The Synthesis of the Elements

The Astrophysical Quest for Nucleosynthesis and What It Can Tell Us About the Universe

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Zu Inhaltsverzeichnis

Chapter 2
Preparing the Ground for Delving into the Stars

2.1 The Long Road to Deciphering the Composition of the Stars

All our knowledge about the composition of cosmic objects is obtained via spectroscopy. Two key disciplines are required to extract this information from observations: the theory of radiative transfer through stellar material and the theory of atomic structure. Spectroscopy is as old as modern science. It began with Johannes Kepler (1571–1630m)[1] and later Isaac Newton (1643–1727m), who knew about the effect of the prism on sunlight.[2] When they cast the outgoing light of the prism on a screen, they discovered all the colors of the rainbow. Naturally, Newton used a circular aperture, and consequently his spectrum was not pure. Despite this early start, progress was slow at the beginning, and even after major breakthroughs, about 400 years were needed before reliable information about stellar composition could be obtained.

In 1752, Thomas Melvill (1726–1753)[3] began to study the spectra of salts placed in a flame. Melvill reported that heating table salt converted the flame to yellow. No explanation of the phenomenon was given.

After Kepler, about 150 years went by before William Wollaston, a London physician, invented the very narrow slit in 1802. This apparently trivial invention allowed him to obtain a pure spectrum by preventing the differently colored lights from over-

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[1] Kepler, J., *Ad Vitellionem Paralipomena*, *Quibus Astronomiae Pars Optica Traditur*, Claudius Marnius, Frankfurt, 1604.

[2] Newton, I., *Treatise of the Reflections*, *Refractions*, *Inflections and Colours of Light*, London, 1704. The discovery was in 1666, according to Newton's letter to the secretary of the Royal Society dated 6 February 1672.

[3] Melvill, T., J. R. Astr. Soc. Can. **8**, 231 (1914). This is a reprint of the original paper from 1752. And so says the special introduction: *Had the ingenious author of this paper* (*who died December*, *1853*, *at the age of 27*) *lived to put the finishing hand to it*, *he would probably*, *have added many things*. I could not discover who wrote the introduction, nor the occasion on which the paper was reprinted.

G. Shaviv, *The Synthesis of the Elements*, Astrophysics and Space Science Library 387,
DOI: 10.1007/978-3-642-28385-7_2,

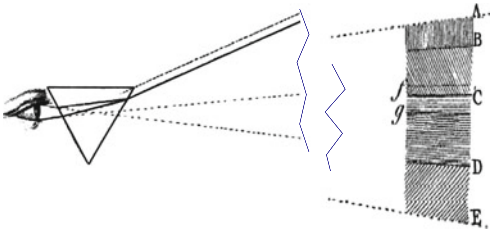

Fig. 2.1 The first description of what is known today as the Fraunhofer line, by Wollaston (1802). Note that the lines appear to separate different regions (what Wollaston called 'images' and 'separation lines') in the continuous spectrum. Wollaston marked the lines by A, B, …, and this is the source of the notation D, for the famous *yellow* sodium line

lapping, as Henri Roscoe (1833–1915) described it in 1862.[4] The narrow slit is still in use today.[5] The fact that the spectrum was now pure enabled Wollaston[6] to make a seminal discovery. He noticed that the colors seen in the spectrum of the Sun (about 5) are separated by dark lines (see Fig. 2.1). At the same time, Wollaston discovered that the light emerging from a candle is not continuous, but exhibits distinct colored lines. Thus, hot gases do not emit continuous light, but lines. Wollaston offered no explanation. In his own words: *I cannot undertake to explain* the dark lines. He made no attempt to explore their origin. Florian Cajori (1859–1930)[7] claimed about a century later that Wollaston's 'explanation' *shows how a most plausible theory may be destitute of all truth*, though Wollaston admitted that he had no explanation.

The next major progress came in 1814, when Joseph Fraunhofer (1787–1826m)[8] added a small telescope of a theodolite after the prism and put the slit at a distance of 30 meters before the prism. As a result, he created a powerful spectrometer. When he examined solar light, he was able to observe a total of 576 dark lines crossing the colorful spectrum, the positions of which he recorded. It was from this moment on that these lines became known as the Fraunhofer lines. Fraunhofer noted that the intensity of the solar continuum radiation is not uniform and that the maximum intensity occurs in the yellow color. Next, Fraunhofer identified the location of the bright lines emitted by hot gases with some dark lines he saw in the spectrum of the Sun. In particular, he noticed that the D line (in Wollaston's notation), which appeared as two very close yellow lines in the spectrum of a hot gas, was present as one of the darkest lines in the spectrum of the Sun. Fraunhofer turned the system

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[4] Roscoe, E.H., The Edinburgh Review **CXVI**, 295 (1862).

[5] Still, the question remains as to how Newton missed the discovery of the Fraunhofer lines in the solar spectrum. There is a claim (Johnson, A., Nature **26**, 572, 12 October 1882) that Newton had to rely on a young assistant with better eyesight, and it was the assistant who missed the lines.

[6] Wollaston, W.H., Phil. Tran. R. Soc. Lond. **92**, 365 (1802), read 24 June 1802. In a paper just after Wollaston's in the journal, Young (Young, M.D.; ibid., 387, read 1 July 1802) describes how he repeated Wollaston's experiment and got 'perfectly' identical results. In particular, he mentions 'the line of yellow'.

[7] Cajori, F., *A History of Physics*, The Macmillan Comp., London, 1899.

[8] Fraunhofer, J. von, Denkschriften de K. Acad. der Wissenschaften zu Munchen, Band **V**, 193 (1817).

of dark lines into standards for the calibration of achromatic lenses. He also tried to discover the source of the lines, but failed.

At first, Fraunhofer thought the dark lines were an artefact of interference caused by the slit. But further experiments convinced him that they were a genuine feature of the Sun's spectrum.[9] Fraunhofer measured the relative distance between the lines and discovered that these distances did not change with the location of the Sun in the sky, or even when the solar light was reflected from planets, like Venus. The positions of the lines were fixed! Moreover, he was able to observe three dark lines in the spectrum of Sirius, the brightest star seen from the Earth. Fraunhofer was thus convinced that the source of the dark lines was in the stars.

The scientific story of the Fraunhofer lines as described above camouflages a rivalry driven by national pride, which took place between the German and English academic communities over a long period of time.[10] The establishment of the Fraunhofer Optical Institute in Bavaria with the financial support of Napoleon's army, destined to produce superb optical instruments needed for the artillery, allowed Fraunhofer to develop the ultimate skill in glasswork and optical instrumentation. He used this to facilitate major discoveries in astronomy in general, and in the spectrum of the Sun in particular. England, on the other hand, decided to impose a tax on flint glass, and in this way strangled any technical progress. As an excuse, some of the leading English scientists began to argue that the art of manufacturing glass was not science. This was an exaggeration because the Fraunhofer calibration system, facilitated by the unrivaled quality of their instrumentation, was described by Babbage in his essay on why English science declined[11] as an example of what high precision instruments, craftsmanship, and above all observation can lead to.[12]

In 1824, Fraunhofer observed the coincidence of the yellow sodium lines with the double D line in the solar spectrum. Unfortunately, the inevitable conclusion that the

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[9] Fraunhofer, Edinb. Phil. J. **9**, 299 (1823); ibid. **10**, 22 (1823).

[10] Jackson, M.W., Studies in History and Philosophy of Science Part A **25**, 549 (1994). An interesting account of the way short-sighted politics on the one hand and military needs on the other affected progress in science on both sides of the English channel.

[11] Babbage, C. *Reflections on the Decline of Science in England and on Some of Its Causes*, London, Printed for B. Fellowes, Ludgate street, 1830, p. 210. Charles Babbage (1792–1871m) was a mathematician.

[12] The irony is that the German scientists thought the same way and expressed contempt for experimental work. When the brilliant self-taught optical inventor Fraunhofer applied for membership to the Bavarian Academy of Sciences, his application was rejected (1819) because Bavarian academics were convinced that the discoveries had only technological significance (what a shame!). Indeed, Fraunhofer regarded himself as an optical engineer. But the telescope lenses produced by Fraunhofer were considered the best in the world. In 1838, Friedrich Bessel (1784–1846m) used a Fraunhofer telescope to determine the first parallax of a nearby star (Bessel, F.W., MNRAS **4**, 152, 1838). The star was 61 Cygni, with a mean annual parallax of 0.3135 arcsec. Johann Galle (1812–1910m) was using a Fraunhofer telescope when he discovered the theoretically predicted planet Neptune in the year 1846 (Galle, J.G., MNRAS **7**, 153, 1846). It was estimated that Fraunhofer's refractors of a given aperture were as effective as reflectors with an aperture three times as big. Better late than never, Fraunhofer was accepted as a member of the Bavarian Academy in 1823 and died three years later, before he turned forty.

Fig. 2.2 Testimony to discoveries made in Heidelberg around 1855–1860. *Left* the plaque in the main street of Heidelberg, on the building where Kirchhoff carried out solar spectroscopy for the first time. *Right* on the other side of the street, in a small garden, stands Bunsen's statue looking at the plaque commemorating Kirchhoff and Bunsen's discoveries. Photos by Shaviv

yellow lines and the dark *D* lines were produced by the same chemical element, but under different physical conditions, never crossed Fraunhofer's mind (Fig. 2.2).

2.2 Why the Sodium *D* Line Appears Everywhere

An annoying problem in spectroscopy was that the usual flames used for heating the substances contained sodium as a trace element from salt, and consequently every spectrum was contaminated with sodium lines. The problem was solved when Robert Bunsen (1811–1899m) invented the Bunsen burner, or in short the Bunsen, which produced a hot flame but without sodium.[13] Using the Bunsen, Joseph Swan (1828–1914) was able in 1857[14] to identify the *D* lines with sodium, because the clean flame simply did not show them. A long list of discoverers had suggested the coincidence between the Fraunhofer *D* line and sodium, but had not been able to verify it. With this discovery, Swan[15] confirmed the suspected discoveries by William Herschel (1738–1822m) in 1823, David Brewster (1781–1868m) in 1835, and Leon Foucault (1819–1868m) in 1849.

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[13] Bunsen invented the Bunsen burner sometime in 1855. The goal was mainly to develop a better heat source for laboratory work. The standard flames used were smoky and produced a low heat intensity. Bunsen's breakthrough was simple: mix the gas with air before combustion instead of during combustion. Two years later in 1857, Bunsen and Roscoe described the new burner in Pogg. Ann. Phys. **100**, 84 (1857). Mixing the air and gas before burning left the salt outside the burning volume.

[14] Swan, J.W., Edinb. Trans. **21**, III, 411 (1857).

[15] Swan did not like the way Kirchhoff and Bunsen attributed the discovery to him, and found it necessary to write a letter to the editor stressing that he found it to be the case in *all flames*. Swan Phil. Mag. **20**, 169 (1860).

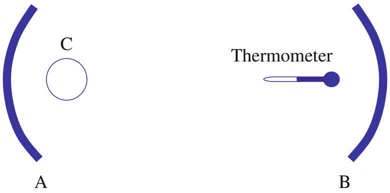

Fig. 2.3 The setup of Pictet's experiment. *A* and *B* are two mirrors. *C* is the hot/cold object. The thermometer and the hot/cold object are placed at the focal points of the two mirrors

It is fascinating to note how the strong line of sodium, present as a trace element almost everywhere, played such a crucial role in the development of spectroscopy.

2.3 The Concept of Equilibrium: Pictet and Prévost

In the middle of the eighteenth century, the concept of 'radiant heat' was still separated from the concept of light. Thomas Young (1773–1829m) wrote in 1803[16] that the first to concentrate radiant heat was Hoffmann, who used mirrors prepared by Wolfe. No further details were given by Young.

Marc-Auguste Pictet (1752–1825m)[17] used the possibility of concentrating heat rays by placing a hot blob of iron at the focus of a concave mirror and observing a thermometer placed at the focus of a second mirror placed about 3 meters away (see Fig. 2.3). After taking all the precautions to isolate the experiment from external perturbations, Pictet discovered that, as the iron blob cooled, the temperature of the thermometer rose. The experiment was conducted ten years before Herschel placed a thermometer behind a spectrometer at a location beyond the red color and discovered infrared radiation, demonstrating how the invisible 'radiant heat' and visible radiation behave and propagate in the same way. Pictet's experiment on the concentration and propagation of radiant heat was not the first in this story, but it was the first to stimulate interest among physicists and consequently incited them to provide a theoretical explanation.[18]

Pictet repeated the experiment with 'cold', i.e., he put snow at the focus of one of the mirrors, and found that the temperature at the other focus went down. In Pictet's language, the experiment demonstrated the 'reflection of cold'.

In the late eighteenth century, heat was assumed to be a kind of weightless fluid called caloric, which pervades everything. Those were the days when the similarly

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[16] Young, T., *A Course of Lectures on Natural Philosophy and the Mechanical Arts*, London, Taylor & Walton, new edition, 1846, p. 489. The original edition was published in 1803. The relevant report is by Wolfe (Phil. Tran. 4, 1769), who stated that the first to concentrate heat like light was Hoffmann, although Buffon (Histoire Naturelle, Supplement, 1774, I, p. 146) gave a more rigorous proof than Hoffmann did.

[17] Pictet, M.A., *Essais sur le feu*, Geneva, 1790. Translated from French by W.B., printed for E. Jeffery, London, 1791.

[18] See Cornell, E.S., Ann. Sci. **1**, 217 (1936) for a survey of previous experiments.

imaginary fluid phlogiston was invented to explain the chemical process during fire. Pictet believed in the caloric, and the two experiments he conducted differed from one another only in the direction of flow of the caloric. Pictet remarked that his explanation would not change if the heat were some vibrations in the elastic fluid of fire, because he argued that such vibrations would be reflected like sound. However, he did not specify who had proven such an effect. No matter how illogical it was, caloric served in those days as the best theory in town and many physicists subscribed to it.

When Pierre Prévost (1751–1839)[19] approached the problem in the 1780s, there were physicists who even believed that 'cold' was a different weightless fluid from caloric fluid, calling it 'frigoric'. Prévost argued, on the other hand, that cold was simply a lack of caloric.

In 1791, Prévost, who was Pictet's colleague at Geneva university, published[20] a seminal interpretation of Pictet's experiment. First, Prévost made the following assumptions:

> Heat is a discrete fluid. […] And this is the effect of the movement of its particles. This movement is caused by the impulse of a much more subtle 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 to another appears instantaneous. […] 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.

We may wonder whether anyone really understood these sentences in full. It reflects how vague the notions of the physical meaning of heat and light were at that time. Yet despite such foggy notions, the important hypothesis put forward by Prévost was based on common sense. It could not have been based on thermodynamics, which did not exist at that time, nor on the as yet unknown microphysics.

Prévost conceived the first thought experiment to consider *two portions to be enclosed in an empty space*, *terminated on all sides by impenetrable walls*. It was this concept that developed into a cavity emitting black body radiation, although the terms 'cavity' and 'black body' did not exist in Prévost's lexicon.

Next, Prévost defined two types of equilibrium:

> Absolute equilibrium of free heat is a state of this fluid in a portion of space which receives as much as it allows to escape it. 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 [that are] precisely equal.

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[19] Prévost was the first known case of a lawyer who turned into a physicist. The other famous cases are Edwin Hubble, who studied law before changing his mind and pursuing a unique career in astronomy, and Lewis Rutherfurd, an attorney and amateur astronomer, who built an observatory at the center of New York city in 1856. Avogadro studied law but reached the conclusion that physics is more interesting.

[20] Prévost, P., J. Phys. **38**, 314 (1791).

The term 'free heat' was not defined by Prévost in this paper, but the definition can be found in his book published in 1809,[21] where it is defined as: *free heat as radiant fluid*. Not a terribly helpful definition.

Prévost conceived the following solution: the two bodies (the hot/cold blob and the thermometer) exchange caloric all the time and tend to a state in which each one absorbs and emits the same amount of caloric. This is the idea of dynamic equilibrium, in which heat flows permanently in both directions (with vanishing net flow), in contrast to static equilibrium, in which case there is no flow at all. According to Prévost's model, the cooling takes place because the hot body receives less caloric than it loses. Prévost hypothesized that, in equilibrium, the net flow vanishes, irrespective of the composition of the two radiating bodies. On the other hand, the emission and absorption do not vanish in equilibrium. It did not seem logical to Prévost that, when the temperature of a body equals that of its surroundings, the body would suddenly stop radiating. No mathematical formulation or proof was provided. Prévost's book was published in 1809, and as the author pointed out, after Herschel's *beautiful demonstration that caloric rays reflect and refract*, which implied that these rays behaved like light. This is the reason for the name Prévost chose for his book, viz., *Du Calorique Rayonnant*, which means, the radiating caloric. While Prévost rejected the explanation of his colleague, he provided an explanation as to why Pictet was led to his own erroneous explanation. There was no mention of Hoffmann and his priority.

Towards 1804, Rumford and Leslie discovered that the nature of the surface of the substances is not less important for absorption and emission. Benjamin Thompson, known as Count Rumford (1753–1814m), discovered that the heat losses are maximal when the substance is painted black and minimal when it is metallic. The particular property of black or blackened surfaces was already discovered in Rumford's first experiments on the nature of heat.[22] Rumford found that black or blackened surfaces cool fast, and hence are the best heat emitters, while polished metallic surfaces are the slowest to cool, and hence are the worst heat emitters.[23] We can trace the birth of the black body as best emitter to this discovery by Rumford.[24]

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[21] Prévost, P., *Du calorique rayonnant*, Paris, Chez Paschoud, J.J., Libraire, Quai des Grands Augustins, no. 11, près du pont Saint-Michel, à Genève, chez le même libraire, 1809. The proof of the radiation law in the book is only verbal. Mathematics appears only in some examples, and the cooling law is expressed algebraically, and not as a differential equation, although the latter techniques had been known since Newton's times. Another interesting part of the book is Chap. VII, p. 298, where the author discusses the importance of the radiative heat exchange of the Earth in determining its global temperature, a key factor ignored by many in those days. This was at the time Fourier began his attempts to calculate the heat balance of the Earth.

[22] Rumford, *An inquiry Concerning the Nature of Heat, and the Mode of Its Communication*, 1804, in *Collected Works of Count Rumford*, Harvard Press, Cambridge, 1970.

[23] In 1796, on the basis of his research results for radiant heat, Rumford invented what is called today the Rumford fireplace. It reflects heat well and eliminates turbulence. The Rumford fireplace was popular until 1850.

[24] In *The Gentleman's Magazine*, p. 394, October 1814, we find the following anecdote about Rumford, who applied his own research results:

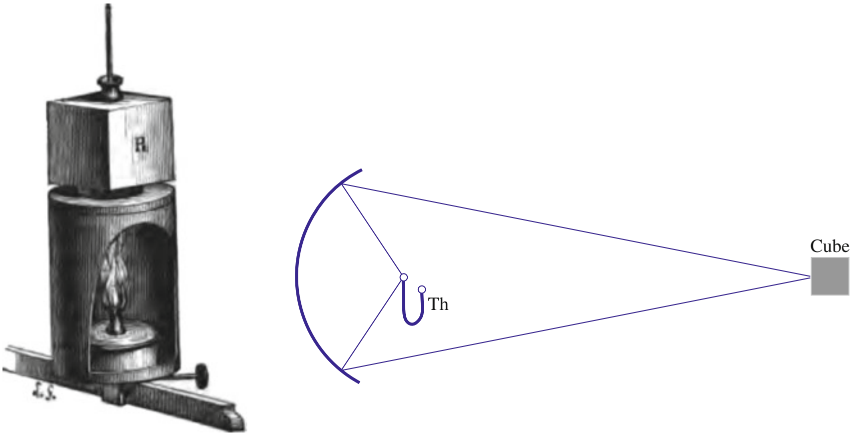

Fig. 2.4 *Left* the Leslie cube used by Leslie in his thermal radiation experiments. *Right* the arrangement applied by Leslie to investigate the emission of various substances. The parabolic mirror concentrates the radiation coming from the heated cube onto a thermometer. The cube is filled with boiling water and painted or coated with the substance to be tested

In 1809, Prévost called his hypothesis *l'équilibre mobile*, or dynamic equilibrium, and it is frequently referred to as *the theory of exchange*. Prévost was interested in heat transfer between bodies. He assumed that space is full of *radiant heat*, because every body radiates and absorbs heat continuously. But the dependence of the rate of cooling on the temperature of the body was unknown at that time.[25] So the implicit, unverified assumption was that the rate of cooling of a hot body is proportional to some monotonic function of the temperature. In equilibrium, the emission equals the absorption, and consequently the temperatures of the two bodies are equal. Prévost's idea was challenged by Rumford[26] in the realm of 'radiant heat', but this discussion would carry us too far afield and is less crucial for the physics of the Fraunhofer lines.

(Footnote 24 continued)

> Nor did any one follow (which is not to be wondered at) his whimsical winter dress, which was entirely white, even his hat. This he adapted agreeably to the law of nature, that more heated rays are thrown from a dark body than a light one; an experiment easily made, by taking two vessels of equal capacity, one blackened, the other white, and filling them with water heated to the same temperature: the water contained in the dark vessel will be found to arrive at the temperature of the surrounding bodies considerably sooner than the white, and vice versa.

The obituary is not signed. However, this is a good example of how physics may be important in fashion, even if it is wrong. Colors are meaningful only in the visible range. In the infrared, which is the relevant radiation in this case, there are no colors, and practically all materials behave the same way.

[25] This was even before 1817, when Dulong and Petit got the first result.

[26] Rumford, C., *The Complete Works*, Pub. Am. Acad. Arts Sci., Vol II, Boston, 1873.

In parallel with Prévost, but completely independently, John Leslie (1766–1832) carried out a long series of experiments and published them as a book[27] in 1804. The book describes 58 different experiments on the propagation of 'radiant heat', mostly carried out with the setup shown in Fig. 2.4. Qualitative conclusions are inferred after each experiment. The most important conclusion for our discussion here was already drawn after the fourth experiment:

> The power of absorbing heat, and the power of emitting it, seem always conjoined in the same degree.

However, he then added:

> […] and this uniform conjunction clearly betrays a common origin, and discovers the evolution of a single fact, which assumes contrary but correlative aspects.

It is not clear what 'common origin' Leslie had in mind, but it is more plausible that the absorption and emission have the same origin and hence are proportional to each other, as was later demonstrated. Leslie's results are plotted in Fig. 2.5. We see that, because the results were related to lampblack[28] (the measurements were relative), Leslie effectively had two data points (two of his three data points were very close to each other). It was therefore daring to state, as he did, that the emission of a body is proportional to its absorption power. But Leslie was proven right, even though he never got the credit for this observation. We may say that Leslie discovered the existence of black bodies as perfect emitters and absorbers when he realized that surfaces coated with lampblack were the best emitters and absorbers he could lay his hands on.

