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ART. I.—1. *Researches on the Solar Spectrum, and the Spectra of the Chemical Elements.* By G. KIRCHHOFF, Professor of Physics in the University of Heidelberg. Translated by HENRY E. ROSCOE, B.A., Professor of Chemistry in Owens College, Manchester. Cambridge and London: 1862.

2. *Chemical Analysis by Spectrum Observations.* By Professors BUNSEN and KIRCHHOFF. Memoirs I. & II. POGGENDORFF'S Annalen (Philosophical Magazine, 4th Series, vol. xx. p. 89., vol. xxii. p. 1.). London, Dublin, and Edinburgh.

IT is unnecessary to insist, at the present day, upon the incalculable value of discoveries in natural science, however abstruse they may be, or however far-distant may appear their practical application. If we put aside for the moment that highest of all intellectual gratifications afforded by the prosecution of truth in every form, the perception of which is one of the chief distinctions of human from mere brute life, and if we look to the results of scientific discovery in benefiting mankind, we find so many striking examples of the existence of truths apparently altogether foreign to our every-day wants, which suddenly become points of great interest to the material prosperity and the moral advancement of the race, that we are less apt to utter the vulgar cry of 'cui bono' respecting any scientific discovery; and if we are not advanced enough to love science for the sake of her truth alone, we at least respect her for the sake of the power she bestows. Not once, but oftentimes in the annals of science, it has turned out that discoveries of the most recondite truths have ere long found their application in the physical structure of the world, and even in the common interests of men; for in the range of scientific inves-

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tigation, it can never be said how near the deepest principle lies to the simplest facts.

A great discovery in natural knowledge, for which no equivalent in direct benefit to mankind has as yet been found, but which nevertheless excites our liveliest interest and admiration, has lately been made in the rapidly advancing science of Chemistry. This discovery, which is one of the grandest and most important of all the recent additions to science, consists in the establishment of a new system of chemical analysis — of a new power to investigate the constitution of matter. This is of so delicate a nature, that, when applied to the examination of the substances composing our globe, it yields most new, interesting, and unlooked-for information. At the same time it is of so vast an application as to enable us to ascertain with certainty the presence in the solar atmosphere — at a distance of 95,000,000 miles — of metals, such as iron and magnesium, well known on this earth, and likewise to give us good hopes of obtaining similar knowledge concerning the composition of the fixed stars. Here, indeed, is a triumph of science! The weak mortal, confined within a narrow zone on the surface of our insignificant planet, stretches out his intellectual powers through unlimited space, and estimates the chemical composition of matter contained in the sun and fixed stars with as much ease and certainty as he would do if he could handle it, and prove its reactions in the test-tube.

How can this result, at first sight as marvellous and impossible as the discovery of the elixir vitæ or the philosophers' stone, be arrived at? How did two German philosophers, quietly working in their laboratory in Heidelberg, obtain this inconceivable insight into the processes of creation? Are the conclusions which they have arrived at logical consequences of bonâ fide observations and experiments — the only true basis of reasoning in physical science — or do they not savour somewhat of that mysticism for which our German friends are famous? Such questions as these will occur to all who hear of this discovery; and it will be our present aim, in reviewing the publications which are placed at the head of this article, to answer these and similar questions, and to show that, far from being mystical, these results are as clear as noon-day, being the plain and necessary deductions from exact and laborious experiment. And here we may express our satisfaction at the change which has occurred within the last few years in the direction given to the powerful intelligence and the indefatigable industry of Germany. The labours of the Germans in physical science have far surpassed in their results those speculative researches

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which had rendered 'German philosophy' the synonym of all that was unintelligible and perplexing: and it is impossible to overrate the services which men like Liebig and Bunsen (the chemist) and Kirchhoff have rendered to mankind. In chemistry, Germany may now be said to take the lead of England, of France, and of Italy: already she has paid an ample contribution to the common stores of human knowledge. It is a remarkable circumstance that although for several years the once productive fields of German literature have been comparatively barren, or have at least presented us with no work of the highest order, the supply of German works on natural science is immense, and the quality of these works excellent.

The only channel through which we on the earth can obtain information of any kind whatever concerning the sun and stars, consists in the vivifying radiance which these luminaries pour forth into surrounding space. The light and heat which we receive from the sun not only supply the several varieties of force which we find in action upon the surface of the earth, thus rendering the whole human family truly children of the sun; but a knowledge of their nature enables us to ascertain the chemical composition of those far-distant bodies upon which the existence of our race so intimately depends. The examination of the nature of sunlight and starlight has led to the foundation of a science of stellar chemistry; and it is likewise upon the examination of the light given off by terrestrial matter, when through heat it becomes luminous, that the new method of spectrum analysis is founded—a method so delicate as to enable the analyst to detect with ease and certainty so minute a quantity as the $\frac{1}{180,000,000}$ part of a grain of substance.

The world owes to the great Newton its first knowledge of the nature of sunlight. In 1675 Newton presented to the Royal Society his ever-memorable treatise on Optics; and amongst the numerous important discoveries there disclosed and recorded, was one demonstrating the constitution of white light. He describes what he observed when he passed a beam of sunlight, from a hole in the shutter of a darkened room, through a triangular piece of glass called a prism. He noticed that, instead of a spot of white light corresponding to the hole in the shutter, a bright band of variously coloured lights, showing all the tints of the rainbow, was thrown on the wall of his room. Newton concluded that these colours were no peculiar effect of the prism, because a second prism did not produce a fresh alteration of the light. He showed that the white light is thus split up into its various constituent parts; and by bringing all these coloured rays together in the eye, and again obtaining the white image of the hole in the shutter, he proved that the kind of light which produces on the eye the sensation we term *whiteness*, is in reality made up of an infinite number of differently coloured rays.

