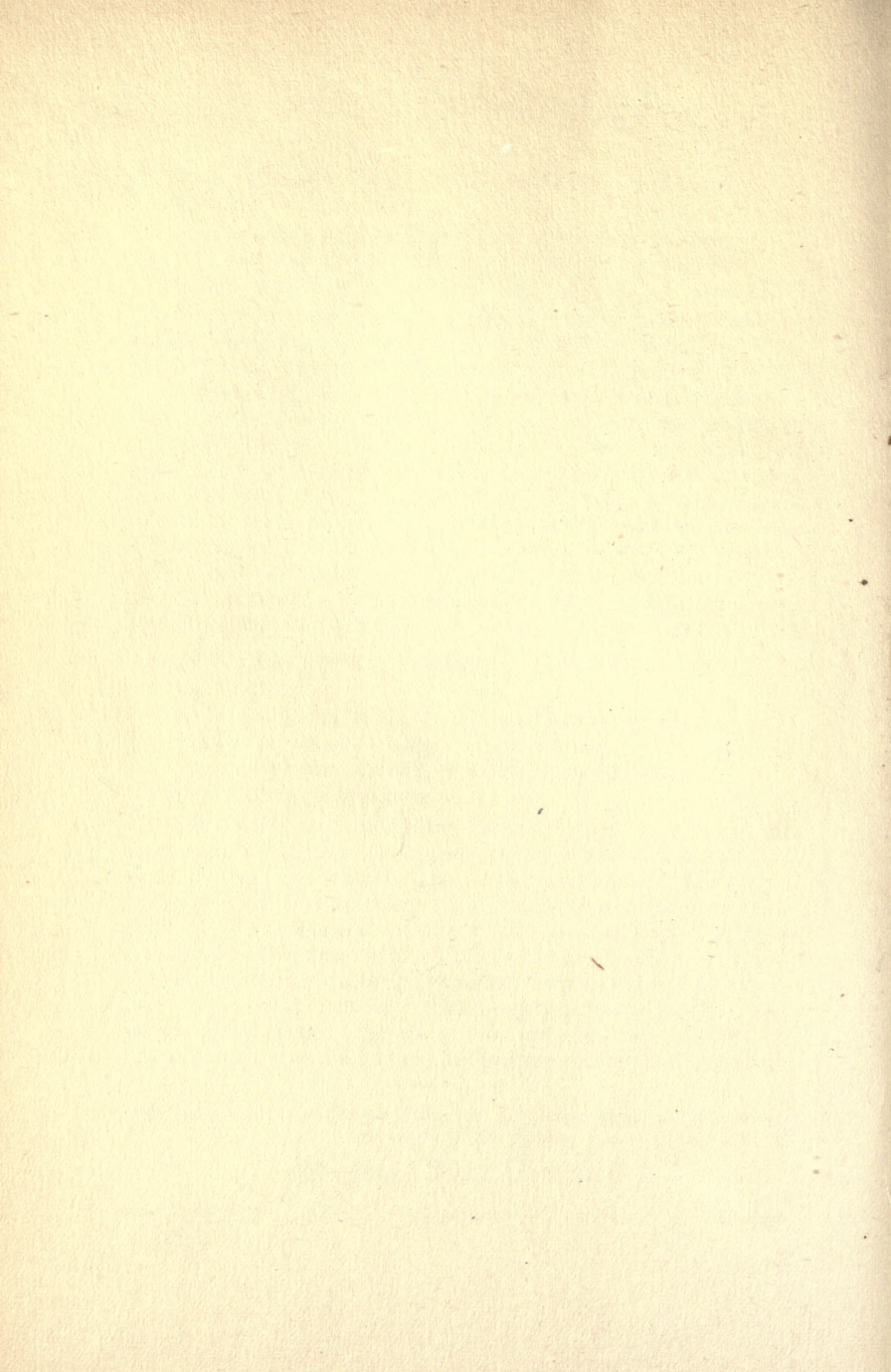
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