2.4 Beyond the Visible Light

In 1800, Herschel[29] took the solar spectrum and put a detector beyond the place where the red light fell (see Fig. 2.6). He thus discovered what is known today as infrared radiation ('infra' means 'coming after'). Herschel also found that about half of the

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[27] Leslie, J., *An Experimental Inquiry into the Nature and Propagation of Heat*, printed for J. Mawman, London, 1804. In 1805, Leslie was elected to the Chair of Mathematics at Edinburgh. His unsuccessful competitor for the chair was backed by some Edinburgh clerics, members of the moderate wing of the Scottish church. This group sought to have Leslie's election overturned, invoking a clause in the university's statutes requiring the electors to take the advice of the Edinburgh clergy! As evidence of Leslie's unsuitability for the job, they cited a footnote from the book in which he agreed with David Hume's view of cause and effect (p. 521), saying that Hume's writings were *a clear model of accurate reasoning*. But Hume was hated by the church. Leslie's opponents objected because his views challenged *traditional arguments for the existence of God*. Leslie denied any connection to Hume, however. What saved him was the fact that the different clerical groups hated each other more than they hated Leslie, and did not want one group (in this case the moderate one) to win the battle to change the decision. (Price, H., *John Leslie*, Oxford, Clarendon Press, 2001).

[28] Fine soot of incompletely burnt coal.

[29] Herschel, W., Phil. Trans. R. Soc. Lond. **90**, 284 (1800).

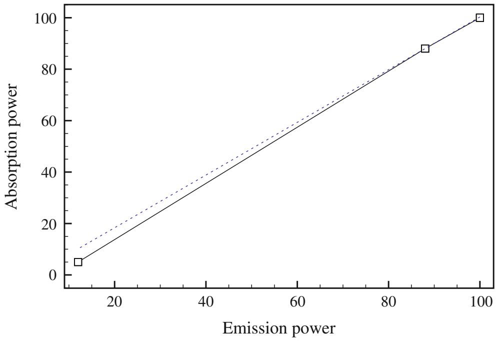

Fig. 2.5 Absorption as a function of emission from Leslie's data. *Squares* are the measured data for a list of materials, and the *continuous line* is the author's eye fit. Effectively, Leslie had three data points. The *straight line* is the *broken line*. Most of the substances at Leslie's disposal were either good emitters or bad ones

solar heating comes in the visible and half past the red color (in the IR). The violet, which is most refracted by the prism, had the least *efficacy*. Herschel concluded:

> If we call light, those rays which illuminate objects and radiant heat those which heat objects, it may be inquired, whether light be essentially different from radiant heat? […] we are not allowed, by rules of philosophizing, to admit two different causes to explain certain effects, if they may be accounted for by one.

While Young[30] thought that Herschel had also had *the good fortune to discover the separation of the rays of heat from those of light*, as if it were a question of luck and not of a physical idea, he also considered that Herschel's discovery *must be allowed to be one of the greatest that has been made since the days of Newton*, *although the theories of some speculative philosophers might have led to it a few years earlier*. On the other hand, Leslie asked:

> What, then, is this calorific and frigorific fluid after which we are inquiring? It is no light, it has no relation to ether, it bears no analogy to the fluids, real or imaginary, of magnetism and electricity. But why have recourse to invisible agent?

Leslie thought that it was all an effect of heating the air, which then gave rise to hot currents. Leslie lost all his supporters of this idea (of hot air)[31] after Davy showed that the intensity of the radiation increased in vacuum and Ritter made his discovery of ultraviolet radiation (see below).

John Ritter (1776–1810) discovered that silver salts darken when exposed to sunlight. So a year after Herschel's discovery, in 1801, Ritter[32] repeated Herschel's experiment, but putting the silver salts beyond the blue solar light, and effectively discovered the ultraviolet range of the spectrum. At first these rays were called 'chemical rays', because it was soon found that they were chemically active and induced chemical reactions, in contrast to heat rays. The exact nature of these rays

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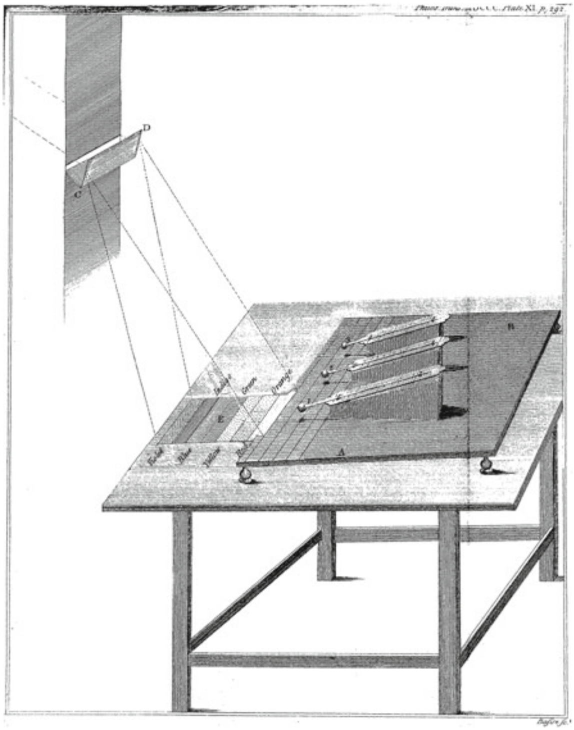
[30] Young, T., *A Course of Lectures on Natural Philosophy and the Mechanical Arts*, printed for Taylor and Walton, London, 1845.

[31] The expression 'full of hot air' meaning nonsense or exaggerated, originated at some time during 1835–1845, but it is not clear to what extent Leslie's idea contributed to it.

[32] Ritter, J.W., Ann. Phys. **7**, 527 (1801).

Fig. 2.6 The way Herschel discovered the infrared radiation by placing a thermometer beyond the place where the *red light* fell on the table



was at the center of a controversy, mainly between John Draper (1811–1882)[33] and his contemporaries. Draper thought that they were special type of rays that differed from visible light.

Returning to Leslie, while most of his conclusions were correct, some appeared strange. For example, experiment XX with the conclusion: *The impressions of heat or cold are*, *therefore*, *propagating through the air*, *with unequal degrees of diffusion*. Why should cold spread at a different speed to heat?

Unfortunately, the book contains no reference to any previous work, and in particular, Pictet and Prévost are not mentioned, although one of the experiments described in the book resembles Pictet's. Leslie made the admission: *I am free to confess that the propagation of heat is still a subject of immense difficulty*, then digressed to philosophy. Thus, 13 years after Prévost had stated his principle about emission and absorption on the continent, word had still not reached Edinburgh.

The book contains philosophical digressions which are relevant to the synthesis of the chemical elements, and for this reason we bring them into the discussion at this point. An example is:

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[33] John was the father of Henry Draper (1837–1882m) from the Henry Draper (HD) catalogue, see Shaviv, *The Life of the Stars*, 2009. John William Draper took the first photograph of the Moon in 1840.

> Nothing seems more chimerical than to indulge a hope that the humans will ever be able to achieve the transmutation of earths into precious metals; but those hapless visionaries who consumed their days in the obscure search after the philosopher's stone, did not, like their fellow labourers who sought the perpetual motion, advance pretensions which involve a physical absurdity.

The connection is a puzzle. Finally, at the end of the book, there appears the conclusion:

> Heat is an elastic fluid, extremely subtle and active. Is it a new and peculiar kind of fluid, we are already in some manner acquainted with? Heat and light are commonly associated. Heat is only light in the state of combination.

Indeed, as Leslie wrote about his own discoveries (p. 115 in Leslie's book):

> We have thus deduced a train of phenomena which must be deemed equally novel and striking.

Many years later, in 1865, the Frenchman Paul-Quentin Desains (1817–1885) published a book[34] in which he wrote that the *principle of the equality between the emission and absorption powers* was due to René-Just Haüy (1743–1822), who first stated it in 1806.[35] However, no reference is given to a paper by Haüy except for his lecture notes. The experiments by Leslie are discussed, but the principle is credited to Haüy. Indeed, on p. 108 of Haüy's lecture notes, he wrote:

> The equilibrium takes place when all the affinities of the bodies for caloric are satisfied, [...] and when, at the same time, each body sends forth to others as much radiant caloric as it received; and this equal repartition continues so long as the system remains at the same temperature.

It is interesting that Haüy, who was a crystallographer, did not carry out experiments with heat, and consequently we may infer that he reached this conclusion logically, without bothering to publish the result. This is also why no reference was given. The only place I could find the name Haüy in this connection is in Desains' book.

In 1826, Henri Talbot (1800–1877)[36] made the important claim that, if his theory that certain bodies gave characteristic lines should prove to be correct, then a glance at the prismatic spectrum of a flame would suffice to identify substances that would otherwise require a tedious chemical analysis for their detection. In 1834, Talbot studied lithium and strontium, both of which paint the flame in red. He then wrote: *The prism betrays between them the most marked distinction which can be imagined*. However, the mission was not simple. In 1845, William Miller (1817–1870)[37] carried out a detailed analysis of the spectra of the alkali metals, but was unable to infer any specific characteristic lines, the reason being the use of impure flames. Moreover,

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[34] Desains, P., *Leçon de Physique*, Tome second, Dezobry, E. Magdeleine et Co., Paris, 1865.

[35] Haüy, R-J., *Traité de Physique*, Berthollet, Daubenton, Paris, 1806. The translation into English by Gregory is from 1807. These are Haüy's lectures at the Ecole Normale, Paris.

[36] Talbot, H.F., Brewster, D., Sci. **5**, Phil. Mag. **3**, 33 (1833); ibid. **9**, 3 (1936).

[37] Miller, W.A., Phil. Mag. **27**, 81 (1845).

it was impossible to state with confidence that the spectral lines were unique for each element, and hence that the spectral identification was unique.

In 1830, the optician William Simms (1793–1860)[38] made a very important improvement in the spectroscope. Instead of merely using a prism and observing the slit with the naked eye, he placed a lens in front of the prism, so arranged that the slit was in the focus of the lens. The light which is allowed to pass through the slit is thus turned into a parallel beam hitting the prism. The beam emerging at each wavelength could then be magnified.

In 1847, Draper[39] concluded that all solids, and probably all liquids too, become incandescent, i.e., red hot, at the same temperature of 525°C. While below this temperature invisible rays are emitted, as the temperature rises above 525°C, rays of greater refrangibility (which in today's parlance means radiation of shorter wavelengths) are continually added. Moreover, all spectra of incandescent solids are continuous. Luminous gases, on the other hand, emit only bright lines. Draper's statement that only solids and liquids emit a continuum spectrum provided support for the then widely accepted conclusion that, as the Sun emits a continuous spectrum, it must be either a solid or a liquid, as 'can be inferred' from its mean density (1.45 g/cm^3). Scientists could not imagine gases at such high densities. Here is an example of the way imagination can sometimes fail us.

2.5 Stewart, the Forgotten Discoverer

Early in 1858, Balfour Stewart (1828–1887)[40] carried out a series of three types of experiment in which he compared the radiation emitted from different types of metal plate. Stewart was able to apply a sensitive radiation detector (see Figs. 2.7, 2.8), developed by Leopoldo Nobili (1784–1835)[41] and Macedonio Melloni (1798–1854),[42] who applied the thermoelectric effect discovered in 1822 by Thomas Seebeck (1770–1831)[43] to the problem of detecting radiation. According to Stewart:

> 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 vibrations or the wavelength.

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[38] Simms was an acclaimed family of opticians who contributed to improvements in spectroscopy and telescopes through the company Troughton & Simms.

[39] Draper, J.W., Phil. Mag., May, 345 (1847).

[40] Stewart, B., *An Account of Some Experiments on Radiant Heat, Involving an Extension of Prévost's Theory of Exchanges*, Trans. R. Soc. Edinb. **XXII**, PART I, 1 (March 1858) and Proc. R. Soc. Edinb. **6**, 93, session of 1857–1858.

[41] Nobili, L., Univ. Sci. et Art Genève **29**, 119 (1825).

[42] Melloni, M., Ann. Chim. Phys. **53**, 5 (1833); also Pogg. Ann. **35**, 112 (1835). His great work on thermal radiation was published in 1850 under the title *La thermochrose, ou la coloration calorifique*, Naples.

[43] Seebeck, T.J., Pogg. Ann. **6**, 1 (1823).

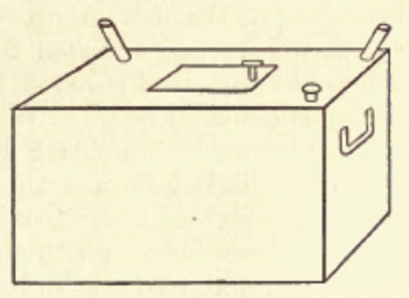

Fig. 2.7 The first cavity to serve as an effective *black body* (Stewart 1858)

Stewart repeated the basic experiments carried out by Leslie, Frédéric Provostaye (1812–1863), Desains,[44] and Melloni, but with greater accuracy. Inevitably, Stewart reached the conclusion already pointed out by Leslie, as Stewart asserted himself,[45] namely that:

> The absorption of a plate equals its radiation, and that for every description of heat.

It seems that 'for every description of heat' was intended to mean 'for every wavelength'. This important addition, however, did not appear in Leslie's conclusion. Neither Leslie nor Stewart applied filters to their experiments, and hence the experiment did not test what went on at particular wavelengths. The wavelength independence of the law came in the theoretical proof provided by Stewart. The novelty here lay in the fact that Stewart provided the first theoretical proof of the law. In this theoretical proof he demonstrated that the law held for every 'quality' of the heat wave, this being the term Stewart used for what we call wavelength today, as can be understood from the context. Finally, the above formulation of the law is incomplete. The correct formulation is this: at a given temperature, the emission of any substance is proportional to the absorption. The constant of proportionality changes with temperature.[46] This particular point was missing in Stewart's formulation.

In his second paper,[47] Stewart discussed the connection between the radiation emitted by a body and its temperature. Stewart found that the radiation of a naked

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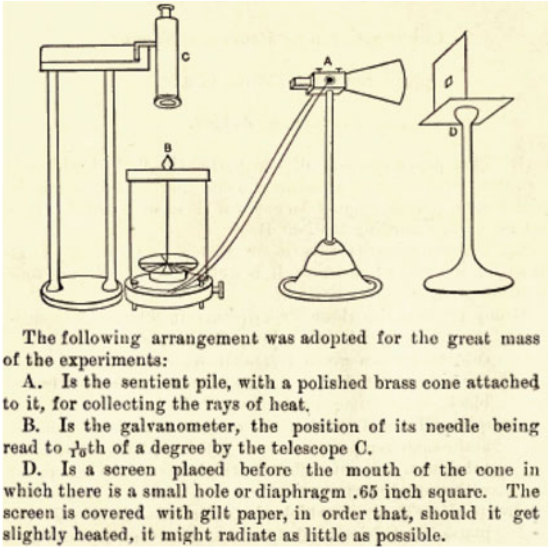
[44] For an extended description of these experiments, see the book by Desains, P., *Leçon de Physique*, Dezobry, E., Magdeleine et Cie., Lib-Éditeurs, Paris, 1860.

[45] In the textbook *Handbook of Natural Philosophy and Astronomy*, by Lardner, D., Second Course, Blanchard & Lea Pub., Philadelphia, published in 1854, we already find a table *showing the absorbing and reflecting power* of various substances, as found by Melloni in the 1830s. The interesting point is that the title of the column is *Radiating and Absorbing Powers*, and a single number is given. This confirms that Melloni showed the emission to be equal to its absorption, as is also explicitly stated in the text. However, although Melloni gave more data than Leslie, Stewart did not mention him. As a matter of fact, in a textbook on physics from 1837, *The Elements of Physics* by Webster, T., Scott, Webster, and Geary Pub., London, 1837, it is stated that, *in a state of equilibrium*, *the absorbing power is always equal to the radiating power* (p. 257).

[46] The coefficient of proportionality is given by the radiation density at equilibrium. See later.

[47] Stewart, B., *Researches on radiant heat*, Trans. R. Soc. Edinb. **XXII**, Part I, 59 (April 1859).



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.

Fig. 2.8 The tools used by Stewart in his radiant heat experiments. Note in particular item *A*, the sensitive detector of radiation (Stewart 1858)

thermometer increased somewhat less rapidly with temperature than that of a silvered thermometer. Dulong and Petit found no difference between the two.

The experiment on how plates of different thickness cool inspired Stewart to comment in the following way:

> 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. [...] We have thus ascertained first that Dulong and Petit's law is not the law of radiation of a material particle, and second that this law increases less rapidly with the temperature than Dulong and Petit's law.

Stewart could not do better because his apparatus was not in vacuum, and heat conduction and convection by air constituted non-negligible cooling processes.

Furthermore, Stewart found 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.

He also defined 'perfectly black bodies', or 'black bodies' for short, as bodies which *completely absorb all rays which fall upon them*, and the substance which was the best approximation for a black body was found experimentally to be lampblack.[48] At the end of the second paper, Stewart reached a pessimistic conclusion:

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[48] Note that lampblack is a perfect absorber in the infrared and was not really tested in the visible. However, in the visible, it has a black color. Colors have no meaning in the infrared as we cannot see in the infrared. So the term 'black body' really emerged from an object which behaved in the infrared as a perfect absorber and emitter, but has a black color in the visible range. Put another way, the name arose from an irrelevant property of the body, because it could have had any color in the visible.

> I am therefore induced to think that it is nearly hopeless to attempt to ascertain the true law of radiation of a material particle, as 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.

Note that Stewart's second paper[49] came out just after Kirchhoff published his first paper on the subject (see later), but Stewart was certainly unaware of Kirchhoff's results when he wrote the paper, and vice versa. Kirchhoff's first paper was read before the Berlin Academy in 1859[50] and published a few months later in the Ann. Phys. It was only in 1860 that the paper was translated into English and published in the Philosophical Magazine.

2.6 Kirchhoff's Law

During the years 1859–1860, Gustav Kirchhoff (1824–1887m) by himself and Kirchhoff together with Robert Bunsen made three independent major discoveries. Kirchhoff explained how the Fraunhofer lines form[51] (see Sect. 2.7) and proved his radiation law,[52] while Kirchhoff and Bunsen[53] promoted the idea of spectral analysis as a tool for identifying chemical elements and even certain compounds.

Kirchhoff proved that:

> The ratio between the emissive and the absorptive power is the same for all bodies at the same temperature in thermal equilibrium.

Note the additional clause 'at the same temperature'. Kirchhoff proved the law first for black bodies and then for general bodies. We describe these seminal discoveries in a logical rather than historical order, so as to emphasize the importance and explain the logic.

Kirchhoff's proof, like Stewart's, hinges on the assumption that there exist bodies which absorb and radiate energy only in a certain restricted wavelength range. In addition, the proof requires the assumption that perfect diathermanous substances exist.[54] The point would arise some thirty years later.

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[49] Stewart, B., Proc. R. Soc. Lond. **10**, 385 (1859–1860).

[50] Kirchhoff, G., Monat. der König. Preussischen Akad. der Wissen. Berlin, October, 1858.

[51] Kirchhoff, G., Ann. Phys. **184**, no. 12, 567 (1859); ibid. Ann. Phys. **185**, no. 1, 148 (1859).

[52] Kirchhoff, G., Ann. Phys. **185**, no. 2, 275 (1860); ibid. Ann. Physik und Chemie **CIX**, 6, 275 (1860); ibid. Ann. Chim. Phys. **LXII**, 3, 160 (1861).

[53] Kirchhoff, G. and Bunsen, R., Ann. Phys. und Chemie **CX**, 6, 161 (1860); ibid. **CXIII**, 7, 337 (1861); ibid. Ann. Chim. Phys. **LXII**, 3, 452 (1861); ibid. **LXIV**, 3, 257 (1862).

[54] Diathermanous means permeable by heat waves, so it describes a body which transmits heat as electromagnetic radiation. The term was apparently invented by Melloni somewhere between 1830 and 1840. Melloni proposed to use 'diathermanous' for bodies that let heat pass easily, and athermanous for those that do not let heat pass. However, see W.D.L.L. Nature **7**, 242 (1873). In general, transparency in the visible and the property of being diathermanous are not related.

When heated, every chemical element or compound emits a set of emission lines and/or continuum radiation. The wavelengths at which these emission lines appear are characteristic of the chemical element. They are like a fingerprint of the element. Hence, we can say that the emission E is given by

$$E = \begin{cases} E(\lambda, T, \text{chemical composition}), & \text{for } \lambda = \lambda_i, \\ 0, & \text{for } \lambda \neq \lambda_i, \end{cases}$$

where the λ_i form a set of wavelengths corresponding to emission lines. Consequently, the spectral lines λ_i can be used for chemical identification. There was no theoretical proof that two different chemical elements cannot have the same set of emission lines. By tedious careful analysis of all known chemical elements and by cataloging the observed spectral lines, it was found empirically that each element has its own series of emission lines. Clearly, it was not known why there are spectral lines and not say, a continuum, let alone what determines the wavelengths of the lines. The question as to why there are lines was not asked in those days, and there was no hypothesis as to their origin. Only when quantum theory was invented and developed was it proven that the spectral lines are unique to each element.

Kirchhoff carried out the following experiment. He first observed the continuum radiation emitted from a very bright source, and then he observed the emission lines λ_i emerging from a faint source. Lastly, he placed the faint source in front of the bright source and discovered that the emission lines in the faint source became dark exactly at the positions λ_i, like Fraunhofer lines at the locations λ_i. There was no case in which one of the Fraunhofer lines did not correspond to an emission line and vice versa.

Kirchhoff formulated the result of the experiment by stating that, when you place a cooler gas in front of a hot one, the spectrum of the cooler gas is 'reversed', i.e., instead of an emission spectrum it becomes an absorption spectrum. The reversal phenomenon of spectral lines (reversal from emission into absorption) was, according to Kirchhoff, the origin of the Fraunhofer lines. This explains why the term 'reversing layer' is used with reference to the solar atmosphere. The hot solar interior is covered by a cooler atmosphere, and the Fraunhofer lines are formed in the cooler atmosphere, or 'reversing layer'. Note that we write 'cooler' rather then 'cold', because the gas may be at a high temperature and emit radiation itself, but it has to be at a lower temperature than the gas behind it.

The possibility of reversing the spectrum of a gas implied that the absorption a could be written as

$$a = \begin{cases} a(\lambda, T, \text{chemical composition}), & \text{for } \lambda = \lambda_i, \\ 0, & \text{for } \lambda \neq \lambda_i. \end{cases}$$

In other words, the absorption takes place at the wavelengths λ_j, and depends on the temperature and the identity of the matter. As the absorption spectrum is the reversed emission spectrum created under unique conditions, it is clear that it can also be used to identify chemical elements. The idea of 'reversing the spectrum' means that

$$\begin{aligned}&E(\lambda=\lambda_j, T, \text{chemical composition})\\&\quad=\alpha(\lambda, T)a(\lambda=\lambda_j, T, \text{chemical composition}),\end{aligned}$$

where $\alpha(\lambda, T)$ is some function of wavelength and temperature. Most importantly, the set of emission lines is identical to the set of absorption lines. What the above formula says is that the positions of the emission lines are identical to the positions of the resulting Fraunhofer lines, but the power of the emission is not necessarily equal to the power of the absorption. This is why α appears in the formula. It is impossible for an emission line to disappear in the reversed spectrum and vice versa. All emission lines are reversed and appear as Fraunhofer lines. This relation does not require equilibrium conditions.