The coloured band thus obtained by Newton did not, however, reveal to him all the characteristic beauties of solar light, because in his spectrum the tints were created by the partial superposition of an infinite number of differently coloured images of the round hole through which the light came. It was not until the year 1802 that Dr. Wollaston, by preventing the different coloured lights from overlapping, and thus interfering with each other, discovered that great peculiarity in solar light which has led to such startling discoveries in the composition of the sun itself. Dr. Wollaston noticed, when he allowed the sunlight to fall through a narrow slit upon the prism, that a number of dark lines cutting up the coloured portions of the spectrum, made their appearance. These dark lines, or spaces, of which Wollaston counted only seven, indicate the absence of certain distinct kinds of rays in the sunlight; they are, as it were, shadows on the bright background.

It is, however, to the celebrated German optician Fraunhofer, that we owe the first accurate examination of these singular lines. By a great improvement in the optical arrangements employed, Fraunhofer, re-discovering these lines, was able to detect a far larger number of them in the solar spectrum than had been observed by Wollaston. He counted no less than 590 of these dark lines, stretching throughout the length of the spectrum from red to violet, and in the year 1815 drew a very beautiful map of them, some of the most important of which he designated by the letters of the alphabet. Fraunhofer carefully measured the relative distances between these lines, and found that they did not vary in sunlight examined at different times. He also saw these same dark fixed lines in reflected as well as direct solar light; for on looking at the spectrum of moonlight and of Venus-light, the same lines appeared quite unaltered in position. But he found that the light of the fixed stars was not of the same kind as direct or reflected sunlight, as the spectra of the starlight contained dark lines entirely different from those which are invariably seen in the solar spectrum. From these observations Fraunhofer, so early as 1815, drew the important conclusion that these lines, let them be caused by what they may, must in some way or other have their origin in the sun. The explanation of the production of these lines was reserved for a subsequent time; but

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Fraunhofer opened the inquiry, and all his conclusions have been borne out by recent and more elaborate investigations.

Since the time of Fraunhofer our knowledge of the constitution of the solar spectrum has largely increased. Professor Stokes, in his beautiful researches on Fluorescence, has shown that similar dark lines exist in that part of the spectrum extending beyond the violet, which require special arrangements to become visible to our eyes; and Sir David Brewster and Dr. Gladstone have mapped with great care about 2000 lines in the portion of the spectrum from red to violet.

But it is to Kirchhoff, the Professor of Physics in the University of Heidelberg, that we are indebted for by far the best and most accurate observations of these phenomena. In place of using one prism, as Fraunhofer did, Kirchhoff employed four prisms of most perfect workmanship, and thus enjoyed the advantage of a far greater dispersion, or spreading out, of the different rays than the Munich optician had obtained. The lines were observed through a telescope having a magnifying power of 40, and when the whole apparatus was adjusted with all the accuracy and delicacy which the perfection of optical instruments now renders possible, Kirchhoff saw the solar spectrum with a degree of minute distinctness such as had never before been attained; and of the beauty and magnificence of the sight thus presented those only who have been eye-witnesses can form any idea.

Kirchhoff's purpose was not merely to observe the fine vertical dark lines which in untold numbers crossed the coloured spectrum, stretching from right to left. He wished to measure their relative distances, and thus to map them, exactly as the astronomer determines the position of the stars in the heavens, and the surveyor triangulates and marks out the main features of a country; so that future wanderers in this new field may find fixed and well-recognised points from which to commence their own excursions. Professor Kirchhoff is far from thinking that his measurements, delicate and numerous though they be, have exhausted the subject. The further we penetrate into the secrets of nature, the more we find there remains to be learnt. He saw whole series of nebulous bands and dark lines which the power of his instrument did not enable him to resolve; and he thinks that a larger number of prisms must be employed to effect this end. He adds—'The resolution of these 'nebulous bands appears to me to possess an interest similar to 'that of the resolution of the celestial nebulæ; and the investi-'gation of the spectrum to be of no less importance than the 'examination of the heavens themselves.' True, indeed, does this appear, when we learn that it is by the examination of these lines that we can alone obtain the clue to the chemical composition of sun and stars!

The exact measurement of the distances between the lines was made by moving the cross wires of the telescope from line to line by means of a micrometer screw with a finely divided head, and reading off the number of divisions through which the screw had to be turned. The breadth and degree of darkness were also noticed, and thus the lines were mapped. In order to give a representation in the drawing of the great variety of the shade and thickness of the lines, they were arranged according to their degree of blackness, and drawn of six different thicknesses. First, the darkest lines were drawn with thick black Indian ink; the ink was then diluted to a certain extent, and the lines of the next shade drawn, and so on to the lightest series. As soon as a portion of the spectrum had been drawn in this manner, it was compared with the actual spectrum, and the mistakes in the breadth and darkness of the lines, as well as in their position, corrected by fresh estimations, and the drawing made anew. A second comparison and another drawing were then made, and this process repeated until all the groups of lines appeared to be truthfully represented. Copies from the same lithographic stones accompany the English edition of the memoir as are appended to the original, and these are masterpieces of German artistic skill. They are printed on six different stones, with ink of six different tints, and reproduce with marvellous fidelity the appearance which the solar spectrum presents when viewed through the magnificent Heidelberg instrument.

These maps extend, however, over only one-third part of the visible portion of the solar spectrum, and it will, we fear, be long before the other two-thirds are completely surveyed, as the following note, telling of the failing eyesight of the ingenious observer, touchingly explains:—'My drawing,' he says, 'is 'intended to include that portion of the spectrum contained 'between the lines A and G. I must, however, confine myself 'at present to the publication of a part only of this, as the re- 'mainder requires a revision, which I am unfortunately unable 'to undertake, owing to my eyes being weakened by the con- 'tinual observations which the subject rendered necessary.'

Before it can be understood how these dark lines reveal the chemical composition of the solar atmosphere, it must be shown how the constitution of terrestrial matter can be ascertained by the examination of the nature of the light which such heated matter emits. That certain substances, when heated or burnt,

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give off peculiar kinds of light, has long been known; and this fact has been made use of by the chemist to distinguish and detect such substances. Thus compounds of the earth strontia, when burnt with gunpowder, produce the peculiar mixture well known as the 'red fire' of the pyrotechnist; the salts of baryta give colour to the green fires of the stage; and we all see in the Christmas game of snap-dragon that a handful of salt (chloride of sodium) thrown into the dish imparts to the flame a yellow colour.

This property of substances to give off certain kinds of light was formerly only known to hold good for a few bodies; but the progress of science has taught us that it is not confined to one substance, but is applicable to all. We only require to examine a body under the proper conditions, in order to see that when heated it emits a peculiar and characteristic kind of light; so that each elementary substance — that is, a substance which has not been split up, or decomposed, or out of which no two or more bodies differing in their properties have been obtained—whether it be a gas, a solid, or a liquid, may by heating be made to emit a kind of light peculiar to itself, and different from that given off by any other substance. Here, then, is the basis of this new method of spectrum analysis — a science which demonstrates the chemical composition of a body by the colour or kind of light emitted from it when heated. We now only need to know, in order to understand the subject, the proper conditions under which bodies can be made to develope this beautiful property, by help of which their chemical natures can be thus easily investigated, and analysis rendered not only independent of test-tubes, but likewise of distance; for it is clear that so long as light can be seen, it matters not how far removed its source may be. The sole condition which must be fulfilled in order to attain the object, is that the body to be analysed must be in a condition of luminous gas or vapour; for it is only in the gaseous state that each kind of matter emits the light peculiar to itself. It is somewhat difficult at first to understand how a gas or air can be heated until it emits light, and yet familiar instances are not wanting of such a condition of things. Flame, indeed, is nothing else than heated and luminous gas; and in the blue part of the flame of a candle, and in the lambent blue flame which plays on the top of a large fire, we have examples of a truly gaseous body heated until it becomes luminous.

The modes in which the various elements can be best obtained in the condition of luminous gases are very different. For the compounds of the metals of the alkalies and alkaline earths, it

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suffices to bring a small quantity of one of their salts into a flame of a spirit lamp, or into a gas flame. The salt then volatilises, or becomes gaseous; and this vapour, heated to the temperature at which it is luminous, tinges the flame with a peculiar colour. For the compounds of the other metals, such as iron, platinum, or silver, a much higher temperature is needed; whilst for bodies such as air and hydrogen, which are gases at the ordinary temperature, a different mode of manipulation is necessary.

In order to become acquainted with the exact nature of the light which bodies in the condition of luminous gases emit, their light must be examined otherwise than by the naked eye. The same kind of apparatus is used in this investigation which Fraunhofer and Kirchhoff applied to the investigation of solar light; in short, the distinctive qualities of these luminous gases are ascertained by their *spectra.* Then only is it that the full beauty of this property of matter becomes apparent, and the character of each elementary body is written down in truly glowing language — language different for every element, but fixed and unalterable for each one, as to the interpretation of which no variety of opinion can possibly exist.

To Professors Bunsen and Kirchhoff science is mainly indebted for the examination of this hitherto hidden language of nature. These philosophers undertook an investigation of the 'Spectra of the Chemical Elements,' and nobly have they carried out their intention; unfolding a vast store of nature's secrets to the knowledge of mankind, and revealing the existence of much more yet to be learnt in unlimited fields which promise a rich harvest of discovery to the patient and exact inquirer. Seldom indeed has it been the privilege of men in a single discovery to found a science, or to open a subject so pregnant with important results as that of spectrum analysis.

Those alone who are acquainted with the practical details of the science of Chemistry will be able fully to appreciate the grand change which the introduction of this new method effects in the branch of their science devoted to analysis. Qualitative analysis thereby undergoes a complete revolution; the tedious operations of precipitation and filtration must now be superseded by the rapid observation of the spectra of the coloured flames by which the presence of the most minute trace of the substance — far too small to be found by the older and coarser methods — can be surely and clearly detected. Let us endeavour to form an idea of the appearance of the peculiar spectra thus obtained; the most complete or eloquent description must, however, fail to give more than a bare idea of the reality.

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In the first place, if we look through the telescope of Kirchhoff's instrument, having placed a flame coloured yellow by a sodium compound in front of the slit through which the light falls on to the prisms, and thence into the telescope, we shall see the spectrum of sodium. We notice that it consists simply of two very fine bright yellow lines placed close together, all the rest of the field being perfectly dark. On investigation we find that all the compounds of the metal sodium give these two lines, and no other substance is met with in whose spectrum these lines occur. So excessively delicate is this indication of sodium — that is, so small a quantity of sodium salt suffices to bring forth a flash of these bright lines—that we discover sodium everywhere; in every particle of dust; in the motes visible in the sunbeam. We cannot touch any substance without imparting to it some soda salt from our hands. Hence it appears that Professor Bunsen was easily able to detect the presence of $\frac{1}{180,000,000}$ part of a grain of soda; and we learn without astonishment that common salt, derived from the ocean which covers two-thirds of the earth's surface, is always present in the atmosphere in a very finely divided solid form, which doubtless produces most important effects on the animal œconomy, and probably on all the phenomena of life.

If a small quantity of a potash salt, instead of the soda, be placed in the flame, it will be tinged purple; the potash spectrum consists of a portion of continuous light in the centre, bounded by a bright red and a bright violet line at either end. This peculiar appearance is alone caused by the compounds of potassium, and is produced by all the salts of this metal. So, too, with each metal we notice peculiar bright coloured bands, or lines, which are so distinct and characteristic that a glance through the telescope reveals, to an experienced eye, the presence of each of the metals of the alkalies and alkaline earths, when they occur or are combined together even in the minutest quantities. For none of these bright lines overlap or interfere with any other; the lines of each metal, when all are present together, appear perfectly distinct. It is a hopeless task to endeavour by words to express the beauty of the phenomena which in this branch of science present themselves to the beholder; as well might we attempt to convey by description, to one who had not witnessed those scenes, the grandeur of the high Alps, or the majesty of the flight of a comet through the heavens. Suffice it to say, with Kirchhoff, that the appearances here noticed 'belong to the most brilliant 'optical phenomena which can be observed.' Professor Bunsen thus describes what he saw when he placed a mixture of the salts of all the metals of the alkalies and alkaline earths into the flame, and observed the spectra thus produced:—

'I took,' he says, 'a mixture, consisting of chloride of sodium, chloride of potassium, chloride of lithium, chloride of calcium, chloride of strontium, chloride of barium, containing at most $\frac{1}{1000}$ part of a grain of each substance. This mixture I put into the flame, and observed the result. First, the intense yellow sodium lines appeared on a background of a pale continuous spectrum; as these began to be less distinct, the pale potassium lines were seen, and then the red lithium line came out, whilst the barium lines appeared in all their vividness. The sodium, lithium, potassium, and barium salts were now almost all volatilised, and after a few moments the strontium and calcium lines came out as from a dissolving view, gradually attaining their characteristic brightness and form.'