In the words of Kirchhoff and Bunsen:

> Within the spectrum, an element absorbs the light at the exact location of the lines which it can emit.

They stated the basic law of elementary spectrometry which is:

> Each element has specific properties as regards the light it emits.

While the emission power (how much energy is emitted per unit time) of the gas depends on the wavelength, temperature, and composition, the absorption power (how much energy is absorbed per unit time) depends on the same parameters, and in addition the intensity of the radiation $J(\lambda)$. The total power absorbed by the gas is therefore given by

$$A = J(\lambda)a(\lambda = \lambda_j, \ldots, T, \text{chemical composition}).$$

In 1858, Stewart, following Leslie and Melloni, carried out experiments which showed that, in thermal equilibrium,

$$\begin{aligned}\text{total emission power} &\equiv \int E(\lambda = \lambda_j, T, c)\mathrm{d}\lambda\\&= \int J(\lambda)a(\lambda = \lambda_j, T, c)\mathrm{d}\lambda = \text{total absorption power},\end{aligned}$$

where c means ‘composition’. The integration is carried out over all wavelengths. The function $J(\lambda)$ did not appear explicitly in Stewart’s paper, but its existence was implied. The result makes a lot of sense. If more power were absorbed than emitted, the object would heat up, and vice versa. All the experiments implied was that the total power of emission and absorption, and not the power absorbed/emitted in a given spectral line, were equal. It was only in their theoretical proofs that Stewart and Kirchhoff established that the integral signs can be removed, whence, in thermal equilibrium,

$$E(\lambda = \lambda_j, T, c) = J(\lambda)a(\lambda = \lambda_j, T, c).$$

Kirchhoff's dramatic and momentous discovery was that, in thermal equilibrium,

$$\frac{E(\lambda = \lambda_j, T, \text{composition})}{a(\lambda = \lambda_i, T, \text{composition})} = J(\lambda_j, T) \equiv e(\lambda_j, T),$$

where $e(\lambda, T)$ is a universal function that does not depend on the material involved. The formula states that the emission at wavelength λ_j divided by the absorption at the same wavelength is given by a universal function $e(\lambda, T)$ evaluated at $\lambda = \lambda_j$. The function $e(\lambda, T)$ is the spectral distribution of the radiation in equilibrium. It is the same function for all materials, provided there is thermal equilibrium.

Let us formulate it slightly differently. The emission of the body depends only on its temperature. On the other hand, the absorption of the body depends on the temperature. However, the absorption power is a product of the properties of the matter and the incident radiation. It is the incident radiation as well as the emission which have, in the case of equilibrium, a universal shape and distribution. Kirchhoff realized how important the function $e(\lambda, T)$ is, but was unable to derive it theoretically because Maxwell's theory of light had not yet been born. Note that the law does not specify the temperature dependence of $E(\lambda = \lambda_j, T, c)$ or $a(\lambda = \lambda_j, T, c)$, but only the ratio between them.

Let us now cross the bridge before coming to it. Forty years later, Max Planck (1858–1947m) discovered the exact form of the function $e(\lambda, T)$, and it is usually denoted in present day textbooks by $B_\nu(T)$, and called the Planck function. In addition to the classical electromagnetic theory of light, the theoretical derivation of this function requires the fundamental assumption of quantum theory, namely the quantization of energy, and it thus opened the gate to quantum mechanics. In the view of the present author, it would be better called the Kirchhoff–Planck function, as Unsöld and Baschek do.[55]

About a year after publishing the first proof of his law, Kirchhoff published a second and more rigorous one.[56] The basic idea of the law emerged from general thermodynamic considerations. Kirchhoff's result was truly astonishing: why should all materials behave in the same way? The reason is that, in thermodynamic equilibrium, there is only one solution for the radiation field, irrespective of the materials out of which the enclosure is made. In stars, we define local thermodynamic equilibrium or LTE to be a situation in which the gas is in equilibrium with the radiation at a given point. Thus, whenever there is LTE in stars, and one can show that this assumption holds perfectly in the stellar interior, the distribution of the radiation field is $B_\nu(T)$. Naturally, such a sweeping discovery resulted in commotion, not so much about the validity of the result as about the priority of the discovery.

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[55] Unsöld, A. and Baschek, B., *The New Cosmos*, 4th edn., Springer, 1991.

[56] Kirchhoff, G., Ann. Chim. Phys. **67**, 160 (1861).

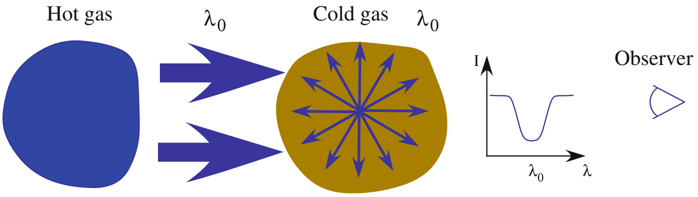

Fig. 2.9 The setup which leads to a reversed spectrum

2.7 A Modern Physical Explanation for the Reversal Phenomenon

Consider a hot gas which emits a continuum. Next consider the photons at wavelength λ_0, the wavelength at which the cold gas absorbs. Assume for simplicity that this is the only wavelength at which the cold gas absorbs.[57] Thus, the strong flux of radiation is absorbed by the cold gas. But the cold gas cannot absorb forever and must eventually re-emit the radiation. The emission takes place in all directions. Ignoring for a moment stimulated emission (to be discussed later), the atom forgets the original direction of the photon it absorbed and emits the newly born photon in any direction without preference. Consequently, the original intensity of the radiation is distributed in all directions and the intensity in the original direction, the direction of the observer, is reduced. When compared with the radiation intensity in wavelengths adjacent to λ_0, where no absorption took place, the intensity in $\lambda = \lambda_0$ is lower and hence appears darker, or more accurately, less bright. This is the Fraunhofer line. It is not that there is no radiation at all at this wavelength, but rather that it is significantly weakened in relation to the absorption/emission power of the hot gas.

The detailed process is more complicated than the above simple explanation and requires solution of the radiative transfer equation in which Kirchhoff's law plays a central role. The radiative transfer equation was not known in Kirchhoff's day, and nor was the atomic physics and detailed structure of the atomic levels, whose difference determines the wavelengths of the spectral lines. Moreover, the shape of the line, which appears very wide in the figure, is in fact quite narrow, and the details of its shape provide valuable information about the physical conditions under which the particular line formed. In the Sun, for example, not all lines form at the same location. A very strong line, which implies high absorption, forms high up in the atmosphere because a small amount of matter (counting from outside) is needed for its formation. On the other hand, a weak line requires a large amount of matter, and hence forms deeper in the star. By comparing the shape and intensity of various lines, the detailed temperature run can be traced through the outer layers of the star (Fig. 2.9).

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[57] This approximation is called the two-level atom. This simplification, which is frequently used even today, was introduced by Milne, E.A., J. Lond. Math. Soc. **1**, 40, 1926.

2.8 Could the Coincidence Be Fortuitous?

Could the coincidence between the Fraunhofer dark lines and the bright emission lines emitted by the heated elements be fortuitous? Kirchhoff calculated, from the number of coincidences he found and from the degree of exactitude with which each coincidence could be determined, that the fraction of chance agreements was less than 10^{-18}. In other words, it was practically certain that these lines had a common origin. And if this were not sufficient, Kirchhoff pointed to the fact that the characteristic lines of elements occurred in groups, which of course appeared as such in the spectra of the Sun. Once quantum theory became available, it was found that the locations of the lines were not accidental but unique to every atom.

2.9 The Priority Debate

So much for the physics behind one of the most important laws in radiation theory. Soon after the German publication of Kirchhoff's radiation laws, several English scientists started to question, not Kirchhoff's scientific results, but the priority in his discoveries. The pages of the 1860 London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science (with Brewster as one of the editors) **20**, July–December 1860, are testimony to the priority dispute, and contain practically no controversy about the physical content.

All sorts of priority claims were raised against Kirchhoff, which were tantamount to plagiarism: that 'Kirchhoff's law' was discovered first by Stewart; that several English researchers had long since proposed spectroscopic analysis as a tool for identification of chemical elements; and that the explanation of the way the Fraunhofer lines form was also put forward before Kirchhoff announced his own explanation.

2.10 The Radiation Law

The controversy over the priority for the proof of the radiation law took place directly between Stewart and Kirchhoff. Although Stewart discussed 'radiant heat' and Kirchhoff discussed 'visible light', they arrived at the same law (except for the clause about the temperature). So who had the priority? Once the dispute had come out into the open, Kirchhoff tried to establish his priority in the Annalen der Physik[58] and Stewart responded in the Philosophical Magazine.[59] In many textbooks today, Kirchhoff is credited with the priority, probably because Kirchhoff provided what was considered to be a more rigorous mathematical/physical proof of the law, while Stewart reasoned in a largely logical way and merely described the law.

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[58] Kirchhoff, G., Ann. Phys. **194**, 94 (1862). The English translation is: Phil. Mag. **25**, 250 (1863).

[59] Stewart, B., Phil. Mag. **25**, 354 (1863).

Kirchhoff began the 1860 de facto reprint in English[60] of the paper first published in German with the following statement:

> A body placed within a covering whose temperature is the same as its own, is unaffected by radiation and must therefore absorb as many rays as its emits.

For the experimental verification, Kirchhoff cited de la Provostaye and Desains,[61] claiming that:

> This was proved for bodies emitting rays of one kind.[62]

But Kirchhoff stressed that:

> Whether the same law holds good when bodies emit rays of different kinds, has never hitherto been determined theoretically or by experiment.

Kirchhoff then argued that:

> The ratio of the radiating and absorbing powers of all bodies at the same temperature is the same.[63]

It is here that Kirchhoff defines the 'perfectly black' body as the perfect absorber. Years later, Wien[64] would redefine it more precisely and call it a black body, which is the term used today.

At the end of the paper, in a postscript, Kirchhoff turned to the argument over priority, writing:

> After the appearance of my paper in the Pogg. Annalen, I received information of a prior communication closely related to my own. The communication in question is by Mr Balfour Stewart […]. The principle enunciated by Mr Stewart is, however, less distinctly expressed, less general, and not altogether so strictly proved as mine.

It is not difficult to imagine that this statement by Kirchhoff did not appease his rivals. Note that Kirchhoff himself was not happy with his first proof (the subject of the priority dispute) and provided another proof. As for Stewart, the proof he gave

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[60] Kirchhoff, G., Phil. Mag. Sect. 4, **20**, 1 (1860).

[61] Kirchhoff wrote that de la Provostaye and Desains did the experiment, but did not provide any published reference. I suspect that he meant: de la Provostaye, F., and Desains, P., Ann. Phys. **150**, 147 (1848), which was a translation from Compt. Rend. **XXVI**, 212 (1848).

[62] Kirchhoff mentions that, in the case of de la Provostaye and Desains, the rays were invisible, while he discussed visible light. The conclusions were nevertheless the same. In 1868, Desains wrote a review about French scientific achievements in *La Théorie de la Chaleur* and did not mention any 'rays of heat'.

[63] Kirchhoff also argued incorrectly as follows: *The wavelengths which correspond to maxima of the radiating and absorbing powers are*, *as will be fully explained in another place*, *altogether independent of the temperature*. This was before the discovery of Wien's displacement law, which is a relation between the temperature of a black body and the wavelength at which its emission power reaches maximum. The existence of such a law became clear once the shape of the spectral distribution had been found. Such a law had been suggested earlier by Wilhelm Weber (1804–1891) in his 1888 paper.

[64] Wien, W., Ann. Phys. **288**, 132 (1894).

in his book, published in 1866,[65] was also a new proof which relied on more general equilibrium considerations. We can summarize this dispute by stating that it began as a controversy about the rigour of the proofs, which was very quickly relinquished. The experimental evidence and the hypothesis for the law belong to Leslie almost fifty years earlier (or even Haüy slightly earlier). It was, however, Kirchhoff's analysis as a theoretical physicist that led to the formulation in terms of a universal function, and that was the wonderful physical essence of the law.

But this conclusion was not universally accepted. As late as 1901, Rayleigh (1842–1919)[66] raised the issue again. Rayleigh, in his fight for the priority of Stewart, admitted that the experiments did not strictly demonstrate what Stewart's conclusion implied. Yet the theoretical proof according to Rayleigh was perfect and no less rigorous than Kirchhoff's. Rayleigh's argument did not convince the entire community, and in 1902, Heinrich Kayser (1853–1940)[67] continued to argue that Stewart's proof was *not a strict demonstration*. However, Kayser did not supply an alternative proof which would be to his satisfaction.

The zeal to protect Stewart's priority continued even as late as 1925, by which time both Stewart and Kirchhoff had met their maker (both passed away in 1887). At this point, Arthur Schuster (1851–1934m) published an article in Nature *which may possibly leave with the ordinary reader an impression that Balfour Stewart's contributions to the establishment of the laws of natural radiation were slighter than was actually the case*. Larmor[68] immediately volunteered to straighten things out. What Larmor did was to direct the reader to Rayleigh's earlier discussion. The interesting fact, which tells us something about how high feelings were running, is that Schuster's article was published on 17 January and the letter Larmor wrote to the editor of Nature was dated 16 January. Note in this respect that Schuster was a German-born English physicist. He became an English citizen in 1875.

2.11 Stewart in Retrospect

In 1866, Stewart published the above-mentioned Rumford Medal winning book about 'Heat' and it is interesting to see his final remark on the subject. Stewart clearly had a hunch about Wien's law when he wrote:

> We have reasons to believe that as the temperature rises the spectrum of a black substance is extended in the direction of greatest refrangibility, so as to embrace more and more of the violet and photographic rays.

This should be contrasted with Kirchhoff's incorrect statement about the effect of the temperature of a body on its color. The formulation of the famous law was now:

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[65] Stewart, B., *An Elementary Treatise on Heat*, Clarendon press, Oxford, 1866.

[66] Rayleigh, Lord, Phil. Mag. **6**, 1, 98 (1901); *Scientific Papers* **4**, 494.

[67] Kayser, H., *Handbuch der Spectroscopie*, Hirzel, Leipzig, 1900.

[68] Larmor, J., Nature **115**, 159 (16 January 1925).

> In an enclosure of constant temperature the heat reflected plus the heat radiated by any substance will be equal to the total lampblack radiation of that temperature.

So Kirchhoff's clause was added.

In Chap. II, in his discussion of the 'theory of exchange' on p. 199, Stewart wrote simply:

> This theory, since its proposal by Prévost, has been developed by Provostaye and Desains, and more recently by the author of this work and by Kirchhoff. [...] Bunsen and Kirchhoff, who have done much more than any one else to introduce and perfect this method of analysis.

Stewart, a man of honor, paid tribute to Kirchhoff:

> Before concluding this chapter we ought to allude to the beautiful discovery of Kirchhoff, by which it has been proved that substances with which we are here familiar exist also in the atmospheres of the Sun and stars.

Regarding the Fraunhofer lines, Stewart stated that:

> The inference naturally drawn from this experiment was that the lines of the solar spectrum do not denote rays originally wanting in the light of the Sun, but are due to the absorption of his light by some substance interposed between the source of light and the spectator. It was doubtful, however, whether this stoppage of light occurred in the atmosphere of the Sun or in that of our Earth, until the matter was finally settled by Kirchhoff, not however before the true explanation had been divined by Professor Stokes.

Stewart did not and could not give a reference to Stokes' discovery, because such a reference does not exist (see later).

2.12 Who Discovered the Source of the D_2 Lines?

Several of Kirchhoff's critics and quite a few textbooks claim that Foucault preceded Kirchhoff in identifying the *D* line of sodium in the spectrum of the Sun. Regarding this point, Kirchhoff wrote (see Fig. 2.10):

> The fact that the bright lines of the spectra of sodium and lithium flames may be reversed, was first published by me in a communication to the Berlin Academy, October 27, 1859. This communication is noticed by M. Verdet in the February number of the Ann. de Chim. et de Phys. of the following year, and is translated by Prof. Stokes in the March number of the Philosophical Magazine. The latter gentleman calls attention to a similar observation made by M. Leon Foucault eleven years ago, and which was unknown to me, as it seems to have been to most physicists. This observation was to the effect that an electric arc between charcoal points behaves, with respect to the emission and absorption of rays of refrangibility answering to Fraunhofer's line *D*, precisely as the sodium flame does according to my experiment. The communication made on this subject by M. Foucault to the Soc. Philom. in 1849 is reproduced by M. Verdet, from the Journal de l'Institut, in the April number of the Ann. de Chim. et de Phys.

He went on to say:

> Foucault's observation appears to be regarded as essentially the same as mine; and for this reason I take the liberty of drawing attention to the difference between the two.

Fig. 2.10 The typical voltaic arc used by Foucault, in which electrical sparks gave rise to spectra with *D* lines

FIG. 33.
Voltaic Arc.

Foucault discussed cold electric discharges while Kirchhoff discussed flames. We know today, but not in Kirchhoff's times, that the excitations of the gas which lead to the formation of the observed lines are different. And so alleged Kirchhoff:

> M. Foucault's observation does not afford any explanation of mine, and could not have led to its anticipation. My observation leads necessarily to the law which I have announced with reference to the relation between the powers of absorption and emission; it explains the existence of Fraunhofer's lines, and lead the way to the chemical analysis of the atmosphere of the Sun and the fixed stars. All this M. Foucault's observation did not and could not accomplish, since it related to a too complicated phenomenon, and since there was no way of determining how much of the result was due to electricity, and how much to the presence of sodium. If I had been earlier acquainted with this observation, I should not have neglected to introduce some notice of it into my communication, but I should nevertheless have considered myself justified in representing my observations as essentially new.

Foucault did apparently challenge Kirchhoff. It seems that Foucault's attention was focused on his experiments about the speed of light.

In view of the controversy about the priority of Kirchhoff's laws, Foucault's work was republished in 1860[69] and later translated in the Philosophical Magazine, publications which did not change the general perception that Foucault's experiment was different from Kirchhoff's, and no general conclusion was drawn.

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[69] Foucault, L., Ann. Chim. Phys. **58**, 476 (1860).

According to Kirchhoff, he knew about the previous attempts to correlate the sodium emission line with the Fraunhofer *D* line, and wanted to either confirm or disprove the connection. However, he gave a reference to Swan 1857. Swan in turn, gave a reference to Auguste-Arthur de La Rive (1770–1834),[70] who wrote about Foucault's identification of the *D* line of sodium as early as 1849. Kirchhoff knew about the work of de la Provostaye and Desains[71] in which they discussed the issue.

2.13 Kelvin and the Reversal Phenomenon

Several times for too many years, William Thomson (1824–1907m), who later became Lord Kelvin, raised the priority issue concerning the discovery of the reversal of the spectrum. Thomson was a celebrity thanks to his contributions to thermodynamics (the second law), his theory about the energy of the Sun, the controversy with Darwin, and the dispute with the entire community of geologists about the age of the Earth.[72]

In his presidential address to the British Association in 1871,[73] Lord Kelvin stated his belief that the application of *prismatic analysis*[74] of light to stellar chemistry had never been suggested directly or indirectly by anyone when George Stokes (1819–1903m) taught it to him at Cambridge University, some time prior to the summer of 1852, and he set forth the conclusions, theoretical and practical, which he learnt from Stokes at that time, and which he afterwards gave regularly in his public lectures in Glasgow. And so wrote Kelvin:

> Professor Stokes mentioned to me at Cambridge some time ago (it was probably 1851 when Stokes apparently discussed a possible solution for the Fraunhofer lines), probably about ten years, that professor Miller had made an experiment testing to a very high degree of accuracy the agreement of the double dark line *D* of the solar spectrum with the double bright line constituting the spectrum of the spirit-lamp burning with salt. I remarked that there must be some physical connexion between two agencies presenting so marked a characteristic in common. He asserted, and said he believed a mechanical explanation of the cause was to be on some such principles as the following: vapours of sodium must possess by its molecular structure a tendency to vibrate in the period corresponding to the degree of refrangibility of the double line *D*. Hence the presence of sodium in a source of light must tend to originate

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[70] De La Rive, A.-A., *A Treatise on Electricity*, London, Longman, Green, and Longman, 1853.

[71] de la Provostaye, F.H., and Desains, P., Compt. Rend. **38**, 977 (1854).

[72] Kelvin was famous for many provocative statements which turned out later to be wrong, in particular in the discussion with Darwin. See Shaviv, G., *The Life of Stars*, Springer, 2009.

[73] Thomson, W., MacMillan's Magazine, March, 1862, and Rep. Br. Assoc. **3**, 27 (1871).

[74] Kelvin used the term 'prismatic analysis' rather than 'spectroscopic analysis' to refer to spectroscopic analysis by means of a prism. Today, spectroscopic analysis can be better carried out with a grating. The first to construct and apply a grating was David Rittenhouse (1732–1796) in 1785, followed later by Fraunhofer in 1821. However, the prisms were still better in those days. The priority of Rittenhouse in the use of a grating was established by Babb as late as 1932. See Cope, T.D., J. Frank. Inst. **214**, 99 (1932). It was not until 1873 that Friedrich Nobert (1806–1881) perfected the grating to reach 9,000 lines per millimeter and eventually produce a superior resolution to prisms.

> light of that quality. On the other hand, vapours of sodium in an atmosphere round a source, must have a great tendency […] to absorb and to have its temperature raised by light from the source, of the precise quality in question. In the atmosphere around the Sun, therefore, there must be present vapours of sodium. […] I have the impression that some Frenchman did make this out by experiment, but I can find no reference on the point.

And he continued:

> I am not sure whether professor Stokes's suggestion of a mechanical theory has ever appeared in print. I have given it in my lectures regularly for many years always pointing out along with it that solar and stellar chemistry were to be studied by investigating terrestrial substances giving bright lines in the spectra of artificial flames corresponding to the dark lines of the solar and stellar spectra.

Kelvin claimed that:

> Although Professor Stokes unfortunately did not publish his theory (I say unfortunately because valuable time has been lost), the world was not long in ignorance of a matter of such general interest, for in 1853 the idea was published by the celebrated Ångström[75] who found that in many cases the Fraunhofer lines were an inversion of bright lines which he observed in the spectra of various metals.[76]

Kirchhoff's reply to Kelvin's letter does not appear in the paper. In any case, Stokes' ideas were apparently considered by him not to merit publication. On the other hand, this phenomenon later became the cornerstone of stellar spectroscopy. So the least one can say is that Kirchhoff recognized the impact of his discovery.