The most striking example of the value of this new power of analysis, and of its probable results, is that of the discovery of two new alkaline metals by Bunsen. This distinguished chemist, in examining the spectra of the alkalies contained in the mineral waters of Dürkheim in the Palatinate, observed some bright lines that he had not seen in any other alkalies which he had investigated. He was sure that no other metals but those of the alkalies could be present, because, by well-known chemical processes, he had separated every other kind of metal. Hence he concluded that these new lines indicated the presence of an alkaline metal whose existence had as yet been overlooked. In fact, just as Adams and Leverrier, from the perturbations of the planet Uranus, predicted the existence of Neptune, so Bunsen, from the perturbations seen in the spectra of the alkalies, predicted the existence of a new member of the large family of the elementary bodies. So certain was Bunsen of his method, and so confident was he that his bright lines could not fail him, that, although the weight of substance from which he obtained his result only amounted to the $\frac{1}{1000}$ part of a grain, he hesitated not a moment, but began to evaporate forty tons of the water, in order to get enough material to separate out his new metal, and examine all its chemical relations. No sooner, however, had he obtained more than a mere trace of the new substance, than he found that with it was associated a second new metal. From the forty tons of the water in question Bunsen got only about 105 grains of the chloride of one metal, and 135 grains of the chloride of the other; in such minute quantities do these substances occur! Yet, thanks to the skill and patient industry of the great chemist of Heidelberg, these difficulties were triumphantly overcome, and we now possess a chemical history of these two new metals as complete and well authenticated as that of the commoner alkalies. The names wisely chosen for these substances indicate the nature of their origin, and point out the property by help of which they were discovered. Bunsen calls one of them 'Cæsium,' from *cæsius*, bluish grey, because the spectrum of this metal is distinguished by two splendid violet lines; the other he named 'Rubidium,' from *rubidus* dark red, owing to the presence of two bright red rays at the least refrangible extremity of its spectrum. Since the publication of the discovery of these metals, their salts have been found to be pretty commonly diffused; but, owing to their close resemblance to the compounds of potassium, they were not recognised as separate substances; in fact, had it not been for this new method, we should not have been able to distinguish them from the well-known alkali potash. Cæsium and Rubidium occur in the water of almost every salt spring; and they have likewise been found in the ashes of plants, especially in those of beet-root, so that they must be contained in the soil; but in all these cases the quantity in which they are found is very minute. The mineral lepidolite contains a certain quantity of Rubidium, which now may be obtained by the pound; but Cæsium is still extremely rare.

It is satisfactory to learn that in a similar way the existence of another new metal has been pointed out by Mr. Crookes. This body is characterised by a spectrum containing one bright green band, and has been called 'Thallium.' *

In an article like the present it is impossible to enter minutely into the details of such discoveries, or even to mention more than the most striking points by way of illustration. Enough has, however, been said to show the enormous fertility of this field of research, and to give an idea of the principles upon which the method depends. We anticipate, more especially, important results to the art of medicine from the application of this analytical process to mineral waters, as they are termed, noted for their therapeutic qualities. The composition of these waters, their apparently inexhaustible faculty of reproduction, their modes of affecting the human frame in various states of health or disease, are only known as yet empirically. Yet it is impossible to doubt or deny that waters, like those of Carlsbad, Aix-la-Chapelle, or Bagnères de Luchon, contain certain agents

* This new element has lately been prepared in somewhat larger quantities by M. Lamy from the residues of the Belgian sulphuric acid chambers. He finds that in its specific gravity and outward properties it closely resembles the metal lead, but that it possesses very peculiar chemical characteristics.

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of the most powerful sanative character, which the means of chemical analysis hitherto employed do not appear to have reached. It is extremely probable that the application of spectral analysis to the elements contained in these springs will bring them within the range of accurate medical knowledge, and perhaps extend the resources of medicine itself.

The field of spectrum analysis was not wholly untrodden until it was explored by the two German professors. Even so long ago as 1826, Mr. Fox Talbot, a gentleman whose name is honourably associated with discoveries in that most beautiful of the modern applications of science to art — Photography — made some experiments upon the spectra of coloured flames, and pointed out the advantages which such a method of analysis would possess. Professor Wheatstone, Mr. Swan, Sir David Brewster, and Professor W. Allen Miller in our own country, and Ångström, Plücker, Masson, and others on the Continent, have likewise contributed to our knowledge of this subject; but, whatever may have been done by others for the establishment of the new method, it must be admitted that the names of Bunsen and Kirchhoff will justly go down to posterity as the founders of the Science of Spectrum Analysis; for they first established it on a firm scientific basis, by applying to it the modern methods of exact research.

For the purpose of obtaining the peculiar spectra of iron, platinum, copper, and most of the other metals, these metals must be exposed to a much higher temperature than that of the gas flame, to which they impart no colour. This high temperature is best attained by the use of the electric spark. So great, indeed, is the heat developed by this agent, that a single electric discharge past through a gold wire dissipates the metal at once in vapour. Our illustrious Faraday — the founder of so many branches of electrical science — first showed that the electric spark was produced by the intense ignition of the particles composing the poles; and Professor Wheatstone proved that if we look at the spark proceeding from two metallic poles, through a prism, we see spectra containing bright lines which differ according to the kind of metal employed. 'These differences,' said Wheatstone, writing in 1834, 'are so 'obvious, that any one metal may instantly be distinguished 'from others by the appearance of its spark; and we have here 'a mode of discriminating metallic bodies more ready than a 'chemical examination, and which may hereafter be employed 'for useful purposes.' This has, indeed, turned out to be a true prediction.

The large number of bright lines which are seen in the spark

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spectrum are not all caused by the glowing vapour of the metal forming the poles; a portion of them proceed, as Ångström first pointed out, from the particles of gas or air, through which the spark passes, becoming luminous also, and emitting their own peculiar light. Thus, if we examine the spectrum of an electric spark passing from two iron poles in the air, we see at least three superimposed spectra, one of the iron, one of the oxygen, and a third of the nitrogen of the air.* By help of a little mechanical device, it is easy to distinguish between the air lines and the true metallic lines, and in this way to detect the various metals. So certain and accurate is this method that Professor Kirchhoff has, without difficulty, been able to detect and distinguish the presence of minute traces of the rare metals Erbium and Terbium, as well as Cerium, Lanthanum, and Didymium, when they are mixed together; a feat which the most experienced analyst would find it almost impossible, even after the most lengthened and careful investigation, to accomplish with the older methods.

In endeavouring to form an idea of the present and future bearings of the science of spectrum analysis as applied to the investigation of terrestrial matter, we must remember that the whole subject is as yet in its earliest infancy; that the methods of research are scarcely known; and that speculations as to the results which further experiments will bring forth, are therefore, for the most part, idle and premature. We may, however, express our opinion that a more intimate knowledge of the nature of the so-called elements, if it is to be attained at all, is to be sought for in the relations which the spectra of these substances present; and if a 'transmutation' of these elementary bodies be effected, as is by no means impossible, it will be effected by help of the new science of spectrum analysis. That we shall thus gradually attain a far more accurate knowledge of the composition of the earth's crust than we now possess, is perfectly certain; nor is it less certain, that with the progress of the investigation, other new elementary bodies will be added to our already somewhat overgrown chemical family.

So long ago as 1815, Fraunhofer made the important observation, that the two bright yellow lines which we now know to be the sodium lines, were coincident with, or possessed the same degree of refrangibility as, two dark lines in the solar spectrum called by Fraunhofer the lines D. A similar coincidence was

* The spectra of the permanent gases, as well as those of the other non-metallic elements, have been accurately examined by Professor Plücker, of Bonn.

observed by Sir David Brewster, in 1842, between the bright red line of potassium and a dark line in the solar spectrum called Fraunhofer's A. The fact of the coincidence of these lines is easily rendered visible if the solar spectrum is allowed to fall into the upper half of the field of our telescope, whilst the sodium or potassium spectrum occupies the lower half. The bright lines produced by the metal, as fine as the finest spider's web, are then seen to be exact prolongations, as it were, of the corresponding dark solar lines.

Although the fact of the coincidence of several bright metallic lines with the dark solar lines was well known, yet the exact connexion between the two phenomena was not understood until Professor Kirchhoff, in the autumn of 1859, investigated the subject. Nevertheless, before he gave the exact proof of their connexion, some few bold minds had foreseen the conclusions to which these observations must lead, and had predicted the existence of sodium in the sun. Foremost among these stand Professors Stokes and William Thomson, and the Swedish philosopher Ångström. It is, however, to Kirchhoff that we are indebted for the full and scientific investigation of the subject, and he must be considered as the founder of the science of solar and stellar chemistry.

Wishing to test the accuracy of this frequently asserted coincidence of the bright metallic and dark solar lines with his very delicate instrument, Professor Kirchhoff made the following very remarkable experiment, which is interesting as giving the key to the solution of the problem regarding the existence of sodium and other metals in the sun:—

'In order to test in the most direct manner possible the frequently asserted fact of the coincidence of the sodium lines with the lines D, I obtained a tolerably bright solar spectrum, and brought a flame coloured by sodium vapour in front of the slit. I then saw the dark lines D change into bright ones. The flame of a Bunsen's lamp threw the bright sodium lines upon the solar spectrum with unexpected brilliancy. In order to find out the extent to which the intensity of the solar spectrum could be increased without impairing the distinctness of the sodium lines, I allowed the full sunlight to shine through the sodium flame, and to my astonishment I saw that the dark lines D appeared with an extraordinary degree of clearness. I then exchanged the sunlight for the Drummond's, or oxy-hydrogen lime-light, which, like that of all incandescent solid or liquid bodies, gives a spectrum containing no dark lines. When this light was allowed to fall through a suitable flame coloured by common salt, dark lines were seen in the spectrum in the position of the sodium lines. The same phenomenon was observed if instead of the incandescent lime a platinum wire was used, which being heated in a flame was

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brought to a temperature near its melting point by passing an electric current through it. The phenomenon in question is easily explained upon the supposition that the sodium flame absorbs rays of the same degree of refrangibility as those it emits, whilst it is perfectly transparent for all other rays.' (*Kirchhoff. Researches, &c.*, pp. 13, 14.)

Thus Kirchhoff succeeded in producing artificial sunlight, at least as far as the formation of one of Fraunhofer's lines is concerned. He proved that the yellow soda flame possesses this—at first sight anomalous—property of absorbing just that kind of light which it emits; it is opaque to the yellow D light, but transparent to all other kinds of light. Hence, if the yellow rays in the spectrum produced by the Drummond's light in the above experiment are more intense than those given off by the soda flame, we shall see in the yellow part of the spectrum shadows, or dark lines; and if the difference of intensity be very great, these shadows may by contrast appear perfectly black. This opacity of heated sodium vapour for the particular kind of light which it is capable of giving off, was strikingly exhibited by Professor Roscoe, in one of a course of lectures on Spectrum Analysis, lately delivered by him in London at the Royal Institution. A glass tube, containing a small quantity of metallic sodium, was rendered vacuous and then closed. On heating the tube, the sodium rose in vapour, filling a portion of the empty space. Viewed by ordinary white light this sodium vapour appeared perfectly colourless, but when seen by the yellow light of a soda-flame the vapour cast a deep shadow on a white screen, showing that it did not allow the yellow rays to pass through.