Not long afterwards, Whitmell,[77] who had been watching the ongoing controversy, obtained Stokes' consent to publish in Nature a letter that Stokes had written to him. And so wrote Stokes:

> Hence the sodium compounds […] are transparent […] and the absorbing vapour was that of sodium itself. Knowing the powerful affinities of sodium, I did not dream of its being present in a free state in the flames of a spirit lamp.

Stokes was confused by the signals from the molecule of salt (NaCl) and from the sodium atom. Finally, Stokes concluded his letter to Whitmell with:

> Reviewing my then thoughts by the light of our present knowledge, I see that my error lay in the erroneous chemical assumption that sodium could not be free in the flame of a spirit-lamp; I failed to perceive the extension of Prévost's theory, afterwards discovered by Stewart, nor perceived that the emission of light of definite refrangibility necessitated (and not merely permitted) absorption of light of the same refrangibility, which would have come in conflict with that error.

Stokes added to his letter to Whitmell a description of the conversation he had with Kelvin:

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[75] Ångström, A.J., Optiska Undersokningar, Trans. R. Acad. Stockholm, 1853. Translated in Phil. Mag., fourth series, v, **IX**, 327.

[76] See Phil. Mag., fourth series, **XXIV**, 2, 3: Monatsberichte Akad. Wissen. Berlin, 1859, p. 662.

[77] Whitmell, C.T.L., Nature, p. 188 (January 1876).

> I mentioned to him [Kelvin] the perfect coincidence of bright and dark *D* [...] and described it using the dynamical illustration of the piano string. [...] I mentioned also, on authority of Sir David Brewster, another case of coincidence. [...] On hearing this Kelvin said something like: "Oh then, the way to find what substances are present in the Sun and stars is to find what substances give bright lines coincident with the dark lines of those bodies." I thought he was generalising too fast. [...] If, as I take it for granted, Kelvin is right as to the dates [1852] when he began to introduce the subject into his lectures at Glasgow [...] he must be mistaken as to the time when I talked with him about Foucault's discovery, for I feel sure I did not know it till 1855.

A most interesting remark by Stokes is:

> I have never attempted to claim for myself any part of Kirchhoff's admirable discovery, and cannot help thinking that some of my friends have been over zealous in my cause. As, however, my name has frequently appeared in print in connection with it, I have been induced to put on paper a statement for the views I entertained and talked about, though without publishing. In ascribing to Stewart the discovery of the extension of Prévost's law of exchange, I do not forget that it was rediscovered by Kirchhoff, who, indeed, was the first to publish it in relation to light, though the transition from radiant heat to light is so obvious that it could hardly fail to have been made, as in fact it was made, by Stewart himself. Nor do I forget that it is to Kirchhoff that we owe the admirable application of this extended law to the lines of the solar spectrum.

We are left to admire Stokes' academic honesty. As a matter of fact, Stokes had so many diamonds in his crown of discoveries that he did not need an additional one.[78]

As a matter of fact, Kelvin argued in favor of his compatriot Stokes, and in his zeal overlooked the priority of his fellow countryman and other English scientists like Brewster, who had identified even earlier[79] many lines that appeared in flames with lines that appeared in the solar spectrum. Obviously, Brewster could not have identified all the lines in the solar spectrum because he did not have the data on the spectra of many elements. Even so, Brewster concluded that the phenomenon was universal long before Swan clinched the identification of the *D* line with sodium.

As late as 1857, Swan[80] published a work on the spectra of carbon compounds. These compounds have a very large number of spectral lines and some coincided with solar lines (at least within the accuracy of the measurements). But Swan nevertheless concluded that the explanation for the reversal was not correct.

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[78] Irony of fate, there exists a Kirchhoff–Stokes equation for sound attenuation. The name was given after both heroes had passed away. Kirchhoff, who is mostly known for his work on electricity and radiation, derived a formula for the absorption of sound due to conduction (Kirchhoff, G., Ann. Phys. **134**, 177, 1868) which is similar to the formula for viscosity deduced by Stokes (Stokes, G.G., Phil. Mag. **I**, 305, 1851) several years earlier.

[79] Brewster, D., Rep. Br. Assoc. **11**, 15 (1842).

[80] Swan, J.W., *On the Prismatic Spectra of the Flames of Compounds of Carbon and Hydrogen*, Royal Society of Edinburgh. Transactions, 1857.

2.14 Kirchhoff's Rebuttal

No doubt, Kirchhoff's proof was more complete than the one given by Stewart. This led Stewart to write to the editor Brewster and pose the dilemma: to what extent should priority go to the first who discovers a law or to the one who provides the more accurate proof? A problem that exists even today when it comes to attributing credit.

According to Kirchhoff,[81] Talbot had already guessed in 1826[82] that there was a connection between a substance and its spectral lines, but careful reading reveals that Kirchhoff did Talbot a great favor in this statement, because Talbot's papers contained many other hypotheses that were later found to be wrong.[83] Herschel on the other hand discussed the Fraunhofer lines in 1836,[84] but did not mention 'such a fantastic idea' of using the spectral lines for chemical analysis of stars. Could it be that Herschel actually missed this great idea?

A letter Kirchhoff wrote to Erdmann was transferred by the addressee to Roscoe.[85] And so reads the letter:

> The Sun possesses an incandescent gaseous atmosphere, which surrounds a solid nucleus having a still higher temperature. If we could see the spectrum of the solar atmosphere, we should see in it the bright bands characteristic of the metals contained in the atmosphere, and from the presence of these lines should infer that of these various metals. The more intense luminosity of the Sun's solid body, however, does not permit the spectrum of its atmosphere to appear, but reverses it, according to the proposition I have announced. So instead of the bright lines which the spectrum of the atmosphere by itself would show, dark lines are produced. Thus we do not see the spectrum of the atmosphere, but we see a negative image of it. This, however, serves equally well to determine with certainty the presence of those metals which occur in the Sun's atmosphere.

A statement valid even today.

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[81] Kirchhoff, G., Pogg. Ann. **118**, 94 (1863).

[82] Talbot, W.H.F., Edinb. J. Sci. **5**, 77 (1826). Talbot discusses experiments carried out by Herschel.

[83] Talbot claimed that the *D* line was due to sulphur and sodium salt. He was correct about the contribution of the sodium to the line, but wrong about the sulphur. Moreover, if two elements can produce the same line, then the lines cannot be used to identify elements.

[84] Herschel, J.F.W., *A Treatise on Astronomy*, 3rd edn., Carey, Lea & Blanchard, Philadelphia, 1835.

[85] Roscoe forwarded part of the letter to the Editor of the Philosophical Magazine and Journal, on 1 February 1860, and wrote: *As it gives a later account of Kirchhoff and Bunsen's most important researches than has yet appeared in the English journal*, *I think it may be of interest to you and to your readers*. […], *signed*: *Henry E. Roscoe*.

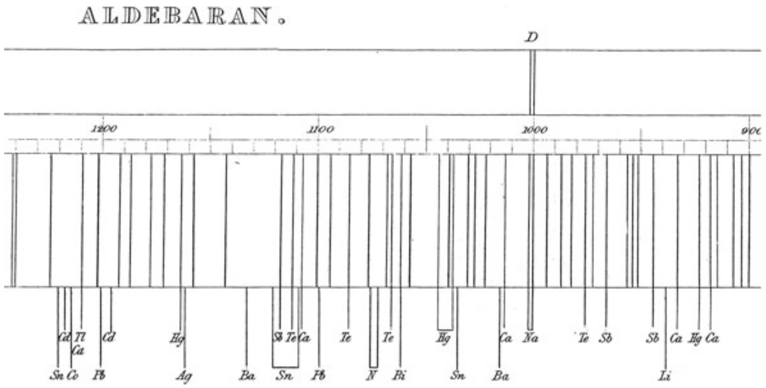

Fig. 2.11 The first ever spectra of the bright star Aldebaran taken by Huggins and Miller, 1862. At the *top* is the spectrum of sodium for comparison, while *below* are the identifications of the spectral lines of metals

2.15 Huggins' Particular View: How Stellar Spectroscopy Came into Being

In 1897, Huggins described how he started stellar spectroscopy in 1864[86]:

> It was just at this time [in 1862] that I happened to meet at a soirée of the Pharmaceutical Society, where spectroscopes were shown, my friend and neighbour, Dr. W. Allen Miller, Professor of Chemistry at King's College, who had already worked much on chemical spectroscopy. A sudden impulse seized me to suggest to him that we should return home together. On our way home I told him of what was in my mind, and asked him to join me in the attempt I was about to make, to apply Kirchhoff's methods to the stars. At first […] he hesitated as to the probability of our success. Finally he agreed to come to my observatory on the first fine evening, for some preliminary experiments as to what we might expect to do upon the stars.

This is the story of the beginning of a long-standing friendship and collaboration, and it probably explains why Huggins felt compelled to defend Miller's priority in using spectral analysis for chemical identification (Fig. 2.11).

The relevant part for the priority Huggins claimed for Miller (1817–1870m) is based on what Miller[87] himself wrote in 1845, namely:

> It may be interesting to remark, in connexion with the speculation on the absorptive action of the Sun's atmosphere, that if solar light be transmitted through a flame exhibiting well-marked black lines, these lines reappear in the compound spectrum, provided the light of day be not too intense compared with that of the coloured flame: this may be seen in the red light of the nitrate of strontia, and less perfectly in the green of chloride of copper. It would therefore be that luminous atmospheres exist in which not only certain rays are wanting, but which exercise a positive absorptive influence upon other lights.

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[86] Huggins, W., *The New Astronomy*, *A Personal Retrospect*, The Nineteenth Century **41**, 911 (1897).

[87] Miller, W.A., Phil. Mag. III, 27, p. 81, 1845.

The grounds for Huggins' claim are not very convincing. If the discovery was already so deeply appreciated, then why there were no follow-up papers?

In his influential textbook, the second edition of which appeared in 1860,[88] just before he met Huggins and before he embarked on his prolonged research on stellar composition, Miller addressed the problem of the Fraunhofer lines in the spectra of stars, writing:

> These lines are independent of the nature of the refracting medium, and occur always in the same colour, and at corresponding points of the spectrum.

While admitting their usefulness for opticians in accurately determining a substance's index of refraction, Miller added:

> No satisfactory explanation has yet been found for the cause of this phenomenon.

His long-standing interest in the Fraunhofer lines should have made Miller more receptive than most to the news of Kirchhoff's theory regarding their cause, but there was no mention of the new discoveries in his book.

2.16 Lockyer 1887: The Chemical Composition of the Sun

In 1887, Norman Lockyer[89] published a book on the chemical composition of the Sun,[90] in which he claimed that the solution for the Fraunhofer lines was found as early as 1823 by two English scientists, Brewster[91] and Herschel,[92] who realized that when a cool absorber is placed in front of a bright light source, dark lines will appear. It was Brewster, according to Lockyer, whose experiments convinced him that the dark lines offered a unique method of chemical analysis. It was also Brewster who claimed (erroneously) to have discovered nitrous acid in the atmosphere of the Sun. This was the first chemical compound to have been claimed to be identified in the solar spectrum.

But the reality or its rigorous interpretation, was a bit different. In 1835, Herschel himself[93] wrote as follows:

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[88] Miller, W.A., *Elements of Chemistry*: *Theoretical and Practical*, Part I. Chemical Physics, 2nd edn. John W. Parker and Son, London, 1860, p. 146.

[89] Publisher Alexander Macmillan chose Lockyer as Nature's founding editor in 1869. As Ruth Barton suggests (Barton, R., *Lockyer's columns of controversy in Nature*, in *History of the Journal Nature*, Nature **16**, October 2007), Lockyer endorsed discussions of controversies. Should we understand his remarks on the priority in terms of his passion for controversy?

[90] Lockyer, N., *The Chemistry of the Sun*, MacMillan, 1887. See Chap. V.

[91] Brewster, D., Edinb. Phil. Trans. **9**, 433 (1823).

[92] Herschel, J.F.W., Edinb. Phil. Trans. **9**, 445 (1823).

[93] Herschel, J.F.W., *A Treatise on Astronomy*, 3rd edn., Carey, Lea, & Blanchard, Philadelphia, 1835, p. 203.

> The prismatic analysis of the solar beam exhibits in the spectrum a series of fixed lines totally unlike those of any known terrestrial flame. This may hereafter lead us to a clearer insight into its origin. But before we can draw any conclusion from such an indication, we must recollect that previous to reaching us it has undergone the whole absorptive action of our atmosphere, as well as of the Sun's. Of the latter we know nothing, and may conjecture everything. [...] It deserves inquiry whether some or all of the fixed lines observed by Wollaston and Fraunhofer may not have their origin in our own atmosphere. [...] The absorptive effect of the Sun's atmosphere, and possibly also of the medium surrounding it (whatever it be), which resists the motion of comets, cannot be thus eliminated.

Two points are worth noting. We observe the Sun through a telescope, so obviously everything we see can be either on the Sun, or in the space between the Sun and the Earth, or in the Earth's atmosphere. But suggesting these three possibilities is not a solution or an explanation of the Fraunhofer lines. Furthermore, everything we see may be used to understand structure and composition, and Lockyer's interpretation of a naive phrase like 'clear insight into its origin' as a prediction of the powerful future methods of spectroscopic analysis, is to my mind, stretching the meaning a bit too far.

In 1840, Herschel published his *Outline of Astronomy*.[94] In 1871, in the 11th edition, he wrote:

> The reference of the dark lines in the solar spectrum to absorptive action in the Sun's atmosphere has of late received a most unexpected confirmation, and it may now be considered as almost certain that they owe their origin to the presence in that atmosphere of the vapours of metals and metalloids identical with those which exist here on Earth. These vapours, or many of them, have been shown by Kirchhoff, Bunsen, and Fizeau to possess the singular property when present in an unburnt (or metallic) state in a flame, of destroying in the spectrum of that flame rays of precisely the refrangibilities of those which they themselves when burning emit in peculiar abundance. Though there is something so enigmatical as almost to appear self-contradictory in the facts adduced, the conclusion, especially as applied to the most conspicuous of all the lines (one double one in the yellow, marked *D* by Fraunhofer, and which owes its origin to sodium) seems inevitable. The spectra of some of the stars seem to indicate the presence of chemical elements not identifiable with any terrestrial ones.

We learn that, even ten years after Kirchhoff's major discoveries, Herschel was quite reserved about the possible scope of spectral analysis and the explanation of the Fraunhofer lines, and in particular he did not mention the explanation attributed to him.

The details in the case of Brewster[95] are not that different. In 1837, Brewster wrote about *the coloured bands of the reflected spectrum*, and did not mention any explanation.

In 1859, a year before Kirchhoff published the English version of his German paper in the journal Brewster edited, Brewster and John Gladstone (1827–1902)[96]

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[94] Herschel, J., *Outline of Astronomy*. The first edition came out in 1840 and the 11th edition was issued in 1871. The 'new edition' came out in 1893, London, Longmans, Green, 1893.

[95] Brewster, D., Phil. Trans. R. Soc. Lond. **127**, 245, 1837.

[96] Brewster, D. and Gladstone, J.H., *On the Lines of the Solar Spectrum*, Proc. R. Soc. Lond. **150**, 339, 1859.

wrote: *The origin of these fixed lines and bands in the solar spectrum is a question still unresolved*. The possibilities mentioned were as follows:

- That the light when emitted from the photosphere (the region in the Sun from which the radiation we see emerges) is itself deficient in these rays. This was evidently Fraunhofer's idea.
- That they are due to absorption by the Sun's atmosphere.
- That they are due to absorption by the Earth's atmosphere.

As noted before, these were the three obvious possible solutions. *The first supposition scarcely admits a positive proof*, the authors wrote. The second supposition implied that there should be a difference between spectra emitted from the center of the Sun and the limb. However, Brewster and Gladstone cited Gladstone, who tried to observe this effect during the eclipse in March 1858:

> Unfortunately clouds prevented the experiment. [...] However, by other contrivances, each of the authors came independently to the conclusion that there is no perceptible difference in this respect between the light from the edge and that from the centre of the solar disk.

With some twist of the exact meaning, one can ignore the first and the third explanations and state that this paper provided the explanation for the Fraunhofer lines. Even so, this solution at best identified a configuration that might produce the lines, but it by no means offered an explanation.

Brewster, however, made an interesting experiment. He passed the solar light through vapors of nitrous acid (HNO_2) and discovered *a multitude of lines crossing the spectrum in the same direction as those observed by Fraunhofer*. Miller tried to repeat Brewster's experiment and did not find any gases that would produce the same lines.[97] He also noticed that the number of lines increased as the gas was compressed. In 1833,[98] Brewster discovered that, when the Sun was low above the horizon, additional Fraunhofer lines appeared in the spectrum, thus favoring a local source for the lines.

At about the same time, John Forbes (1787–1861)[99] was determined to take advantage of the opportunity presented by the forthcoming eclipse to examine the spectrum of the edge of the Sun without any disturbance from the central rays. He argued that, if the absorption was due to the solar atmosphere, it ought to be more marked at the edge of the Sun, because the light has to pass through a thicker stratum of atmosphere than at the centre, from which the rays proceed vertically and through a minimum of atmosphere. The general darkening of the Sun's limb was a well-known fact that could be observed at any time by examining the Sun through a dark glass (see Fig. 2.12[100]). Forbes was probably aware of this, and expected to find the limb-darkening accompanied by an increased selective absorption, i.e., stronger Fraunhofer lines.

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[97] Miller, W.A., Phil. Mag., Ser. III, **27**, 81, published in German Ann. Phys. **145**, 404 (1846).

[98] Brewster, D., Phil. Trans. Edinb., 1833.

[99] Forbes, J.D., Phil. Trans. R. Soc. Lond. **126**, 453 (1836).

[100] Pierce, A.K. and Slaughter, C.D., Solar Phys. **51**, 25 (1977).

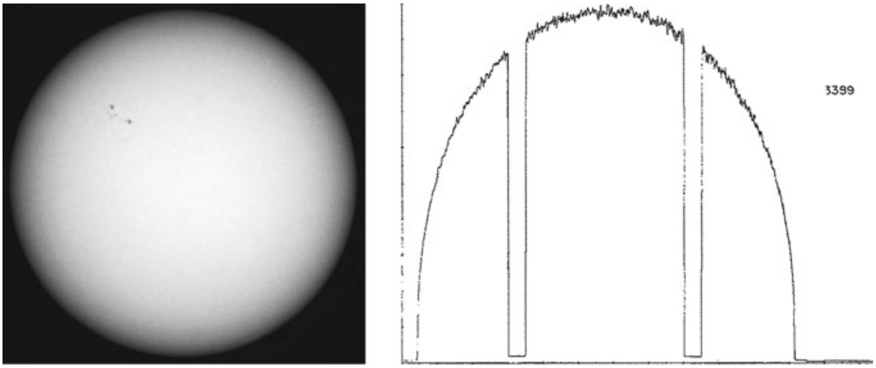

Fig. 2.12 *Left* Limb-darkening. Note how the brightness decreases towards the limb of the Sun. *Right* a modern result for limb-darkening of the Sun at a wavelength of 3,389 Å, after Pierce and Slaughter, (1977)

The result of the observation was that, as the eclipse progressed and the proportion of lateral to central light consequently increased, no change was observed in the number, position, or thickness of the lines, and from this observation Forbes concluded that[101]:

> This result proves decisively that the Sun's atmosphere has nothing to do with the production of this singular phenomenon.

Lockyer dismissed Forbes' observations and wrote that his conclusion *was at variance with that held by his predecessors*, which is not a scientifically valid argument, *and we now know that Prof. Forbes' conclusion was wrong*. He also presented it as an example illustrating *how near one may be to a most important discovery and yet miss it*, because of poor weather.

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[101] In a footnote to his paper Forbes wrote:

> I do not know with whom the idea of the absorptive action of the Sun's atmosphere originated. The editors of the London and Edinburgh Phil. Mag. have, however, referred me to the mention of Sir John Herschel's writings, particularly his *Elementary Treatise on Astronomy*, from which I extracted the following remarkable passage: "The prismatic analysis of the solar beam exhibits in the spectrum a series of fixed lines totally unlike those of any known terrestrial flame. This may hereafter lead us to clearer insight into its origin. But before we can draw any conclusions from such an indication, we must recollect that previous to reaching us it has undergone the whole absorptive action of our atmosphere, as well as of the Sun's. [...] It deserves inquiry whether some or all of the fixed lines observed by Wollaston and Fraunhofer may not have their origin in our own atmosphere. [...] The effect of the Sun's atmosphere, and possibly also of the medium surrounding it (whatever it be), which resists the motion of comets, cannot be eliminated."

If we continued in this way, we would conclude that Herschel even predicted the effect of the solar wind on comets.

But the situation was not as trivial as Lockyer had depicted it. In 1887, the same year as Lockyer published his book, Clerke[102] published a popular book on astronomy in which she claimed that the problem of the formation of Fraunhofer lines across the solar disk *still remains an anomaly of which no satisfactory explanation has been offered*. Indeed, she was quite right.

In 1902, Very (1852–1927)[103] attempted to measure the absorption coefficient of the solar atmosphere, about which practically nothing was known. He measured the intensity across the disk (see Fig. 2.13). The results allowed him to check various models and to find that none of them was particularly successful. So he suggested that irregularities in the photosphere might explain his results, namely that:

> The photosphere is made up of brilliant 'rice-grains' and their component 'granules', separated by a relatively dark reticulation in which the light having come from greater depths suffers larger absorption than where it proceeds from the summits of the photosphere clouds, or granules.

A comparison between the predictions of such a model and the observations turned out to be good, according to Very.

In 1902, Schuster attacked the problem of limb-darkening. He found that:

> The radiation received from different portions of the solar disk is known to diminish from the center towards the limb in a manner which is generally considered not to be consistent with the assumption of a uniformly absorbing solar atmosphere. [...] The difficulty is easily removed. It is only necessary to place the absorbing layer sufficiently near the photosphere and to take account of the radiation which this layer, owing to its high temperature, must itself emit.

The end equation Schuster got was

$$A = (I - F)z^{\sigma} + F,$$

where A (not to be confused with the absorption discussed earlier) is the radiation leaving the absorbing layer in the direction of the Earth, I is the intensity of the radiation which is incident on the absorbing shell, and F is the radiation of a perfect black body at the temperature of the shell. z and σ are two geometrical factors associated with the Sun.[104] The equation can be solved if the radiation is measured at three points across the solar disk, because there are three unknowns: I, F, and z.

Two years later, Very[105] was unhappy with Clerke's statement that the problem had not yet been solved and claimed that he had offered a solution. He repeated Forbes' argument that *a critical examination of the appearances of the Fraunhofer*

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[102] Agnes Mary Clerke (1842–1907) was an astronomer and a well-known writer, mainly in the field of astronomy. She wrote a popular book on astronomy (Clerke, A.M., *A Popular History of Astronomy During the Nineteenth Century*, Edinburgh, A. & C. Black, 2nd edn. 1887).