This remarkable property of luminous gases to absorb the same kind of light as they emit, is not without analogy in the cognate science of Acoustics. Sound is produced by the vibration of the particles of gravitating matter, whilst light is supposed to be produced by a similar vibration of the particles of a non-gravitating matter, called the luminiferous ether. In the case of sound, a similar phenomenon to the one under consideration is well known. We are all acquainted with the principle of resonance; if we sound a given note in the neighbourhood of a pianoforte, the string capable of giving out the vibrations producing that note takes up the vibrations of the voice, and we hear it answering the sound. The intenser vibrations proceeding in one direction are absorbed by the string, and emitted as waves of slighter intensity in every direction.

Not only did Professor Kirchhoff show experimentally that luminous gases absorb the kind of light which they emit, by

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reversing the spectra of several of the metals, but by help of theoretical considerations he arrived at a very important general formula concerning the emission and absorption of rays of heat and light, which includes these phenomena as a particular case. The general law is called the *law of exchanges,* and it asserts that the relation between the amount of heat or of light which all bodies receive and emit is for a given temperature constant. Somewhat similar results were arrived at independently by Mr. Balfour Stewart in this country.

In order to determine and map the positions of the bright lines produced by the electric spectra of the various metals, Kirchhoff employed the dark lines in the solar spectrum as his guides. Much to his astonishment, he observed that dark solar lines occur in positions coincident with those of all the bright iron lines. Exactly as the sodium lines were identical in position with Fraunhofer's lines D, for each of the iron lines (and Kirchhoff examined more than sixty) a dark solar line was seen to correspond. Not only had each bright iron line its dark representative in the solar spectrum, but the breadth and degree of distinctness of the two sets of lines agreed in the most perfect manner; the brightest iron lines corresponding to the darkest solar lines. These coincidences cannot be the mere effect of chance; in other words, there must be some causal connexion between these dark solar lines and the bright iron lines. That this agreement between them cannot be simply fortuitous is proved by Kirchhoff, who calculates—from the number of the observed coincidences, the distances between the several lines, and the degree of exactitude with which each coincidence can be determined—the fraction representing the chance or probability that such a series of coincidences should occur without the two sets of lines having any common cause; this fraction he finds to be less than $\frac{1}{1,000,000,000,000,000,000}$, or, in other words, it is practically certain that these lines have a common cause.

'Hence this coincidence,' says Kirchhoff, 'must be produced by some cause, and a cause can be assigned which affords a perfect explanation of the phenomenon. The observed phenomenon may be explained by the supposition that the rays of light which form the solar spectrum have passed through the vapour of iron, and have thus suffered the absorption which the vapour of iron must exert. As this is the only assignable cause of this coincidence, the supposition appears to be a necessary one. These iron vapours might be contained either in the atmosphere of the sun or in that of the earth. But it is not easy to understand how our atmosphere can contain such a quantity of iron vapour as would produce the very distinct absorp-

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tion-lines which we see in the solar spectrum; and this supposition is rendered still less probable by the fact that these lines do not appreciably alter when the sun approaches the horizon. It does not, on the other hand, seem at all unlikely, owing to the high temperature which we must suppose the sun's atmosphere to possess, that such vapours should be present in it. Hence the observations of the solar spectrum appear to me to prove the presence of iron vapour in the solar atmosphere with as great a degree of certainty as we can attain in any question of natural science.' (*Kirchhoff. Researches, &c.*, p. 20.)

This statement is not one jot more positive than the facts warrant. For to what does any evidence in natural science amount to, beyond the expression of a probability? A mineral sent to us from New Zealand is examined by our chemical tests, of which we apply a certain number, and we say these show us that the mineral contains iron, and no one doubts that our conclusion is correct. Have we, however, in this case proof positive that the body really is iron? May it not turn out to be a substance which in these respects resembles, but in other respects differs from, the body which we designate as iron? Surely. All we can say is, that in each of the many comparisons which we have made the properties of the two bodies prove identical; and it is solely this identity of the properties which we express when we call both of them iron. Exactly the same reasoning applies to the case of the existence of these metals in the sun. Of course the metals present there, causing these dark lines, *may* not be identical with those which we have on earth; but the evidence of their being the same is as strong and cogent as that which is brought to bear upon any other question of natural science, the truth of which is generally admitted.

We do not think we can give our readers a more clear and succinct account of the development of this great discovery than by quoting from Kirchhoff's admirable memoir the following passage:—

'As soon as the presence of *one* terrestrial element in the solar atmosphere was thus determined, and thereby the existence of a large number of Fraunhofer's lines explained, it seemed reasonable to suppose that other terrestrial bodies occur there, and that, by exerting their absorptive power, they may cause the production of other Fraunhofer's lines. For it is very probable that elementary bodies which occur in large quantities on the earth, and are likewise distinguished by special bright lines in their spectra, will, like iron, be visible in the solar atmosphere. This is found to be the case with calcium, magnesium, and sodium. The number of bright lines in the spectrum of each of these metals is indeed small, but those lines, as well as the dark lines in the solar spectrum with which they coincide,

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are so uncommonly distinct that the coincidence can be observed with great accuracy. In addition to this, the circumstance that these lines occur in groups renders the observation of the coincidence of these spectra more exact than is the case with those composed of single lines. The lines produced by chromium, also, form a very characteristic group, which likewise coincides with a remarkable group of Fraunhofer's lines; hence, I believe that I am justified in affirming the presence of chromium in the solar atmosphere. It appeared of great interest to determine whether the solar atmosphere contains nickel and cobalt, elements which invariably accompany iron in meteoric masses. The spectra of these metals, like that of iron, are distinguished by the large number of their lines. But the lines of nickel, and still more those of cobalt, are much less bright than the iron lines, and I was therefore unable to observe their position with the same degree of accuracy with which I determined the position of the iron lines. All the brighter lines of nickel appear to coincide with dark solar lines; the same was observed with respect to some of the cobalt lines, but was not seen to be the case with other equally bright lines of this metal. From my observations I consider that I am entitled to conclude that nickel is visible in the solar atmosphere; I do not, however, yet express an opinion as to the presence of cobalt. Barium, copper, and zinc appear to be present in the solar atmosphere, but only in small quantities; the brightest of the lines of these metals correspond to distinct lines in the solar spectrum, but the weaker lines are not noticeable. The remaining metals which I have examined—viz., gold, silver, mercury, aluminium, cadmium, tin, lead, antimony, arsenic, strontium, and lithium—are, according to my observations, not visible in the solar atmosphere.' (*Kirchhoff. Researches, &c.*, p. 21.)