[103] Very, F.W., Astrophys. J. **16**, 73 (1902).

[104] $z = e^{kt_0}$, $\gamma = r/R_\odot$, and $\sigma = 1/\sqrt{1-\gamma}$, where t_0 is the thickness of the absorbing layer, k the coefficient of absorption, r the perpendicular distance between any point on the Sun and the line drawn from the Sun's surface towards the observer on the Earth, and $R_\odot$ the radius of the Sun.

[105] Very, F.W., Astrophys. J. **19**, 139 (1904).

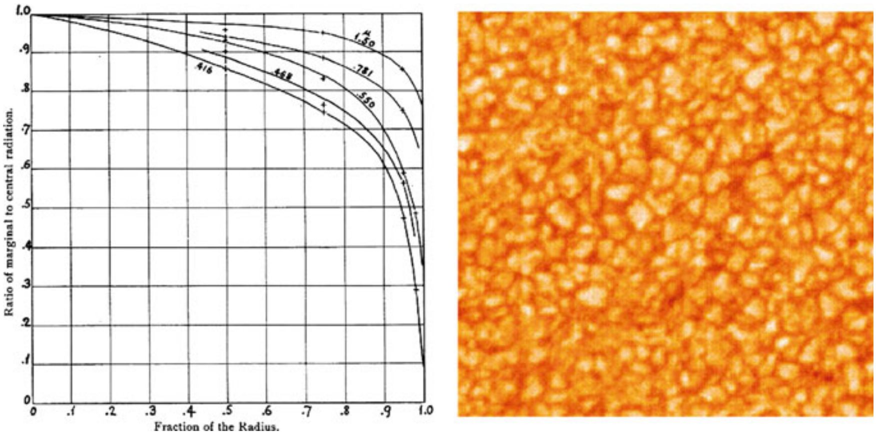

Fig. 2.13 *Left* Very's observation of the change in the solar intensity as a function of the distance from the center and the wavelength. After Very (1902). *Right* a close-up view of the solar surface shows the granules and the dark boundaries between them

lines from different parts of the solar disk discloses the remarkable fact that they do not vary appreciably at any point of the unspotted surface, and can have nothing to do with the progressively increasing selective absorption, with the obvious (but incorrect) conclusion about how the dark lines form.

Very's claim, as presented in the previous paper, was:

> The failure of the Fraunhofer lines to become intensified at the Sun's limb is to be attributed chiefly to the corrugation of the photospheric surface, and to the fact that the efficient absorbing layer is of a depth not great in relation to the vertical dimension of these irregularities.

Then Very attacked Schuster's solution[106] which asserted that:

> Solar radiation comes from an absorbent and radiating layer, distinct from and immediately above the photosphere, and the apparent change of absorption at different distances from the Sun's limb is explained as due to the varying relative preponderance of the two sources—photosphere and atmosphere—in producing the radiation.

Very referred to certain observations, claiming that *Schuster does not avail himself of this evidence*. As for Schuster's assumptions, he assumed a coefficient of absorption which was independent of wavelength. But, so claimed Very:

> Anyone who has compared the strongly contrasted colors—blue at the center and reddish-brown at the limb of the Sun—will recognize that, if this explanation is to be accepted, the radiation at the limb must come almost entirely from the red-hot particles of the envelope, while the blue-hot photosphere is mainly in evidence at the center.

The discussion by Very is quite long and completely rhetorical, without any modeling. Moreover, he claimed to find an error in Schuster's analysis.

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[106] Schuster, A., Astrophys. J. **16**, 320 (1902).

The story about solar limb-darkening is compounded with the question: what is the solar radius? The final answer to this question appeared to require a satisfactory solution and attracted astronomers even as late as the beginning of the twentyfirst century.[107]

2.17 More Creditors?

Among the English scientists on whose behalf credit was requested for discoveries in spectroscopy was Charles Wheatstone (1802–1875).[108] As early as 1835, Wheatstone made some important observations about the origin of the lines as well as their position, and also established that all the elements could be identified by their spectral lines. It would have been virtually impossible for Kirchhoff and Bunsen to know of this, for the lecture in which Wheatstone publicly announced the results of his investigation was held in 1835 and was not published until 1861, when Crookes, in the wake of Kirchhoff's publication, found it appropriate to straighten out the story. Only a summarized extract was published in 1835. According to Huggins, Wheatstone's words in that lecture were:

> We have here a mode of discriminating metallic bodies more readily than by chemical examination, and which may hereafter be employed for useful purposes.

In another publication during that year, Wheatstone[109] described the spectra of Cd, Sn, Pb, Hg, and Zn. No statement about the future or the potential of the method was made in this single reference by Wheatstone.

Similarly, we should mention Anders Ångström (1814–1874m)[110] who reported a relation between absorption and emission. Volkert van der Willigen (1822–1878)[111] discovered in 1859 that the same metal produces the same spectrum whether it is in the form of nitride or chloride. It is thus possible to identify the metal even if it is in a chemical compound.[112]

As in all other branches of science, the discovery of Kirchhoff and Bunsen did not come out of the blue, but rested on significant layers of experiments, ideas, failures, thinking, etc. Few today would argue with the statement that Kirchhoff and Bunsen's

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[107] See for example, Livingston, W.C., Milkey, R., and Sheeley, N., Jr., AAS meeting, no. 211, **159.06**, 2008; Neckel, H., Solar Phys. **229**, 13 (2005).

[108] Wheatstone, C., *Prismatic decomposition of electric light*, Reports to the British association for the Advancement of Science **5**, 11 (1835); Crookes, Chem. News **3**, 198 (1861).

[109] Wheatstone, C., Phil. Mag. **7**, 299 (1835).

[110] Ångström, A.J., Pogg. Ann. **117**, 290 (1862); Phil. Mag. **9**, 327 (1855).

[111] Willigen, V.S.M., Ann. Phys. **182**, 610 (1859).

[112] Roscoe (Roscoe, H.E., *The Edinburgh Review or Critical Journal* for July 1862 to October 1862, p. 295) gives the following example about the unbelievable way in which scientific discoveries are interpreted by laymen, and suggests that it could be *an interesting branch of study to the psychologist*: Kirchhoff and Bunsen got a letter form a Silesian farmer who thanked them for proving his theory that no inorganic materials should be added to plants as all the required minerals exist in solar light.

research was imperative in converting spectroscopic analysis into a paramount tool for analytical chemistry. However, it was only after Kirchhoff and Bunsen recognized the enormous potential of spectroscopy that the community started to appreciate the power of the method.

2.18 An Unimaginable but True Story: No Life on the Sun

Soon after the publication of the great papers, Kirchhoff published a memoir on the *Solar spectrum and the spectra of the chemical elements*, which was quickly translated into English by Roscoe.[113] Kirchhoff credited Swan, Brewster, Gladstone, and Miller, and stressed that his discoveries were due to the excellent apparatus he obtained from the company Steineil-Söhne in Munich.[114]

It is interesting to note that in this first analysis of the solar spectra, Kirchhoff inverted the logic. Hence, having problems with measuring the exact location of certain lines seen in the laboratory, he claimed that:

> The dark lines of the solar spectra afford invaluable assistance in determining the position of the bright lines of the various elementary bodies.

Thus, instead of finding the composition of the Sun, the solar spectrum was used to provide accurate spectroscopic data for chemical elements on Earth. This situation was repeated several times in the following years (like the discovery of helium on the Sun).

To explain the formation of the dark lines Kirchhoff assumed that:

> […] the solar atmosphere encloses a luminous nucleus, producing a continuous spectrum, the brightness of which exceeds a certain limit. The most probable supposition […] 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.

So, on top of explaining the origin of the dark lines, Kirchhoff concluded that the composition of the Solar System and the Sun must therefore be alike, and argued that geology tells us that the Earth was once hot and liquid. Hence, he concluded that all bodies in the Solar System were hot in the past and were now cooling. Small objects like the Moon and the Earth would cool relatively fast compared to the age of the Earth, while big objects like the Sun would cool more slowly. So far, Kirchhoff's assumption was in agreement with Kelvin's incorrect theory of the Sun.

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[113] Kirchhoff, G., *Solar Spectra and the Spectra of the Chemical Elements*, MacMillan, Cambridge, 1862.

[114] Recall the power of the excellent optical equipment produced by Fraunhofer. Similarly, the Steineil-Söhne company was founded in 1855 by Carl (1801–1870) and his son Adolf (1832–1893) Steineil, and excelled in spectrographs.

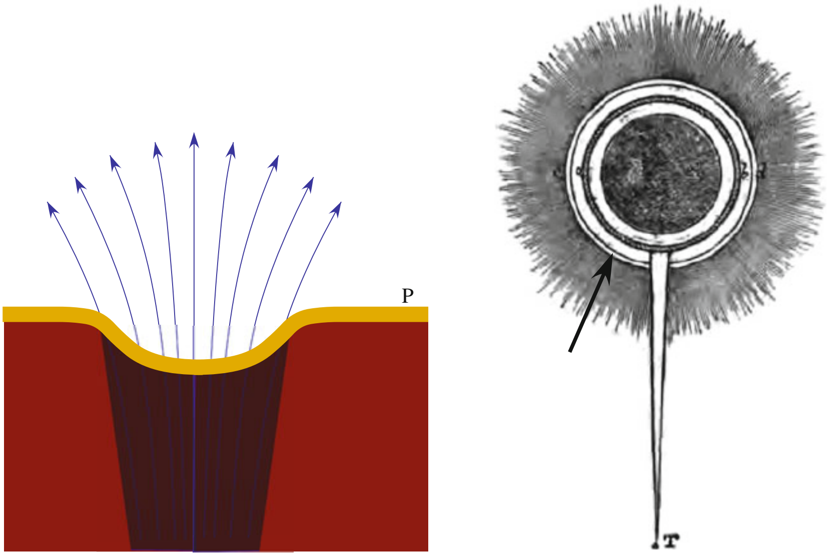

Fig. 2.14 *Left* the Wilson depression was discovered by Wilson in 1769. The photosphere is the region from which the radiation we see emerges from the Sun. In other words, the region where the probability of a photon escaping from the star is high. The *dark area* is a sunspot. Wilson did not know that sunspots contain strong magnetic fields. *Right* Arago invented the term 'photosphere' in his book *Popular Astronomy*. The caption in Arago's book is *Formation of a spot without a nucleus*. The *arrow* marks the photosphere. The 'solid' nucleus of the Sun is seen through the spot without nucleus

Like Galileo before him, Kirchhoff observed the spots on the Sun and accepted Galileo's explanations that they were clouds in the solar atmosphere. But the cloud theory for sunspots was relinquished by many astronomers on account of some peculiarities in the spots which were brought to light by further observations. According to François Arago (1786–1853m),[115] the Sun consisted of a dark nucleus surrounded by an opaque and reflecting atmosphere, this being enclosed by a luminous atmosphere or photosphere,[116] which was in its turn surrounded by a transparent atmosphere. Arago declared:

> If I were asked whether the Sun can be inhabited by beings organized in a manner analogous to those which people on our globe are, I should not hesitate to reply in the affirmative. The existence of a central obscure nucleus, enveloped in an opaque atmosphere, far beyond which the luminous atmosphere exists, is by no means opposed, in effect, to such a conception.

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[115] Arago, F., *Popular Astronomy*. Translated by Smyth and Grant, Longman, Brown, Green and Longman, London, 1955. From 1813 and until 1845, Arago gave very popular non-technical lectures on astronomy. Chapter XXIX of the book is entitled: *Is the Sun inhabited*?

[116] The term photosphere was invented by Arago in *Popular Astronomy*, p. 411:

> All the phenomena of which we have just been speaking, may be explained in a satisfactory manner, if we assume that the Sun is an obscure body surrounded to a certain

The physical nature of sunspots remained a topic of controversy for nearly three centuries. In 1774, Alexander Wilson (1714–1786) observed the asymmetric appearance of sunspots when seen near the solar limbs. The phenomenon, called Wilson depression (see Fig. 2.14) was discovered in 1769. When a spot reaches the limb of the Sun due to solar rotation, the penumbra[117] of a spot appears wider than when observed at the center of the Sun. The entire effect is very small,[118] but Wilson became convinced that the depressions were regions located beneath the general surface of the Sun, in contrast to mountains, as many astronomers thought at that time:

> Is it not reasonable to think that the great and stupendous body of the Sun is made up of two kinds of matter, very different in their qualities; that by far the greater part is solid and dark and that this immense and dark globe is encompassed with a thin covering of that resplendent substance from which the Sun would seem to derive the whole of his revivifying heat and energy?

Herschel was convinced by this argument, and his first paper on the Sun, published in 1794, was based on this supposition. By 1801, Herschel concluded that there were even two types of clouds on the Sun:

> The solid body of the Sun beneath these clouds appears to be nothing else than a very eminent, large and lucid planet, evidently the first, or in strictness of speaking, the only primary one of our system.

And so he was led to claim that: *We need not hesitate to admit that the sun is richly stored with inhabitants.* As hallucinatory as this idea may seem in our view today,

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> (Footnote 116 continued)
> distance by an atmosphere, which may be compared to the terrestrial atmosphere when the latter is occupied by a continuum stratum of opaque and light reflecting clouds. If moreover, we place above this first stratum a second luminous atmosphere which will assume the name of a photosphere, this photosphere, more or less remote from the interior cloudy atmosphere, determines by its contour the visible limits of the body.

Since then, this term has been adopted to describe the 'last luminous visible layer of the Sun'.

[117] Penumbra literally means dim light, in this case, the outer filamentary region of a sunspot.

[118] The existence of magnetic fields in sunspots was demonstrated in 1908, shortly after the Zeeman effect was discovered. The Zeeman effect, the splitting of spectral lines in the presence of a magnetic field, was discovered by Zeeman (1865–1943m) in 1896 (Zeeman, P., Phil. Mag. [5], **43**, 226, 1897; Astrophys. J. **5**, 332, 1897). He observed in the laboratory how the two sodium D lines (the D lines played an important role once again) broaden when the flame is placed between the magnetic poles of a strong electromagnet. Hale used the Zeeman effect to identify the magnetic field in sunspots in 1908 (Hale, G.E., PASP **20**, 287, 1908; Astrophys. J. **28**, 315, 1908). In the wake of this discovery, Hale asked Zeeman to send his views about the discovery to Nature. While Hale was rather cautious about the discovery and its implication, Zeeman stated that:

> Hale has given what appears to be a decisive evidence that sunspots have strong magnetic fields, the direction of these fields being mainly perpendicular to the Sun's surface.

The effect was expected by Faraday (Maxwell, J.C., Collected Works, II, 790, Cambridge Press, 1890), who tried in vain to detect it as early as 1862. The temperature in the spot is about 4,000 K. The magnetic fields in the spots are about 1,000 times greater than the mean solar magnetic field, and may reach 1,000–4,000 gauss, while the magnetic field of the Earth is 0.3–0.6 gauss.

some regard it as the first attempt to provide a coherent explanation for isolated pieces of data seen on the surface of the Sun. Several historians of astronomy claim that this is almost the only point on which Herschel was first mistaken,[119] but later corrected.

Kirchhoff claimed that this theory:

> […] 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 formation of sunspots. 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 in the focus of a circular mirror exposed to the Sun's rays, whose surface seen from the focus is larger than a hemisphere.

Kirchhoff argued that the atmosphere keeps the nucleus of the Sun at least as hot as the temperature of the atmosphere (heated to the point of incandescence). So Kirchhoff rejected this theory and returned to the cloud hypothesis:

> A local diminution of temperature must give rise to the formation of clouds, only that the solar clouds will be of a different chemical composition from terrestrial ones. When a solar cloud is formed, all the portions of the atmosphere lying above it will be cooled down, because a portion of the rays of heat which are emitted from the incandescent surface of the Sun are cut off by the cloud. […] The temperature of the cloud sinks below the point of incandescence, it becomes opaque, and forms the nucleus of the solar spot.

Kirchhoff claimed that he could fully explain Wilson's apparent depression of spots. But Kirchhoff noticed that sunspots are observed only close to the equator and admitted that *this fact cannot be explained by my theory*.

Despite Kirchhoff's rather convincing arguments, several years later, we find people like George Stoney (1826–1911)[120] who had other ideas about the Sun, describing it in the following way:

> The true surface of the Sun is the outer boundary of this enormous atmosphere. […] Within this luminous film there is a dark body, glimpses of which are occasionally seen as the umbrae of spots.

Stoney dedicates a special section to the *clouds in the outer atmosphere*, which were made, according to his hypothesis, of carbon. This section contains an extensive description of the clouds, their size, and what exists between them.

2.19 Final Comments on the Kirchhoff Saga

It is difficult to detach the controversy around Kirchhoff's discoveries from parallel discussions which took place across the English channel at about the same time. Consider, for example, the controversy between the Scotsman Peter Tait (1831–1901)

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[119] Macpherson, H., *Century Progress in Astronomy*, William Blackwood and Sons, Edinb. and Lond. 1906.

[120] Stoney, G.J., Proc. R. Soc. **XVII**, 1, 1867.

and the German Herman Helmholtz (1821–1894m)[121] about the contributions to the basic laws of thermodynamics, and the claim for priority by the Englishman James Joule (1818–1889) against the claim by the German Julius Mayer (1814–1878) that he had established the energy conservation law,[122] or the dispute about the contributions to thermodynamics of the Irishman Lord Kelvin (1824–1907) and the German Rudolf Clausius (1822–1888m) to thermodynamics.

As for Kirchhoff himself, it is important to note that he was not so satisfied with his own proof of the radiation law.[123] So, only a few weeks later, Kirchhoff apparently changed his view that a general proof could be attained by the simple theoretical considerations he had invoked. In January 1860, he submitted a second, much more involved proof without initially commenting on the fate or rigour of the first. Two years later, he published a structurally improved version of this second derivation, which the editors chose for his collected works.[124] In this revision, he commented on the supposition that bodies emit or absorb only at one specific wavelength[125]:

> 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 wavelength lies between l and $l + \mathrm{d}l$ and whose plane of polarization is parallel to the plane a; but which completely reflects rays of other wavelengths or of an opposite polarization.

He now regarded this supposition as inadmissible. Instead, he relied on an even more intricate object:

> [A] plate is possible which, of the rays striking it at the same angle, transmits and reflects them in different degrees according to their wavelengths 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.

In 1877, John Tyndall (1820–1893m),[126] who succeeded the great Faraday, gave a series of 6 lectures in the USA, and the fifth lecture was devoted to spectral analysis.

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[121] Knott, C.G., *Life and Scientific Work of Peter Guthrie Tait*, Cambridge University Press, 1911.

[122] Shaviv, G., *The Life of the Stars*, Springer, Heidelberg, 2009.

[123] Kirchhoff, G., *On the relation between emission and absorption of light and heat*, which was presented to the Berlin Academy of Sciences on 15 December 1859: Gustav Kirchhoff, *Ueber den Zusammenhang von Emission und Absorption von Licht und Wärme*, Akad. der Wissen. Berlin, pp. 783, 784, 786, reprinted in Gustav Kirchhoff, *Untersuchungen über das Sonnenspektrum und das Spektrum der chemi schen Elemente und weitere ergänzende Arbeiten aus den Jahr en 1859–1862*, *Osnabrück*, *1972*, *ed. Kangro. The more detailed paper was published in Ann. Phys.*, *January 1860*.

[124] Gustav Kirchhoff, Untersuchungen über das Sonnenspektrum und die Spektren der chemischen Elemente (2nd edn., Berlin, 1962), appendix, *Über das Verhältnis zwischen dem Emissionsvermögen und dem Absorptionsvermšgen der Körper für Wärme und Licht*, 22–39; also in Gesammelte Abhandlungen. Vol. 1 (Leipzig, 1882) 571, English trans. in D.B. Brace, ed., *The Laws of Radiation and Absorption*: *Memoirs by Prévost, Stewart, Kirchhoff, and Kirchhoff, and Bunsen*, New York, 1901, p. 75.

[125] Note that Kirchhoff's one-wavelength plate is a perfect mirror for all radiation with a wavelength different from the specified one.

[126] Tyndall, J., *Six Lectures on Light Delivered in America in 1872–1873*, Appleton and Comp., New York, 1877.

So who did the Irishman Tyndall, who worked in England, consider to have explained the Fraunhofer lines? Tyndall's version was as follows:

> The explanation of these lines was, as I have said, a problem which long challenged the attention of philosophers, and to Kirchhoff, Professor of Physics in the University of Heidelberg, belongs the honour of having first conquered this problem.

By 'lines' Tyndall meant the Fraunhofer lines. It should be mentioned that Tyndall did not adopt the English version in other priority squabbles that took place at the same time.

2.20 Epilogue

The radiation law practically ceased to be a point of contention between the English and German scientific communities when, in 1862, Kirchhoff won the Rumford medal. The citation was: *For his researches on the fixed lines of the solar spectrum, and on the inversion of the bright lines in the spectra of artificial light*. The citation failed to mention his law of radiation. When Balfour Stewart got the Rumford medal in 1868, the citation said: *For his researches on the qualitative as well as quantitative relation between the emissive and absorptive powers of bodies for heat and light, published originally in the Transactions of the Royal Society of Edinburgh, and the Proceedings of the Royal Society of London, and now made more generally accessible by the publication in 1866 of his treatise on heat*. It is not sure that Kirchhoff would concur.[127]

In 1868 Kirchhoff was elected Fellow of the Royal Society of Edinburgh, and in 1875 Fellow of the Royal Society. As a further recognition by the English scientific

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[127] The Rumford Medal is awarded by the Royal Society every other year for *an outstandingly important recent discovery in the field of thermal or optical properties of matter made by a scientist working in Europe*. The medal is based on a donation by Rumford, who was the first to be awarded the prize! Of the names mentioned so far, the following were winners:

establishment, a year before his death, Kirchhoff was awarded a gold medal by Queen Victoria in 1887.[128]

The doltish non-scientific controversy driven by nationalistic feelings between the English and German scientific communities did not end with the recognition of the German Kirchhoff by the English scientific establishment, and even perdured beyond World War I. The details, though interesting historically, are beyond the scope of this book (for details see, for example, Heilbron[129]).

2.21 The Late Kirchhoff Grilled by His Compatriots

Naturally, the debate in the German scientific community was not about priority. Kirchhoff's priority was obvious in Germany. However, claims about the rigour of the proof were raised. Forty years after the declaration of Kirchhoff's law, Voigt[130] still found it necessary to prove it theoretically and experimentally. It just so happened that the criticism of the rigour of Kirchhoff's proof by German scientists was no

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(Footnote 127 continued)

1804 Leslie	For his Experiments on Heat, published in his work, entitled, An Experimental Enquiry into the Nature and Propagation of Heat.
1816 Davy	For his Papers on Combustion and Flame, published in the last volume of the Philosophical Transactions.
1834 Melloni	For his discoveries relevant to radiant heat.
1838 Forbes	For his experiments on the polarization of heat, of which an account was published in the Transactions of the Royal Society of Edinburgh. Not for spectroscopy.
1842 Talbot	For his discoveries and improvements in photography. Not for heat research.
1852 Stokes	For his discovery of the change in the refrangibility of light.
1872 Ångström	For his researches on spectral analysis.
1874 Lockyer	For his spectroscopic researches on the Sun and on the chemical elements. Not for the helium discovery (it was too 'risky').
1876 Janssen	For his numerous and important researches in the radiation and absorption of light, carried on chiefly by means of the spectroscope. Not for discovering helium!
1880 Huggins	For his important researches in astronomical spectroscopy, and especially for his determination of the radical component of the proper motions of stars.
1886 Langley	For his researches on the spectrum by means of the bolometer.

Note those who did not get the prize, in particular, Herschel, Prévost, Pictet, Wheatston, Miller, de la Provostaye, Desains, and Bunsen. (Source: Rumford archives, 1800–1898.) Prize committees are driven by internal politics.

[128] The following story is amusing. Kirchhoff (Smithsonian Report, p. 537, 1889) once told his banker about the discovery of terrestrial metals on the Sun. The banker responded somewhat indifferently, with: *Of what use is gold on the Sun if I cannot get it down to Earth*? Later, after Queen Victoria of England had presented Kirchhoff with a medal and a prize in gold sovereigns for work on the solar spectrum, he took the gold sovereigns to the banker and retorted: *Here is some gold from the Sun*!

[129] Heilbron, J.L., *The Dilemmas of an Upright Man*: *Max Planck and the Fortunes of German Science*, Harvard University Press, 1996.

[130] Voigt, W., Ann. Phys. **67**, 366 (1899).

different from Kirchhoff's criticism of the accuracy of Stewart's proof. But by then, the early 1890s, Kirchhoff was long dead.

In 1894, Wilhelm Wien (1864–1928)[131] thought he had found a flaw in Kirchhoff's assumptions.[132] In his proof, Kirchhoff had assumed the existence of a material with optical properties that the experimentalist Wien argued could not exist. Even as late as 1909, Wien[133] claimed that Kirchhoff's proof was 'artificial' or contrived.

In 1894, Friedrich Paschen (1865–1940m)[134] used a spectrobolometer[135] to measure the total intensity of the two *D* lines emitted by salt placed in the flame of a Bunsen burner. All other things being equal, he then measured the corresponding intensity of a selected region in the spectrum of a black body, a region completely contained within the two *D* lines. Assuming incorrectly an excessive value for the width of the sodium lines, Paschen then calculated a maximum value for the intensity of the part of the spectrum of the black body corresponding to the lines. The value he found was not even half the value found with the lines given by the burner. Paschen reached the inevitable conclusion that Kirchhoff's law was inapplicable. Paschen conjectured that the brightness of these lines was due, at least for a large part, to a phenomenon of luminescence. Using a different method, Gustav Wiedemann (1826–1899)[136] arrived at the same conclusion. Thus, even the experiments were problematic.

The status of Kirchhoff's law was reviewed by Aimé Cotton (1869–1951) in 1899.[137] The need for such a review forty years after the discovery reflects the difficulties in accepting this far-reaching physical law. Cotton attempted to prove Kirchhoff's law by starting with Prévost's assumption (see Sect. 2.3), and complained that *we have no method of studying a radiation without causing it to disappear*. Next he assumed that *the emission depends solely on the temperature*, *and conversely*, *the absorbed radiation is converted wholly into heat*. Cotton pointed to the fact that Kirchhoff's first proof was not sufficiently general while the second proof was much better. However, as Cotton remarked, the proofs by assuming certain plates with unique optical properties did not make a theory because it was not connected with a theory of light. Hence, Cotton tried to combine the law with the properties of the ether. Cotton ended his paper with the statement:

> The law which connects together so many experimental facts brings an important contribution to the theoretical study of the relationship between ether and matter, which is still so mysterious.

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[131] Wien, W., *Temperatur und Entropie der Strahlung*, Ann. Phys. **288**, 132 (1894).

[132] Wien was very nationalistic, and a defender of German science, so for him to raise such a claim was no a trivial matter.

[133] Wien, W., Encyklopadie del mathematische Wissenschaften **5**, 282 (1909), Leipzig.

[134] Paschen, F., Wied. Ann. **51**, 41 (1894).

[135] A spectrometer which splits the light, combined with a bolometer which measures the power emitted in a certain wavelength range.

[136] Wiedemann, G.H., Wied. Ann. **37**, 180 (1893). In 1877, Wiedemann became the editor of the Annalen der Physik und Chemie, succeeding Johann Christian Poggendorff. Consequently, the journal is frequently cited as Wiedemann Annalen.

[137] Cotton, A., Astrophys. J. **9**, 237 (1899).

Similarly, Ernst Pringsheim (1859–1917)[138] requested further proof in 1903, but neither offered nor performed any new experiments.

2.22 A Mathematical Proof (if Needed): Hilbert

At the beginning of the twentieth century, and in particular after the death of Henri Poincaré (1854–1912m), David Hilbert (1862–1943m) became the leading mathematician in mathematical physics.[139] Hilbert was interested in establishing the whole of physics on axiomatic grounds, and the problem of Kirchhoff's law was no exception to this.

The delicate question of the axiomatic approach versus a genuine physical approach was the subject of a debate between Hilbert who, as a mathematician, favoured the axiomatic approach, and a group of physicists, headed by Pringsheim (and including Kayser and Wien) who, as physicists favored the physical approach. But this debate, which is very important for physics, had no effect on the application of Kirchhoff's law either to the transfer equation or to abundance determinations of chemical elements in stars. For this reason, we shall leave the discussion at this point.[140]

In 1912, Hilbert[141] proved Kirchhoff's law using an axiomatic approach to radiative transfer. But Kirchhoff's law had become a standard assumption in radiative transfer well before Hilbert's proof, with almost no questions raised about its applicability or validity. Physicists, even theoreticians like Karl Schwarzschild, took it for granted. The foundations of radiative transfer were secured at long last.

2.23 The French View

In 1860, Desains published his book *Leçon de Physique*,[142] and in Chap. VIII discussed *Chaleur Rayonnante*. It is interesting to see the French version of the above events. According to Desains, the experiments on the transmission of radiant heat were carried out by François Delaroche (1781–1813) in 1811.[143] Pictet is not

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[138] Pringsheim, E., *Herleitung des Kirchhoffschen Geset zes*, Zeit. f. Wiss. Photographie **1**, 360 (1903).

[139] The two volume book by Courant, R. and Hilbert, D., *Methods of Mathematical Physics*, first published in 1924 and updated in 1953, Interscience Pub., served for many years as the 'bible' for mathematical physicists.

[140] For more details on this interesting and important debate, see Schirrmacher, A., *Experimenting theory*: *The proofs of Kirchhoff's radiation law before and after Planck*, Historical Studies in the Physical and Biological Sciences **33**, 299 (2003).

[141] Hilbert, D., Phys. Zeit. **13**, 1056, 1912; ibid. 1885 **14**, 592 (1913).

[142] Desains, P.Q., *Leçon de Physique*, Dezobry, E., Magdelenine et Cie., Lib-Éditeurs, Paris, 1860.

[143] Delaroche, F., J. Phys. **25**, 201 (1812); ibid. Ann. Phil. Lond. **2**, 100 (1813).

mentioned. Desains emphasised all the results of de la Provostaye and himself which confirmed the equality of the absorption and emission. The heroes were Melloni and de la Provostaye and Desains. Melloni studied in France, but returned to his home country, Italy, after completing his studies.

Desains attributed the discoveries in radiant heat to de la Provostaye and his collaborator.[144] However, the reader will easily recognize that the formulation is Kirchhoff's, although Desains wrote that he repeated the proof by de la Provostaye. The omission of Kirchhoff may be just about justified by the fact that Kirchhoff discussed light, while this book discussed heat. But what about Stewart? After all, the controversy between Stewart and Kirchhoff was run out on the pages of the best scientific journals of the time. And these are not the only inaccuracies in the book. For example, according to Desains, Kirchhoff repeated Foucault's experiment. But Kirchhoff never used a voltaic arc.

2.24 One Can Never Foresee the Future

The discoveries by Fraunhofer did not impress the French philosopher August Comte (1798–1857), who claimed in 1835[145] that it would never be possible to discover the composition of the stars. This 'prophecy' was repeated in the second edition of the course of lectures, which appeared in 1864, after the publication of Bunsen and Kirchhoff's discoveries and Kirchhoff's paper about the solar composition.

2.25 Getting the Black Body Function: Maxwell

The equations of electromagnetism were discovered by various authors and over many years. These appeared as separate equations for the magnetic and electric fields, and for the interaction between them. It was the Scotsman James Clerk Maxwell (1831–1879m) who unified the electric and magnetic fields into the electromagnetic field and formulated modern electrodynamics. Maxwell showed that light is a propagating electromagnetic field composed of inseparable and varying electric and magnetic fields. It seems that Faraday had entertained this idea before Maxwell expressed it in writing, but it was Maxwell who found the theoretical expression and calculated the resulting speed of propagation. The theory of light as an electromagnetic field provided the basis for the forthcoming discovery by Planck. Assuming that light propagated in the 'luminiferous aether', Maxwell derived its properties about 40 years before Einstein buried the idea of the hypothetical aether, which had been assumed to permeate all matter.

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[144] de la Provostaye, *Considérations théoriques sur la chaleur rayonnante*, Ann. Chim. Phys., série 3, **67**. This is the reference given by Desains. The full reference is: p. 5, 1863.

[145] Comte, A., *Cours de Philosophie Positive* **2**, 6, Pub. Baillière, Paris, 1864.

It is interesting to note that Maxwell wrote his equations in a form that was consistent with the special theory of relativity, long before Einstein discovered his theory in 1905. Einstein's special theory of relativity did not change anything in Maxwell's theory.

The basic Maxwell equations are:

- An equation for the connection between the electric charge and the electric field it produces.
- An equation for the connection between the magnetic charge and the magnetic field.
- An equation for Faraday's law of induction, which describes how a changing magnetic field can create an electric field.[146]
- An equation for Ampère's law[147] (with Maxwell's correction) which states that magnetic fields can be generated in two ways: by electrical current (this was the original Ampère law) and by changing electric fields. This is the inverse equation of the previous one. However, Maxwell realized that the equation had to be corrected.

Maxwell's theoretical correction to Ampère's law is described in *A Dynamical Theory of the Electromagnetic Field*, where he commented that[148]:

> The agreement of the results seems to show that light and magnetism are affections of the same substance, and that light is an electromagnetic disturbance propagated through the field according to electromagnetic laws.

Maxwell's equations can be found in almost present day notation in Vol. 2 of Maxwell's book.[149]

2.26 Attempts to Obtain Kirchhoff's Function

Towards the end of the eighteenth century several physicists attempted to find the complete behavior of the universal function $e(\nu, T)$ of black bodies. During the years 1897–1899, Otto Lummer (1860–1925) and Pringsheim[150] accurately measured the energy distribution as a function of wavelength emitted by a black body. The first realization of a black body, and the once and for all disposal of the lampblack, was carried out by Lummer and Wien,[151] using Kirchhoff's idea that a cavity is a good

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[146] The equations for the electric field **E** and magnetic field **B** are $\nabla \cdot \mathbf{E} = \rho/\varepsilon_0$, $\nabla \cdot \mathbf{B} = 0$, $\nabla \times \mathbf{E} = -\partial \mathbf{B}/\partial t$, $\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \partial \mathbf{E}/\partial t$, where ε_0 and μ_0 are the permittivity of free space and the permeability of free space, respectively, and ρ is the total charge density.

[147] For historical justice, we mention, Ampère, Weber, and Robert Thomson (1822–1873).

[148] Maxwell, J.C., *A Dynamical Theory of the Electromagnetic Field*, Phil. Tran. Lond. **155**, 459 (1865).

[149] Maxwell, J.C., *A Treatise on Electricity and Magnetism*, MacMillan, 1873.

[150] Lummer, O.R., and Pringsheim, E., Wied. Ann. **63**, 395 (1897).

[151] Lummer, O.R. and Wien, W., Wied. Ann. **56**, 451 (1895).

approximation for a black body. Kirchhoff slightly confused the problem when he wrote:

> In an enclosure or a cavity which is enclosed on all sides by reflecting walls, externally protected from exchanging heat with its surroundings, and evacuated, the condition of 'black radiation' is automatically set up if all emitting and absorbing bodies at the walls or in the enclosure are at the same temperature.[152]

2.27 Getting the Integral of an Unknown Function First

The first attempts to find the radiative cooling law were by Dulong and Petit in 1817.[153] They heated a thermometer in a vacuum and watched how it cooled (see Sect. 1.14). The problem was that the air pressure in the vacuum was 2–3 mm of mercury, and this is not sufficient to suppress heat losses by air conduction relative to radiation losses. Dulong and Petit found that they could approximate their results with a cooling law of the form $E = m \times a^T$, where T is the temperature and m and $a = 1.0077$ are constants.

It was Draper who, in 1847,[154] discovered that, as the temperature increases, the emission takes place at shorter and shorter wavelengths. This observation was confirmed by Desains in his book.

The experiment was repeated with some improvements by Provostaye and Desains,[155] who managed to reduce the air pressure until no changes in the cooling were measured, and in this way obtained the 'cooling in vacuum'. Provostaye and Desains claimed that the cooling, as given by Dulong and Petit, should be corrected by adding a constant which depended on the radiation. Moreover, they remarked that the numerical coefficient in the cooling law changed with the dominant wavelength of the cooling body. However, the variations were not given.

Alexander-Edmond Becquerel (1820–1891)[156] first confirmed Dulong and Petit's result, and then discovered that the emission at a certain given wavelength increased with temperature. Becquerel found that the constant a in Dulong and Petit's law varied with color as shown in Table 2.1.

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[152] If matter is not completely evacuated from the cavity, the squared index of refraction of the matter enters the law. Here we leave this point aside and assume unity for the index of refraction (vacuum). If the walls are perfect reflectors, the radiation does not interact with the walls. If the radiation is to 'feel' the temperature of the walls, they must absorb at least part of the radiation (and then re-emit it). As for stars, the 'enclosure' is not empty, but full of matter and there are no walls to speak of.

[153] Dulong, P.L. and Petit, A.T., Ann. Chim. Phys. **vii**, 225, 237 (1817).

[154] Draper, J.W., Phil. Mag. **XXX**, 345 (1847). This is basically the displacement law formulated by Wien in 1894.

[155] Desains, P., *Leçons de Physique*, Tome second, Dezobry, E. Magdeleine et Co., Paris, 1865, pp. 704–705.

[156] Becquerel, A.E., J. Phys. **VII**, November, 1878. *La Lumière*, Vol. I, 61. His father was Antoine César Becquerel (1788–1878), a pioneer in the study of electric and luminescent phenomena, and his son was Henri Becquerel (1852–1908), the discoverer of radioactivity.

Table 2.1 Becquerel's radiation law

a	Color	Wavelength
1.01180	Red	6,700 Å
1.01371	Green	5,260 Å
1.01660	Blue	4,600 Å
1.00770	Total	Dulong and Petit

In 1878, André Crova (1833–1907)[157] tried to use the published formulae to obtain an expression which included the wavelength and the temperature. However, it was just an interpolation between known results. The matter and the radiation were treated as ensembles of oscillators, the simplest physical system. Each oscillator has a different frequency or wavelength. The cooling takes place through each oscillator radiating away its energy. The question was, in Crova's words, how much would each oscillator of wavelength λ radiate at a given temperature? Oscillators with different wavelengths radiate different amounts of energy.

The next known attempt was by Francesco Rossetti (1833–1885),[158] who repeated Leslie's cube experiment. He essentially found that the rate of cooling goes as $aT^2(T-\theta)+b(T-\theta)$, where T is the absolute temperature of the body, θ that of the surroundings (lampblack enclosure), and a and b are two constants for the body.

Only in 1879 did Joseph Stefan (1835–1893m)[159] correct the Dulong and Petit result for the disturbing convection and found that $E = \sigma T^4$ provides a better approximation. Dulong and Petit's results extended between the temperatures of 273 and 573 K, which is a relatively small range. To check how the approximation works at higher temperatures, Stefan took the results of Tyndall[160] for platinum at two temperatures, viz., 273 + 525 K and 273 + 1,200 K. The observed ratio of emissions was 10.4, while the ratio of the fourth powers of the temperature was 11.6. Though 10.4 is not equal to 11.6, Stefan considered the agreement satisfactory. But now contemplate the irony of fate: the fact that platinum is a poor black body at this temperature combined with the errors in Tyndall's experimental results (the emission ratio is 18.6 and not 11.6) played in Stefan's favour: all the errors compensated each other to produce the right result! Stefan did not evaluate the constant σ and his result was not accepted because of the crude way it was obtained, until it was proven theoretically about 5 years later by Boltzmann.[161]

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[157] Crova, A., J. Phys. **7**, 357 (1878).

[158] Rossetti, F., Phil. Mag. **viii** (1879).

[159] Stefan, J., Math. Naturw. Akad. Wiss., Wien, Classe Abteilung 2 **79**, 391 (1879).

[160] Tyndall, J., *Heat Considered as a Mode of Motion*, Longman, Green, Longman, Roberts and Green, London, 1865. The book contains the experimental results.

[161] Boltzmann was a PhD student of Stefan and got his PhD in 1866, long before Stefan found his law empirically.

The first theoretical attempt to prove the law was by Adolfo Bartoli (1851–1896), who, in 1875, published a monogram and a short article[162] in which he used pure thermodynamics reasoning and analysis of Crookes' experiments to reach the fundamental conclusion that the radiation in an enclosure operates like a Carnot thermodynamic machine and that light must exert pressure in the direction of propagation. Bartoli's result was overlooked by the community. In contrast, the astronomer Henry Eddy (1844–1921) devised a thought experiment from which he concluded that radiant heat might not obey the second law of thermodynamics.[163] Moreover, Eddy claimed that the prediction of the thermal death of the Universe was wrong.

By pure chance,[164] Bartoli's results became known to Ludwig Boltzmann (1844–1906m).[165] Boltzmann showed, using Maxwell's kinetic theory of gases, that if Stefan's law is valid and the radiative energy losses $\phi(T)$ go as $\phi(T) \approx T^{\alpha}$, then the radiation pressure in thermodynamics goes as $p(T) = (\pi/3c)\phi(T)$. The radiation obeys Maxwell's relation between the energy density and pressure in thermodynamic equilibrium, namely $p = u/3$, where p is the radiation pressure and u the energy density of the radiation. Thus, while the rate of cooling at every wavelength was not yet known, the functional dependence of the total losses (sum over all wavelengths) was already known, and given by what is known today as the Stefan–Boltzmann law. In other words, the integral of Kirchhoff's function $e(\nu, T)$ over all frequencies was known without knowing the shape of the function.

Once the Stefan–Boltzmann law had been established, Stefan could calculate the surface temperature of the Sun. The amount of energy received at the Earth (1,366 W/m^2) was measured by Samuel Langley (1834–1906) in 1884. Langley's result was 2,903 W/m^2, or about a factor of two higher than the present day value. Langley must have erred in the data reduction, since his assistant, Charles Abbot (1872–1973m), who used Langley's original data, found a value of 1,465 W/m^2. The distance to the Sun was known, so it was a simple matter to calculate its emissivity. Use of the new law gave a temperature range of 5,600–11,000K, depending on the exact value of σ, while previous estimates had been significantly lower. The details of the solar spectra were first obtained by Langley (1834–1906m) in 1886.[166] Langley also invented the bolometer in 1878, and this allowed measurement of the total energy arriving at the Earth from stars.[167]

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[162] Bartoli, A., *Il calorico raggiante e il secondo principio di termodynamica*, Nuovo Cimento **15** 196 (1876); ibid. *Sopm i movimenti prodotti dalla luce e dal calore e sopra il radiometro di Crookes*, Firenze, 1876.

[163] Eddy, H.T., J. Franklin Inst. **115**, 182 (1883).

[164] Boltzmann wrote that the editor Wiedemann drew his attention to Bartoli's paper, which was then translated from Italian.

[165] Boltzmann, L., Wied. Ann. **22**, 31 (1884); ibid. 291 (1884).

[166] Langley, S.P., Ann. Chim. Phys. **9**, 433 (1886). Previous attempts had been made by Müller (Müller, J.H., Ann. Phys. **11**, 337, 1858) and Lamanky (Lamanky, S.I., Ann. der Phys. **146**, 200, 1872).

[167] After Langley's death, Abbot continued to measure the solar constant and searched for places with clear sky. Abbot discovered that the southern mountainous region of the Sinai Peninsula enjoyed excellent weather conditions all year round and established an observatory on Mount St.

In 1894, Wien[168] carried out the following thought experiment. Consider a cavity with a piston. Let the cavity be closed so that no radiation can escape from it. As the piston moves slowly inward, the radiation reflected by the slowly moving piston undergoes a small Doppler shift.[169] Calculating the effect on the energy of the enclosed electromagnetic waves with frequency ν, Wien succeeded in showing that the universal function $e(\nu, T)$ must have the form

$$e(\nu, T) = \frac{\nu^3}{c^2} G\left(\frac{\nu}{T}\right),$$

where c is the speed of light in vacuum. Regarding the function G, Wien could only state that it must be a function of ν/T. Obviously, the function G could not increase forever, so at higher and higher frequencies (at a given T), the body must radiate more and more, and consequently must reach a maximum, or else the total emitted radiation would be infinite. Hence, there had to be a value of ν/T for which the maximum emission (per unit frequency) was reached. If the maximum is reached for ν_{max}/T, then

$$\nu_{\text{max}} = c_1 T,$$

where c_1 is a constant. So although Wien did not know the exact form of the function G, he could predict that it reached a maximum value, the location of which could be measured. This simple law, which quantifies Draper's observations in 1847, became known as Wien's displacement law.

Next, assuming the validity of Maxwell's law for the distribution of velocities among the molecules of gas,[170] Wien succeeded in showing that

$$G\left(\frac{\nu}{T}\right) = \alpha\, \mathrm{e}^{-\beta\nu/T},$$

where α and β are constants. So when Wien combined the two results, he found

$$e(\nu, T) = \alpha \left(\frac{\nu^3}{c^2}\right) \mathrm{e}^{-\beta\nu/T},$$

Katherine, only a few kilometers from the famous Santa Katherina monastery. One can still see the stairs with the sign 'to the observatory'. The mountain on which, according to tradition, the ten commandments were announced provides an excellent place for measuring the solar constant! The observatory, established in 1931, operated for about 6 years and was then shut down. The reason for the consistent effort to measure the solar constant accurately was the belief by Langley and Abbot that the energy flux from the Sun dictates the weather on the Earth, so that an exact knowledge of this quantity would be a prerequisite for Earthly weather predictions. Langley suspected the solar radiation of varying periodically.