We are now in a position to understand why the discovery of the existence of these metals in the sun is no myth, no vague supposition, or possible contingency. We now see that this conclusion is derived, by a severely correct process of inductive reasoning, from a series of exact and laborious experiments and observations, and that the presence of these metals in the solar atmosphere has been determined with as great a degree of certainty as is attainable in any question of physical science. But it is only to those who have witnessed the spectacle of the coincidence of the bright iron with the dark solar lines, shown in such an apparatus as that of Kirchhoff's, that it is given adequately to feel the force of this conclusion; and the impression made by such a sight is not one likely to be easily effaced from the mind.

The mode in which new and perhaps startling facts in science, such as those we are now considering, are unwittingly misinterpreted and misapplied by certain minds to suit their own preconceived notions, must be an interesting branch of study to

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the psychologist. The Heidelberg Professors received a letter from a worthy farmer in Silesia thanking them for the great discovery they had made; it had particularly interested him, as it confirmed in a remarkable manner a theory which he had himself long held respecting the nutrition of plants; he believed that all artificial addition of inorganic materials to the plants in the shape of manure, was quite unnecessary, as the plants obtained the alkalies, the phosphorus, and the silica, &c., which they require, if a sufficient supply be not present in the soil, from the *sunlight!* The Heidelberg Professors, he continues, had clearly proved the presence of sodium, potassium, iron, and magnesium (all substances needed by plants), in the *sunlight*, and he felt sure that his theory of vegetable nutrition now required no further proof, but must at once be adopted by the previously incredulous world.

As a similar instance of this unconscious perversion of facts, we may mention the case of an English gentleman who believed that by a series of elaborate experiments he had proved the presence of iron in the *sunlight!* In spite of the previous caution of an eminent man of science, this gentleman was induced to publish his views, because, as he says, 'the whole scope and 'object of Bunsen's and Kirchhoff's experiments are to prove 'the possibility of the most minute particles of metal existing 'in light, and the probability of certain dark lines in the solar 'spectrum being formed by iron!' Thus, the fact of the existence of iron in the body of the sun, at a distance of 95,000,000 miles, is represented by these scientific fanatics — we really can use no milder term — as being identical with the existence of iron in the sunlight, which, travelling at the rate of 192,000 miles per second, bathes the whole universe in its vivifying beams.

Of stellar chemistry applied to other self-luminous celestial bodies, we have at present but little knowledge. Fraunhofer, as we have already stated, observed that the spectra of the fixed stars contained dark lines differing from those seen in the solar spectrum. The half-century which has elapsed since Fraunhofer made these observations has not brought us further knowledge on this point, although it has assured us of the truth of his statements. In the spectrum of Sirius he observed no dark lines in the orange-coloured region; but in the green there was a distinct line, and in the blue two dark bands, none of which were seen in solar light. The spectra of other stars were likewise examined by Fraunhofer, and they appeared each to differ from the other. The difficulties attending the exact observation and measurement of the dark lines in the spectra of the stars are, of course, very great: but, with the aid of the vastly improved optical instruments of the present day, we believe that astronomers will overcome these difficulties; and we look forward with interest to no far distant time, when we shall receive some clue to the cause of the colour of those wonderful blue and red stars which appear to be confined to certain quarters of the heavens.*

In the last chapter of Professor Kirchhoff's memoir he leaves the sure road of inductive reasoning, and puts forward a theory on the physical condition of the sun. Doubtless the Professor is as well aware as any one can be of the great difference between his discovery of the existence of the metals in the sun and his physical theory of the solar constitution. One is an ascertained fact, the other is a mere hypothesis. It is, however, necessary to point out this difference, lest many who may not agree with the theory of the physical constitution of the sun proposed by Kirchhoff should think themselves at liberty to discard his discovery of the presence of the metals in the solar atmosphere. It is not possible to give here the arguments which may be adduced in favour of, or in opposition to, Professor Kirchhoff's theory. Scarcely, indeed, can we do more than quote one or two passages from his memoir, to give an idea of his views respecting the structure of the sun:—

'In order to explain,' he says, 'the occurrence of the dark lines in the solar spectrum, we must assume that the solar atmosphere encloses a luminous nucleus, producing a continuous spectrum, the brightness of which exceeds a certain limit. The most probable supposition which can be made respecting the sun's constitution is, that it consists of a solid or liquid nucleus, heated to a temperature of the brightest whiteness, surrounded by an atmosphere of somewhat lower temperature. This supposition is in accordance with Laplace's celebrated nebular theory respecting the formation of our planetary system. If the matter, now concentrated in the several heavenly bodies, existed in former times as an extended and continuous mass of vapour, by the contraction of which sun, planets, and moons have been formed, all these bodies must necessarily possess mainly the same constitution. Geology teaches us that the earth once existed in a state of fusion; and we are compelled to admit that the same state of things has occurred in the other members of our solar system. The amount of cooling which the various heavenly bodies have undergone, in

* We rejoice to see, from his last annual report, that the Astronomer-Royal is about to undertake the examination of the spectra of the fixed stars. He remarks—'I have prepared a prism-apparatus to be 'used in conjunction with the SE. Equatorial for the examination of 'the fixed stars; but hitherto I have been able to do little more than 'adjust its parts.'

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accordance with the laws of radiation of heat, differs greatly, owing mainly to the difference in their masses. Thus, whilst the moon has become cooler than the earth, the temperature of the surface of the sun has not yet sunk below a white heat.