[168] Wien, W., Wied. Ann. **52**, 132 (1894).

[169] The Doppler effect, namely the shift in wavelength due to the relative velocity between the source and the observer, was discovered by Doppler in 1842.

[170] According to Maxwell, the energy distribution of the molecules in a gas is given by an exponential law, namely, $\mathrm{e}^{-E/kT}$, where k is a constant.

which is Wien's famous radiation law.

Very soon afterwards, these results of Wien and Stefan–Boltzmann were confirmed by the experiments of Lummer and Pringsheim,[171] but only for high frequencies or short wavelengths. A systematic deviation from Wien's law was discovered at small frequencies (long wavelengths).[172] The mere existence of deviations between theory and observation was controversial. Paschen[173] insisted that he had succeeded in proving the universality of Wien's radiation law. Planck[174] on the other hand, rederived Wien's law from the theory of irreversible processes and provided *a more rigorous proof*. Planck's basic idea was to consider the radiation field as a collection of harmonic oscillators[175] exchanging energy with the walls of a cavity. The idea of presenting the radiation field as a collection of oscillators was crucial.

Planck's proof went in two steps. In the first, he showed that the unknown function was given by

$$e(\nu, T) = \frac{\nu^2}{c^2}\overline{U},$$

where $\overline{U}$ is the mean energy of an oscillator. In the next step, he proved that $\overline{U}$ was given by

$$\overline{U} = \alpha\nu\, \mathrm{e}^{-\beta\nu/T},$$

and in this way he proved Wien's law. Planck was pleased with the result.

While Wien's radiation formula was the only one derived on the basis of classical physics, several phenomenological formulae were proposed as well. One of the better known amongst these was invented in 1888 by Weber,[176] who found a simple interpolation formula which described a wide range of experiments. The formula was

$$\frac{c}{\lambda^2}\exp\left(aT - \frac{1}{b^2\lambda^2T^2}\right).$$

Mysteriously at that time, this empirical formula described some of the available data better than the theoretically derived Wien formula.

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[171] Lummer, O.R. and Pringsheim, E., Wied. Ann. **63**, 395 (1897).

[172] Lummer, O.R., and Pringsheim, E., Verh. Dtsch. Phys. Ges. **1**, 215 (1899).

[173] Paschen, F., Berliner Ber. 405 and 959 (1899).

[174] Planck, M., Wied. Ann. **57**, 1 (1896). There exists a report on the same subject a year earlier: Sitzunsber. Berliner Akad. Wiss., 21 March, 289 (1895).

[175] A harmonic oscillator is any physical system that behaves like a spring attached to a mass or a pendulum, i.e., a system which, when displaced slightly from its equilibrium position where it would remain without motion, feels a restoring force proportional to its displacement from equilibrium. This is the simplest mechanical system one can conceive of, and many physical systems behave this way upon sufficiently small perturbation from their steady state. Hence, it was natural to assume the simplest possible system for the emitters and absorbers of radiation.

[176] Weber, H.S., Phys. Rev. **2**, 112 (1894), Sitzungsberichte der Akad. Wiss. Berlin 933 (1888).

2.28 A Black Body Does Not Necessarily Look Black

The term ‘black body’ may wrongly imply that it looks black, since it absorbs all incident light. However, a black body is also a perfect emitter, and its color changes with temperature according to the Wien displacement law. As the temperature reaches about 500 K the body starts to glow with a red color. This was what Draper had already found in 1847. As the temperature of the black body continues to rise, the color changes gradually, passing through all the colors in the spectrum, until at very high temperatures all such bodies shine with a blue–white color. Stars behave to a good approximation like black bodies, and the color they exhibit is an indication of their surface temperature. Paradoxically, one may say that there are black bodies which appear red (when they are at the relevant temperature) and there are yellow black bodies (our Sun for example!), and even blue black bodies (stars with surface temperatures above 15,000 K).

2.29 Buried in the Finer Details

But the experimentalists Lummer and Pringsheim were not happy with the result of the theoretician Planck. In 1900, they returned to experiment[177] and showed convincingly that Wien’s law deviates more and more from observation at short wavelengths. It was only then that Planck went back to the problem[178] and came up with his seminal paper, in which the energy of the oscillators was assumed to be quantized. It is extremely instructive to see how this physics-shaking idea was born.

Planck proceeded as follows. He imagined that the walls were composed of small oscillators which radiate. The energy of each oscillator was divided into a discrete number of ‘energy quanta’ of magnitude ε and it was supposed that these energy quanta were distributed randomly among the individual oscillators. We are not concerned here with which particular energy lies in which particular oscillator, but with the number of energy quanta that each oscillator has.[179] Then Planck calculated the number of ways that each particular distribution of energy quanta could be realized (following the standard procedure in statistical mechanics to find the distribution). From this point on it only required the standard mathematics of permutations to obtain $\overline{U}$. Using Boltzmann’s relation between the entropy and the probability for the realization of a state, Planck obtained

$$\overline{U} = \frac{\varepsilon}{\mathrm{e}^{\varepsilon/kT} - 1},$$

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[177] Lummer, O.R. and Pringsheim, E., Verh. Dtsch. Phys. Ges. **x**, 163 (1900).

[178] Planck, M., Verh. Dtsch. Phys. Ges. **x**, 202, 237 (1900). The derivation of Wien’s law already appeared in the first report, but was not accompanied by explanations.

[179] Ehrenfest, P. and Kamerlingh-Onnes, H., Ann. Phys. **46**, 1021 (1915).

where ε is the energy of the oscillator. But from Wien's displacement law and the expression for $e(\lambda, T)$, it follows that

$$\overline{U} = \nu G\left(\frac{\nu}{T}\right).$$

How could Planck provide a bridge between the two results? By inspection, they can be made to agree with one another if one assumes that ε is proportional to ν. In other words, to get agreement with Wien's law, Planck had to assume that

the energy of an oscillator with frequency ν is $\varepsilon = nh\nu$,

where h is known today as the Planck constant[180] and n is a positive integer. In other words, an oscillator with natural frequency ν can only have an energy that is a whole number multiple of $h\nu$. The natural frequency of an oscillator does not depend on temperature, but the number n does. The complete formula then becomes

$$e(\nu, T) = \frac{h\nu^3}{c^2}\frac{1}{\mathrm{e}^{h\nu/kT} - 1},$$

and this is the function Planck derived in 1900, which started the quantum revolution.

The result was soon confirmed experimentally by Heinrich Rubens (1865–1922) and Ferdinand Kurlbaum (1857–1927)[181] for long wavelengths and by Paschen[182] for short wavelengths. Further confirmations were carried out by Warburg and his associates.[183]

But even success left skeptics. Walther Nernst (1864–1941m) and Theodor Wulf (1868–1946)[184] insisted that the accuracy of the experiments (estimated at 7%) was not sufficient to convince them of the correctness of the new revolutionary theory. As a matter of fact, many, including Planck himself and Einstein, had difficulty swallowing the new theory with its unimaginably far-reaching implications.

Attempts by Max Thiesen (1849–1936)[185] and Eugene Jahnke (1863–1921)[186] to improve agreement with experimental results by playing around with Wien's formula failed.

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[180] Planck, M., Ann. Phys. **4**, 553 (1901) found that $h = 6.548 \times 10^{-27}$ erg s.

[181] Rubens, H. and Kurlbaum, F., Sitzunsber. Berliner Akad. Wiss. 929 (1900), Ann. Phys. **4**, 649 (1901).

[182] Paschen, F., Ann. Phys. **4**, 277 (1901). Paschen had by now changed his mind and accepted the new result.

[183] Warburg, E., with 3 coauthors, Ann. Phys. **40**, 609 (1913); Warburg, E. and Müller, C., Ann. Phys. **48**, 410 (1915).

[184] Nernst, W. and Wulf, T., Berliner Dtsch. Phys. Ges. **21**, 294 (1919).

[185] Thiesen, M., Verh. Dtsch. Phys. Ges. **2**, 65 (1900).

[186] Jahnke, E., Ann. Phys. **3**, 283 (1900).

2.30 Rayleigh: Give Classical Physics a Chance

It was only after Planck got his incredible result that Rayleigh[187] set out to discover what traditional physics had to say about the problem. Rayleigh therefore calculated the energy distribution in a cavity, assuming Maxwell's classical theory. The crucial assumption Rayleigh made was that the energy of the small oscillators in the walls, those oscillators which radiate the energy, varied as kT, where k is a constant.[188] In other words, the energy varies continuously and is proportional to the temperature, as classical physics dictates. Rayleigh's result for $e(\nu, T)$ was

$$e_{\text{class}}(\nu, T) = \frac{\nu^2}{c^2} kT.$$

A comparison with Planck's formula shows that this result corresponds to the limit of long wavelengths, i.e.,

$$e_{\text{class}}(\nu, T) \quad (\text{for} \ \ kT \gg h\nu) = \lim_{kT \gg h\nu} \left(\frac{h\nu^3}{c^2} \frac{1}{\mathrm{e}^{h\nu/kT} - 1} \right) = \frac{\nu^2}{c^2} kT.$$

Note that the new constant h, which was introduced by Planck, disappears from the Planck formula in this limit. So there was no sign of a new constant in what is known as the classical limit. Thus, Planck's formula combines nicely with Wien's law on the one hand and Rayleigh's result on the other. However, it would be a grave mistake to consider Planck's formula as an interpolation between two formulae. The actual situation is quite the other way round: Wien's and Rayleigh's results should be considered as approximations to the full, true result given by Planck's law.

2.31 Jeans: No Way of Saving the Classical Picture

Planck's idea was so radical that it was too much even for physicists to swallow. So many attempts were carried out to escape from Rayleigh's result, which was based on the pure classical theory of electricity and statistical mechanics. The most famous of these attempts was the one by Jeans,[189] carried out five years after Planck's publication. Jeans dropped the idea of radiating oscillators in the wall and assumed that the radiation energy inside the cavity was distributed among the 'degrees of

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[187] Rayleigh, Lord, Phil. Mag. **49**, 539 (1900).

[188] According to Maxwell's classical theory of a gas of molecules, or any collection of particles or systems, the distribution of energy of the molecules is exponential ($\mathrm{e}^{-E/kT}$) and the mean energy is $3/2kT$. This may sound complicated, but it can be shown that, if we bring two systems together and the energy of the new bigger system is the sum of the energies of the individual systems, then this law must follow.

[189] Jeans, J.H., Phil. Mag. **10**, 91 (1905).

freedom of the radiation'. The radiation was considered as an infinite collection of waves.[190] The degrees of freedom were simply the amplitudes of the waves.[191] In other words, while Rayleigh considered the radiators in the wall, Jeans considered the radiation in the cavity. However, in both cases one had oscillators: in the first case material oscillators and in the second radiative oscillators. But the classical treatment of the oscillator's energy was the same in Rayleigh's and in Jeans' calculations. The fundamental difference was that, in classical physics, the energy of a wave depends on the amplitude squared, while in quantum physics the energy depends on the frequency of the oscillator, whatever it is (material or radiation), and as described in Sect. 2.29, only insertion of the frequency dependence by Planck resulted in an expression that agreed with observation.

2.32 Classical Physics is Ruled Out for Microscopic Phenomena

But to no avail, Jeans recovered the Rayleigh result once again. Less well known attempts were carried out by Hendrik Lorentz (1853–1928),[192] Albert Einstein (1879–1955) and Ludwig Hopf (1884–1939),[193] Adriaan Fokker (1887–1972),[194] and even Planck.[195] Physicists were reluctant to accept such a revolutionary step. All attempts to evade the new hypothesis led to the same Rayleigh result. Note that Einstein and Hopf's paper was published five years after Einstein published his explanation for the photoelectric effect in 1905,[196] which required as a prerequisite Planck's idea of discrete energies. Although Einstein implemented the idea, he was unhappy with it.

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[190] Strictly speaking, the wavelengths were discrete and of the form $L/2n$, where L was the size of the cavity and n an integer. But these fine details make no difference for the final result and were added here for physical accuracy only.

[191] A degree of freedom of a physical system is a parameter needed to determine the state of the system uniquely. In the case of a monochromatic wave, there is one degree of freedom, the amplitude, and for a general wave there can be an infinite number of degrees of freedom.

[192] Lorentz, H.A., Proc. Kon. Akad. v. Wet., Amsterdam 666 (1903). See also *The Theory of Electrons*, Teubner, Leipzig, 1909, Chap. 2.

[193] Einstein, A. and Hopf, L., Ann. Phys. **33**, 1105 (1910).

[194] Fokker, A.D., Ann. Phys. **43**, 810 (1914).

[195] Planck, M., Ber. d. Berliner Akad. Wiss. 8 July (1915).

[196] The irony is that much of the experimental work on the photoelectric effect on which Einstein based his theory was discovered by Lenard (1862–1947). Lenard, who got the Nobel prize in 1905, was an adamant promoter of the 'Deutsche Physik' idea and a declared anti-semite. As such, he did not believe in the 'Jewish physics' as reflected in the special theory of relativity. For him it was a bitter pill to watch Einstein being awarded the Nobel prize in 1921 for explaining the data obtained by an Aryan. Add to this his annoyance over the fact that the effect was named after Einstein and himself, since he did the experiment, and you will appreciate the rumor that he was even ready to declare his results wrong.

The final death blow to the idea that there might be an alternative assumption that could salvage classical physics came in the 1911 Solvay congress, when Lorentz[197] provided a general proof that the classical concepts of energy distribution among particles, or degrees of freedom as Jeans would have it, lead unavoidably to the Rayleigh result. There was no way to escape from Planck's dramatic assumption, if one wanted to obtain the Planck distribution.

2.33 The Photoelectric Effect: A Further Success for the Quantum Theory

A dramatic confirmation of Planck's result came when Einstein[198] attacked the problem of the photoelectric effect.[199] He realized that, in order to explain the effect, he had to assume that *radiation, when propagated through a vacuum or any medium, possesses a quantum-like structure*. Einstein retreated from the wave description of light back into the massless particle picture. But like Planck, Einstein did not reach the idea of quanta in a straightforward way. Consider a volume v_0 filled with molecules. The probability that n molecules will be found at a certain moment in time in volume $v < v_0$ is given by

$$w = \left(\frac{v}{v_0}\right)^n.$$

Einstein found that, if the radiation satisfies Wien's radiation law, then the probability that the entire radiation converge into a volume $v < v_0$, leaving no radiation in the volume $v - v_0$, is given by

$$w = \left(\frac{v}{v_0}\right)^{E/h\nu}.$$

A comparison with the previous classical result shows that the results agree if

$$n = \frac{E}{h\nu},$$

where n is an integer, since it is the number of particles. But this is exactly what Planck discovered.

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[197] Lorentz, H.A., *Die Theorie der Strahlung und der Quanten*, Abhandlungen d. Deut. Bunsen-Ges. no. 7, 10 (Eucken, 1914). This is a summary of the first Solvay meeting which took place from 30 October to 3 November 1911.

[198] Einstein, A., Ann. Phys. **17**, 132 (1905).

[199] In the photoelectric effect, a metal is illuminated by monochromatic light. Only when the frequency of the light is above a certain value are electrons emitted from the metal. Each metal has a different threshold frequency. A high intensity of light, but at a frequency below the threshold, does not release electrons.

2.34 Are the Positions of the Fraunhofer Lines Random?

Spectral lines seemed to appear in quite chaotic positions. Lockyer, for example, thought that for some mysterious reason every element had its own lines, and that they would not change whatever happened, like human fingerprints. Moreover, it was not clear at all why two different elements could not have the same set of spectral lines. However, there was no attempt to explain the positions of the lines.

So the obvious thing people tried to do was to find some systematics. The first attempt was made by Paul Lecoq de Boisbaudran (1838–1912)[200] for the case of nitrogen lines. But his conclusions, which were based on insufficiently accurate line positions, were not confirmed by others.[201] Stoney[202] was the first to observe some regularity. He found that the wavelengths of the hydrogen lines, denoted by H_α, H_β, and H_γ, were related to each other in the ratios 1/20:1/27:1/32, to very high accuracy. It was not clear what these 'nice' fractions could mean.

Well-known investigators like Osborne Reynolds (1842–1912),[203] Charles Soret (1854–1904),[204] and others tried various combinations of formulae, until Schuster[205] showed in 1881 that, even if there were absolutely no connection between the positions of the lines, the chances were in favor of finding a harmonic relationship if the spectrum was rich in lines. Consequently, the interest in finding a connection between the positions of the lines faded away. How statistics can be misleading!

In 1885, Johann Balmer (1825–1898m)[206] made a travesty of statistics when he discovered a formula that described the then known spectral lines of hydrogen to very high accuracy. The formula was

$$\lambda = A\frac{m^2}{m^2-2^2}, \quad \text{or} \quad \nu = \frac{4}{A}\left(\frac{1}{2^2}-\frac{1}{m^2}\right) \quad \text{for} \quad m = 3, 4, \ldots,$$

where A is a constant and m an integer greater than 2. Balmer had the problem that the wavelengths of the hydrogen lines were not very accurately known, so he had to compare the results obtained by different experiments and use the average values of the latter for comparison between the formula and observation. Yet the errors in the

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[200] Lecoq de Boisbaudran, P.E., Compt. Rend. **69**, 610, 694 (1869).

[201] Thalen, T.R., Svenska. Vetensk. Akad. Handl. **8**, 1 (1869). See also, Landauer, J., *Spectrum Analysis*, Wiley, 1898, Chap. I.

[202] Stoney, G.J., Phil. Mag. **41**, 291 (1871).

[203] Reynolds, O., Phil. Mag. **42**, 41 (1871).

[204] Soret, C., Phil. Mag. **42**, 464 (1871).

[205] Schuster, F.A., Proc. R. Soc. Lond. **31**, 337 (1881).

[206] Balmer, J.J., Verh. Naturforsch. Ges. Basel **7**, 548 (1885); ibid, 750. The name 'Balmer series' was given to this series because Balmer discovered the phenomenological law that yields the frequencies of the lines, and not because he discovered the lines themselves as was the case for the names of the other hydrogen series.

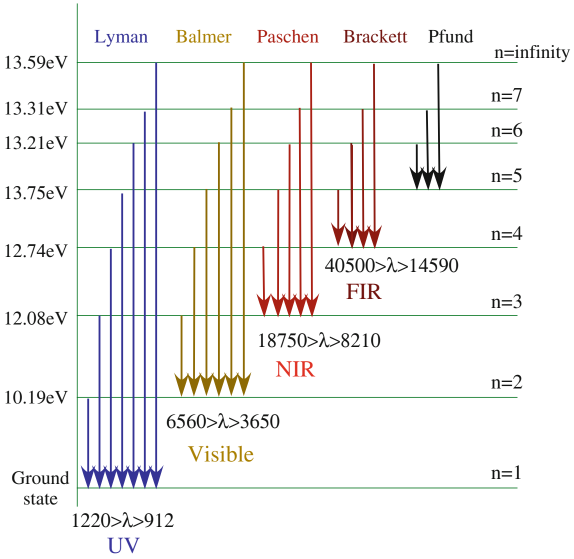

Fig. 2.15 The hydrogen series. Note the ranges in which the series are observed. The energies of the levels are not to scale. There are no energy levels between 0 and 10 eV and all levels lie between 10 and 13.56 eV. There is an infinite number of levels crowding together towards 13.56 eV

fit were about 3 Å, which were considered to be very small in those days. The known lines at the time corresponded to $m = 3$–11. Balmer wrote the equation in the first form (the one on the left), but to display the similarity with Rydberg's formula (see below), it has been rewritten here in the second form. The spectral lines represented by this formula are known today as the Balmer series. Once Balmer had published his formula, Marie Cornu (1841–1902)[207] discovered a similar relation for aluminum and thallium, and later Henri Deslandres (1853–1948m)[208] found additional elements that satisfied this rule. After the success with hydrogen, Balmer attempted to find a formula for the helium lines,[209] but luck did not strike twice (Fig. 2.15).

In 1887, Heinrich Kayser (1853–1940)[210] and Carl Runge (1856–1927m)[211] started their investigation and managed to find various formulae which 'reproduced' the positions of the lines. First, Runge found that

$$\nu = A + \frac{B}{m} + \frac{C}{m^2}, \qquad m = 3, 4, \ldots,$$

provides good agreement with the spectrum of lithium. Then Runge and Kayser found that the following formula provides excellent agreement with the observed positions of the lines of the alkali metals (lithium, sodium, potassium, rubidium, and cesium):

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[207] Cornu, M. A., Compt. Rend. **100**, 1181 (1885).

[208] Deslandres, H.A., Compt. Rend. **103**, 375 (1886); ibid. **104**, 972 (1887).

[209] Balmer, J.J., Astrophys. J. **5**, 199 (1897).

[210] The physical unit of wave number was formerly called the kayser.

[211] Kayser, H. and Runge, C., Ann. Phys. **41**, 302 (1890).

$$\nu = A + \frac{B}{m^2} + \frac{C}{m^4}, \qquad m = 3, 4, \ldots .$$

Janne Rydberg (1845–1919m) attempted to find an empirical expression for the lines of the alkali metals. These were the days after Mendeleev's discovery of the periodic table in which the alkali metals occupied a well defined group. The spectra of the alkali elements were relatively simple when compared for example with that of iron. So it was natural to start with their spectra. At the time it was not known that these metals have a single electron in the outermost shell, and for this reason resemble hydrogen. What Rydberg saw were many lines in the visible. Today we know that this arises because the last electron in the alkali metals is bound to the nucleus with an energy of less than 5 eV. Consequently, most of the spectral lines are in the visible range and had already been observed at that time. The binding energy of the electron in hydrogen is 13.5 eV, so many of the lines lie in the UV and hence were not known at the time Rydberg began his investigation.

Balmer's discovery led Rydberg to attempt in 1889[212] the complete formula (all values of n and not just $n = 2$), which includes all the lines of the alkali metals. Rydberg realized that Balmer's formula was a special case of the following expression:

$$\nu = R_y \left(\frac{1}{n^2} - \frac{1}{m^2} \right), \qquad m \geq n = 1, 2, \ldots, \quad m \text{ integer},$$

which applied nicely to the alkali metals. R_y is a constant known today as the Rydberg constant.

It was a mystery why the hydrogen lines required just $n = 2$, and it was not known what the other values of n implied. Interestingly, Rydberg himself was not sure of the general validity of his formula. In 1897,[213] Rydberg participated in a debate about the nature of the hydrogen lines observed in stars, and claimed that:

> The two series of hydrogen are to be represented by two distinct formulae, even if it may be possible to unite them with great approximation in a single equation.

Moreover, the spectra were classified into two types, those with a clear structure following Rydberg's formula (class I, like the alkali metals) and those which did not follow such a structure (class II).[214]

The enlightenment came when spectroscopy extended its domain to the UV and the far IR. In 1906, Lyman[215] discovered a new set of hydrogen lines in the UV. These lines are 'predicted' by the Rydberg formula if one inserts $n = 1$. In 1908, Paschen[216] discovered a new series of hydrogen lines in the far IR. This series corresponds to $n = 3$. These three series were known to Bohr when he modelled the structure of the

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[212] Rydberg, J.R., K. Svenska Vetensk. Akad. Handl. **23**, 1 (1889).