'Our terrestrial atmosphere, in which now so few elements are found, must have possessed, when the earth was in a state of fusion, a much more complicated composition, as it then contained all those substances which are volatile at a white heat. The solar atmosphere at this present time possesses a similar constitution. The idea that the sun is an incandescent body is so old, that we find it spoken of by the Greek philosophers. When the solar spots were first discovered, Galileo described them as being clouds floating in the gaseous atmosphere of the sun, appearing to us as dark spots on the bright body of the luminary. He says, that if the earth were a self-luminous body, and viewed at a distance, it would present the same phenomena as we see in the sun.' (*Kirchhoff.* *Researches, &c.*, p. 24.)

Certain appearances connected with those spots on the sun's surface have induced astronomers in general to adopt a different theory of the constitution of the sun from that proposed by Galileo and supported by Kirchhoff. This theory supposes, according to Sir William Herschel, that the centre of the spot reveals a portion of the dark surface of the sun, seen through two overlying openings — one formed in a photosphere, or luminous atmosphere, surrounding the dark solid nucleus, and the other in a lower, opaque, or reflecting atmosphere. The supposition of the existence of such an intensely ignited photosphere surrounding a cold nucleus is, according to Kirchhoff, a physical absurdity. He puts forward his views on this point clearly and forcibly in the following passage : —

'The hypothesis concerning the constitution of the sun which has been thus put forward in order to explain the phenomena of the sun-spots, appears to me to stand in such direct opposition to certain well-established physical laws, that, in my opinion, it is not tenable, even supposing that we were unable to give any other explanation of the sun-spots. This supposed photosphere must, if it exists, radiate heat towards the sun's body as well as from it. Every particle of the upper layer of the lower or opaque atmosphere will therefore be heated to a temperature at least as high as that to which it would be raised if placed on the earth, exposed to the sun's rays, in the focus of a circular mirror whose surface, seen from the focus, is larger than a hemisphere. The less transparent the atmosphere is, the quicker will this temperature be attained, and the smaller will be the distance to which the direct radiation of the photosphere will penetrate into the mass of the atmosphere. What degree soever of opacity the atmosphere may possess, it is certain that in time the heat will be transmitted, partly by radiation, partly by conduction and convection, throughout the whole mass; and if the atmosphere ever had been cold, it is clear that in the course of ages it must have become intensely heated. This atmosphere must act on the nucleus in the same way as the photosphere acts upon it; the nucleus must likewise become heated to the point of incandescence. It must therefore give off light and heat; for all bodies begin to glow at the same temperature.' (*Kirchhoff: Researches, &c.*, pp. 25, 26.)

Our author then proceeds to account for the phenomena of the solar spots by the supposition of two superimposed layers of clouds being formed in the solar atmosphere. One of these, being dense and near the sun's surface, does not allow the light of the underlying portion of the sun to pass, and forms the nucleus of the spot; whilst the other, being produced at a higher elevation, is less dense, and forms what we term the penumbra.

It is unfortunate for Kirchhoff's theory that the unanimous verdict of all who have examined these singular phenomena is in favour of their being funnel-shaped depressions. Preconceived notions have, however, so powerful an influence over the mind, and it is so difficult to obtain a truthful estimate of relative depression and elevation at such distances, that we are willing to believe that astronomers may possibly be mistaken in their views on this subject. There is, however, one method of observation which would seem qualified to settle the disputed question. If the astronomers' view of the construction of the spots is correct, the dark nucleus never can be seen beyond the penumbra, when the spot moves round towards the sun's limb. On Kirchhoff's view such a separation of the two clouds forming nucleus and penumbra is perfectly possible, and when they have nearly reached the edge of the sun's disc, we ought to see the dark cloud below, and separate from the upper one. Such a separation, however, has not been noticed, and on the other hand we may adduce the following observation of Sir William Herschel as leading to a directly opposite conclusion:—

'Oct. 13, 1794.—The spot in the sun, I observed yesterday, is drawn so near the margin, that the elevated side of the following part of it hides all the black ground, and still leaves the cavity visible, so that the depression of the black spots and the elevation of the faculæ are equally evident.'

The more the question of the physical constitution of the sun is considered, the more does it appear that we have no right to make up our minds concerning it, either in one way or the other. Seeing how little is really known about the matter, with the true spirit of scientific inquirers, we hold ourselves open to conviction as soon as satisfactory evidence shall be brought forward. The singular observations first made by Mr. James

Nasmyth*, a few months ago, concerning the physical condition of the sun's surface — observations so novel that astronomers were loth to receive them as facts until they were confirmed by other observers — need only to be mentioned in order to show that we are not in a position to uphold any theory whatever of the physical constitution of our great luminary. Mr. Nasmyth asserts, and his assertion has been confirmed by the subsequent observations of more than one competent observer, that the well-known mottled appearance which the surface of the sun exhibits is due to the presence of 'willow-leaf-shaped' luminous bodies, which, interlacing as it were, cover the whole surface of the sun. These most singular forms can be well observed, according to Mr. Nasmyth, in the 'bridges' or streaks of light which cross the dark spots, and they are there seen to move with an astonishing velocity. Imagination itself fails to give us the slightest clue to the probable constitution of these most recent of astronomical novelties!

The beautiful red prominences seen projecting from the sun's disk during a total solar eclipse, and reaching to a height of 40,000 miles above the sun's visible surface, are likewise objects whose existence cannot be reconciled with any of the proposed theories of the sun's structure. Thanks to Mr. De la Rue, we have attained some knowledge concerning these wonderful flames, as, by the help of photography, this gentleman has succeeded in proving that the prominences really belong to the sun, and are not caused in any way by the light passing over the interposed surface of the moon, as was by some imagined.

In considering the subject of solar chemistry, or indeed of any other novel branch of science, we cannot be too frequently reminded of the incompleteness of our knowledge. This is especially the case with reference to the subject to which we have now directed the attention of our readers. But although the results of these agencies are still very imperfect, and leave ample space for the labours of future investigators, yet the discovery of this new method of analysis is at once so original and so important, that we do not hesitate to rank it among the greatest achievements of science in this age, and we await with great curiosity its further application.

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* Memoirs of the Literary and Philosophical Society of Manchester. 3rd Series, vol. i. p. 407.