[213] Rydberg, J.R., Astrophys. J. **6**, 233 (1897).

[214] Rydberg, J.R., *Rapports Présentés au Congrès International de Physique*, *Paris* **2**, 200 (1900).

[215] Lyman, T., Astrophys. J. **23**, 181 (1906).

[216] Paschen, F., Ann. Phys. **332**, 537 (1908).

hydrogen atom in 1913. When Brackett (1897–1974m) discovered the $n = 4$ series in 1922 and Pfund (1879–1949) discovered the $n = 5$ series in 1924, the existence of these series could be predicted by Bohr and constituted an outstanding victory for the new theory.

2.35 The Structure of the Atom: Only Complete Solutions Are Acceptable

Once Einstein's and Planck's ideas were in the air, it became clear that quantization should prevail. The problem was the source of the spectral lines. It was evident that atoms should be treated as oscillators, but the idea of simple oscillators did not help. According to Planck, simple oscillators radiate at a single frequency ν and emit an energy quantum of $h\nu$. If atoms behaved like such oscillators, they would yield a single spectral line with frequency ν, which is obviously not the case. Hence, various attempts were carried out to formulate an atomic oscillator that would oscillate at the observed frequencies of the spectral lines. Among these attempts, probably the best known is the one by Arthur Haas (1884–1941).[217] Haas adopted the Thomson pudding model for the atom in which the negatively charged electrons are immersed in a positively charged jello, and tried to quantize it. This was a year before Rutherford showed, in 1911, that there is a small condensed nucleus and the electrons move around it, like planets around the Sun.

Haas assumed that the maximum frequency of the electron in an atom occurs when it revolves around the atom along its surface (note the contradiction, since the electrons do not move in Thomson's model). Next, he assumed that this negatively charged electron had one energy quantum and revolved around a positively charged sphere. Haas' result for the maximum frequency was

$$\nu_{\max} = \frac{4\pi^2 e^4 m_{\mathrm{e}}}{h^3},$$

where m_{e} is the mass of the electron. He identified this maximum frequency with the series limit, i.e., he substituted $m \to \infty$ in Balmer's formula

$$\nu = R_y\left(\frac{1}{2^2} - \frac{1}{m^2}\right),$$

from which it follows that

$$\upsilon_{\max} = R_{\mathrm{Haas}} = R_y/4.$$

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[217] Haas, A.E., Jahrb. d. Rad. u. El. **vii**, 261 (1910). Other attempts were made by Schidlof, A., Ann. Phys. **340**, 90 (1911); Wertheimer, E., Phys. Zeitschr. **xii**, 409 (1911), Verh. Dtsch. Phys. Ges. 1912, p. 431; Lindemann, F.A., Verh. Dtsch. Phys. Ges. **482**, 1107 (1911); Haber, F., Verh. Dtsch. Phys. Ges. **482**, 1117 (1911); and Nicholson, J.W., MNRAS **130**, 49 (1912).

Had Haas taken the Lyman series, he would have obtained $R_{\rm Haas} = R_y$. But there was no way he could reproduce the following lines in the series. Deriving the Rydberg constant approximately may appear to be a success, but the only parameters in the problem are the charge e and mass $m_{\rm e}$ of the electron and the Planck constant. The simplest unit of frequency (inverse time) that one can build from these three constants is $R_{\rm dim} = e^4 m_{\rm e}/h^3$, so it was no wonder that playing around with the problem would yield the value $R_{\rm dim}$ times a constant of the order of unity for the Rydberg constant. The problem did not lie here, but rather with the relation between the frequencies of the lines!

In contrast to Haas' model, Nicholson's model took the force between the particles to vary inversely as the square of the distance and related the energy of the particles to Planck's theory. The atoms were supposed to consist of a ring of a few electrons surrounding a positive nucleus of negligibly small dimensions. The ratios between the frequencies corresponding to the lines in question were compared with the ratios between the frequencies corresponding to different modes of vibration of the ring of electrons. As Bohr wrote[218]:

> Excellent agreement between the calculated and observed values of the ratios between the wavelengths in question seems a strong argument in favour of the validity of the foundation of Nicholson's calculations.

So what was the problem? Bohr answered:

> In Nicholson's calculations the frequency of lines in a line spectrum is identified with the frequency of vibration of a mechanical system, in a distinctly indicated state of equilibrium, [...] but systems like those considered, in which the frequency is a function of the energy, cannot emit a finite amount of homogeneous radiation [as is observed].

In other words, a certain principle has to be violated or a new one invented.

Why can atoms only radiate at certain frequencies? As well as failing to predict the sequence of spectral lines, all models which assumed atoms in which the positive charge was distributed over the volume completely failed to explain the Geiger (1882–1945m) and Marsden (1889–1970)[219] experiment with scattering of α particles. In this experiment, Geiger and Marsden bombarded a piece of gold foil with α particles. They discovered that:

- The vast majority of the α particles passed through the gold as though through a vacuum.
- Those very few particles that were deviated from the straight line were scattered through a very large angle.

If as Thomson assumed the electric charge is smeared over the whole atom, then the probability that the α particle will hit a constituent of the atom is high, in contradiction with the experiment. The experiment indicated primarily that most of the atom is empty.

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[218] Bohr, N., Phil. Mag. **26**, 1 (1913).

[219] Geiger, H. and Marsden, E., Proc. R. Soc. Ser. A **82**, 495 (1909).

Rutherford[220] explained the experiment with a new model. In Rutherford's model, the positive charge was concentrated at the center and the electrons moved freely through the volume of the atom. The atom as a whole is neutral, but inside the atom the electric field of the nucleus prevails and causes those α particles that pass close to the nucleus to scatter in a special way. Rutherford succeeded in nicely predicting the distribution of the scattered particles. Today the experiment is called the Rutherford scattering experiment, although the experiment was conducted by Geiger and Marsden, while Rutherford provided the theoretical breakthrough regarding the atomic structure.[221]

According to van den Broek,[222] the charge of the nucleus is Ze, where Z is half the atomic weight of the atom. The electron moves in a Keplerian orbit around the nucleus. The atoms are neutral, and hence the number of electrons is equal to the charge of the nucleus.[223]

Rutherford's model explained the scattering but not the emission lines. Moreover, the atom according to Rutherford could not emit a sharp spectral line, thereby introducing the problem that all previous models tried to avoid, namely that an accelerating electron must radiate continuously and hence lose energy and eventually collapse into the nucleus. In short, the atom was unstable.[224]

Bohr adopted the Rutherford model and overcame the problems by revolting against classical physics. He took the liberty of making three bold assumptions which contradicted the notions and spirit of classical physics. His postulates were[225]:

- The electrons cannot revolve around the nucleus in arbitrary orbits, but only in certain discrete orbits determined by quantumtheory.

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[220] Rutherford, E., Phil. Mag. **6**, 21 (1909).

[221] Note the coincidence of facts that helped Rutherford. The atomic weight of gold is 200 while that of the α particle is 4. Thus, when the α particle is scattered by the nucleus of the gold atom, the recoil of the nucleus is very small and the assumption that the scatterer has an infinite mass is a good one. Under this assumption, Rutherford's calculation was simple, while taking the recoil into account would have greatly complicated the theoretical modelling. Gold was chosen because it can be stamped into very thin foils in order to have the smallest number of atomic layers in the target.

[222] van den Broek, A., Phys. Zeit. **14**, 32 (1913).

[223] There are claims that van den Broek suggested in 1911 [Nature **87**, 78 (1911)] that the number of an element in the periodic table corresponds to the charge on its nucleus. But in fact, what van den Broek said was that *if the charge is equal to half the atomic weight*, *than one can infer from the existence of uranium that there are* $238/2 \sim 120$ *elements*. This claim was repeated in Nature **92**, 372 (1913), the year when Mosley published his correct results with 92 elements.

[224] As the Rutherford atom resembles the Solar System and the central force behaves in much the same way, the reader may ask whether the Solar System is stable. The answer is that, according to the general theory of relativity, the Earth emits gravitational wave radiation exactly like the electron which moves around the nucleus. The planets thus lose energy and gradually approach the Sun. In due time, they will therefore collapse into the Sun. However, the rate of energy loss is so small that we can forget this process on the scale of the age of the Universe. But in close binary stars, where the mass of the companion is large and the separation between the two stars is quite small, the collapse happens on a time scale shorter than the age of the Universe. In all likelihood, the collapse triggers a supernova and/or the formation of a black hole.

[225] Bohr, N., Phil. Mag. **26**, 1 (1913).

- If we restrict the motion to circular orbits, then only orbits with angular momentum (mass times radius times circular velocity) equal to a whole multiple of $h/2\pi$ are permitted. This assumption restricts the possible orbits to those which relate to each other like the squares of integer numbers (namely, 1:4:9:16, and so on). These allowable orbits are stationary.

Bohr did not explain why there was a ground state, let alone why the ground state was stable and allowed the electron to stay in it forever, but simply assumed this to be the case. If Bohr was correct, then clearly Maxwell's electrodynamic theory would have to be revised in a substantial way to permit the existence of such orbits, since they violate classical electrodynamics.

- The electrons can jump from one orbit to the other, and when the electron jumps from a level with energy E_2 down to a level with energy E_1, it emits a photon[226] (a quantum of electromagnetic energy) with frequency

  $$\nu = \frac{E_2 - E_1}{h}.$$

  This is called the Bohr frequency condition. What happened during the jump from one energy level to the other remained unknown.

These three assumptions allowed Bohr to derive the Rydberg formula for the hydrogen atom, along with the accurate value of the Rydberg constant. The theory also explained the spectral lines of ionized helium, namely an atom with double the charge but only one electron. The problem of atoms with more than one electron remained unsolved.

Although Bohr's theory introduced new unsolved questions, the victory in the explanation of the existing hydrogen line series, and the prediction of those series that were discovered shortly after, was sweeping.

2.36 Einstein: An Explicit Expression for the Kirchhoff Law

A dramatic change in the attitude to Kirchhoff's law was brought about by Einstein in 1916–1917.[227] By now, Bohr had the explanation for the discrete frequencies at which the hydrogen atom emits radiation, including a full explanation for the position of the emitted lines. So for simplicity, Einstein considered an atom with two energy levels (see Fig. 2.16).

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[226] The term 'photon' appeared for the first time in Lewis, G.N., Nature **118**, 874 (1926) and was quickly adopted. It is surprising that, despite the fact that the concept of a particle of light was known to Newton and was the subject of a centuries long controversy between the supporters of wave theory and the advocates of particle theory, it was such a long time before a proper name was invented.

[227] Einstein, A., Verh. Dtsch. Phys. Ges. **18**, 318 (1916); Mitt. Phys. Ges. **16**, 47 (1916); Phys. Zeit. **18**, 121 (1917).

Let A_{21} be defined by

$$A_{21} = \begin{array}{c}\text{transition probability per unit time}\\ \text{for spontaneous emission per second}\end{array}$$

That is to say, an electron staying in the upper level eventually jumps back to the lower level and this process is spontaneous. It is not known when the electron will jump, but it does so with a certain probability per unit time. Einstein simply assumed that the 'decision' to jump down is statistical. Then define the absorption by

$$B_{12}J = \begin{array}{c}\text{transition probability per unit time}\\ \text{for absorption}\end{array}$$

where J is the mean intensity. The spontaneous jump of the atom from the high to the low energy level does not depend on the radiation that the atom is immersed in. On the other hand, the rate of absorption depends on the mean intensity of radiation and is also probabilistic. The assumptions about these two processes were not sufficient to yield the Planck distribution. Worse than that, they yield Wien's law.

So Einstein found that he had to assume the existence of an additional term, namely, that on top of the spontaneous downward jump of the atom from the high to the low energy level, the transitions are stimulated by the external radiation. Hence, the additional term is

$$B_{21}J(\nu) = \begin{array}{c}\text{transition probability per unit time}\\ \text{for stimulated emission}\end{array}$$

In other words, there is an additional probability to jump down, and this probability is proportional to the intensity of the radiation. The existence of stimulated emission was another major discovery by Einstein. Radiation of a certain frequency induces the oscillator with the same frequency to radiate more. In the simple case, with probability A_{21}, once the electron jumps down, the photon can be emitted in any direction. However, the photon produced by the stimulated electron jump is always emitted in the direction of the stimulating photon. Stimulated emission is not predicted by classical physics, and is a pure quantum phenomenon.

In the steady state, we have

$$n_1 B_{12} J = n_2 A_{21} + n_2 B_{21} J,$$

where n_1 and n_2 are the numbers of atoms/oscillators in the corresponding levels.

From here Einstein rederived Planck's function. To obtain the Planck function, Einstein had to assume that $B_{12} = B_{21}$, a result that does not depend on the properties of the matter. Moreover, Einstein required that $A_{21} = (2h\nu^3/c^2)B_{21}$. This result implies that the coefficient of spontaneous emission is always related to the absorption in the opposite direction, and for all possible materials. In particular, there is no

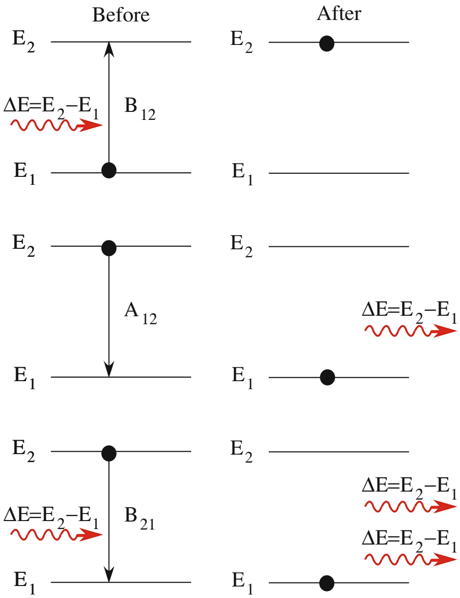

Fig. 2.16 Radiation absorption and emission according to Einstein's phenomenological theory. The *top* process is simple absorption of a photon, with transition of the electron to the upper level. The *second* process is spontaneous emission of a photon, with transition of the electron to the lower level. The *third* process, discovered by Einstein, is stimulated emission. A photon induces the transition of the system to the lower level. Thus for any incoming photon, two photons come out

temperature dependence in this relation. The stimulated photon is coherent with the photon that stimulated the emission.

From the above relation, it follows that the mean radiation intensity is given by

$$e(\nu, T) \equiv J = \frac{n_2 A_{21}}{n_1 B_{12} - n_2 B_{21}}.$$

The strict Kirchhoff relation is

$$e(\nu, T) \equiv J = \frac{n_2 A_{21}}{n_1 B_{12}},$$

namely, without the stimulated emission. If we want to recover Kirchhoff's relation, we must correct the absorption for the stimulated emission. In this way Einstein proved and corrected Kirchhoff's law. But why did Kirchhoff and the others not discover stimulated emission during 40 years of research, and why was it left to Einstein to discover it? There are in fact two reasons. Firstly, Kirchhoff spoke only of the effective absorption and not the theoretical probability of light being absorbed. And secondly, the stimulated effect becomes important only at very short wavelengths, such as UV, and UV spectroscopy was in its infancy or non-existent in Kirchoff's day.

To proceed, Einstein needed the ratio n_1/n_2 between the numbers of atoms in the two levels. He assumed that the ratio satisfied the Boltzmann relation $n_2/n_1 = \exp\left[-(E_2 - E_1)/kT\right]$ and this was sufficient to prove that

$$e(\nu, T) \equiv J \equiv B_\nu(T).$$

Note that the Boltzmann relation is a classical expression, and it is not clear a priori why it should hold in the quantum domain. Thus, the proof was a kind of a mixture between classical physics and the new quantum theory. Moreover, Einstein assumed that the transition of the electron between the energy levels was a probabilistic process, long before the quantum wave function was discovered by Schrödinger and its statistical interpretation given by Born.

The connection between the atomic energy levels, the frequency of the emitted photons, and Kirchhoff–Planck's universal function was finally established. Note that, while the coefficients A and B introduce the probabilistic element of quantum mechanics, Einstein did not draw upon any other results from quantum mechanics. In particular, the structure of the energy levels of the atom, e.g., the Rydberg formula, played no role in the derivation. The matter out of which a cavity is made is irrelevant!

2.37 A Physical Note

The description so far is ideal. Consider a cavity with temperature T and a substance composed of certain kind of two-level atom. Moreover, assume that the cavity is also composed of two-level atoms, but a different kind, so that the two frequencies are different. Clearly, such a system cannot reach thermal equilibrium, because there is no process which converts the radiation energy into thermal energy. Does this mean that there are theoretical systems that cannot reach equilibrium? In principle it does, although in practice it probably does not. If we allow some dissipation to take place, like recoil of the absorbing atom, the cavity will eventually approach thermal equilibrium with the body inside. How long it would take to reach such an equilibrium is another question that will not be discussed here.

2.38 Not All Are Quick to Accept

Not everyone was happy with the new discoveries about the radiation mechanisms. Gilbert Lewis (1875–1946m) was one of the most influential American chemists around the turn of the nineteenth century. As late as 1925, Lewis stated[228] that the number of photons was conserved. He was led to this conclusion from considerations of detailed balance between absorption and emission. Lewis himself asserted that the principle contradicted existing notions of light absorption. The idea was that, in the emission process, only one photon should appear. Likewise, Lewis[229] advocated *the law of entire equilibrium*, which he formulated as:

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[228] Lewis, G.N., Nature **118**, 874 (1925).

[229] Lewis, G.N., PNAS **11**, 179 (1925).

> Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process.

This appears to be what had been demonstrated long before, but just in case the reader was not clear about it, Lewis wrote:

> I believe that some of the ideas contained in this paper have been suggested by the work of Einstein, but he has not proposed this law of equilibrium.

Einstein simply wrote the equation without the accompanying fanfare.

A couple of pages after Lewis' paper in Nature, Ralf Fowler (1889–1944) and Edward Milne (1896–1950)[230] referred to this paper with the remark:

> It may […] be helpful to the reader of Lewis' note to call attention to the considerable amount of recent work in physics, under the name of the 'principle of detailed balancing'. It seems unnecessary that the relevant parts of these investigations should be worked through anew.

In short, the chemist should look at what the physicists had been doing before. On this occasion Fowler and Milne cited a long list of researchers who had investigated this principle: Owen Richardson (1879–1959),[231] Einstein,[232] James Franck (1882–1964),[233] Günther Cario (1897–1984),[234] Cario and Franck,[235] and many others. This is one of the rare cases in which the journal Nature bothered to correct a paper published in its own pages.

2.39 New Elements in the Sun

The discovery of helium in the Sun was an impressive manifestation of Kirchhoff's and Bunsen's discovery that each atom and molecule has its own characteristic spectrum. However, the contribution of luck cannot be ignored.

Indeed, helium was first discovered on the Sun, for which reason it was named after the Greek word *helios*. In 1868, Pierre-Jules Janssen went to India to study the total solar eclipse of 18 August 1868. During the eclipse, he was able to take a spectrum of the prominences, which are usually too faint to be observed at full

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[230] Fowler, R.H. and Milne, E.A., PNAS **11**, 400 (1925).

[231] Richardson, O.W., Phil. Mag. **27** (1914).

[232] Einstein, A., Phys. Zeit. **18**, 121 (1917).

[233] Franck, J., Phys. Zeit. **9**, 289 (1922).

[234] Cario, G., Phys. Zeit. **10**, 185 (1922).

[235] Cario, G., and Franck, J., Phys. Zeit. **11**, 161 (1922).

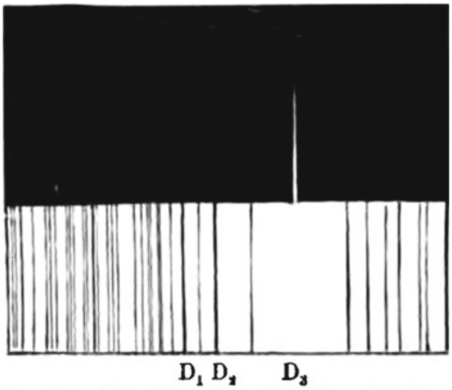

Fig. 42.—Line D_3 (yellow), with radial slit.

Fig. 2.17 The *upper panel* is the famous D_3 line as depicted by Lockyer in 1887 in his book. The *lower part* is the laboratory spectrum attached to the telescope and used to calibrate the observed spectra. The D_1 and D_2 sodium lines are marked as well. Note that the D_3 appears in emission

Sun. And in the spectra of these prominences[236] and the corona, he discovered an unfamiliar single(!) yellow spectral line in emission (see Figs. 2.17, 2.18).[237]

The setting was perfect for Kirchhoff's explanation of the Fraunhofer lines, i.e., a very bright source of radiation, the Sun, surrounded by a faint corona. Yet the observed yellow line in the prominences and the corona, was not seen as a dark Fraunhofer line, but as an emission line. So what was it? Lockyer measured the location of the lines so accurately that there was no room for confusion. The reason, as we know today, is a streak of luck. Helium needs high temperatures (of the order of 2.5×10^5 K) to excite the electron so as to produce spectral lines by jumping back to a lower energy level. The temperature of the corona is about 2×10^6 K, and at this high temperature, a few helium lines remain possible. One of them is the yellow line. At a lower temperature such as 5,800 K, which prevails in the reversing layer of the Sun, the electron of the helium is not excited at all and no spectral line appears. On the other hand, the corona is so much hotter than the solar surface that no reversal of the line takes place. The line was designated D_3 because of its proximity to the sodium D_2 lines.

Janssen informed Lockyer[238] in England about the mysterious line. On 20 October 1869, Lockyer pointed his 6-inch telescope at the Sun and verified Janssen's discovery

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[236] A prominence is a large, bright torus extending outward from the Sun's surface. Prominences are anchored to the Sun's surface in the photosphere, and extend outwards into the Sun's corona. A prominence forms over timescales of about a day, and particularly stable prominences may persist for several months. It is believed that, when the prominences break the energy released heats the corona.

[237] Janssen, P.J.C., Compt. Rend. **67**, 838 (1868).

[238] Lockyer also won a crater on Mars.

Fig. 2.18 The famous sodium D_1 and D_2 lines, and the D_3 line of helium which was identified by Lockyer and Janssen in the Sun. The conditions in the solar corona allow only for the D_3 line to appear

of a yellow line. Edward Frankland (1825–1899) and Lockyer[239] tried to discover the element in the laboratory, but to no avail.

Janssen and Lockyer announced the discovery of a heavenly element never seen before. This was too much for the 'sophisticated' scientific community. Lockyer and Janssen were ridiculed in scientific circles[240] for many years. The idea that there might be elements in stars that do not exist on Earth seemed absurd.

In 1874, Lockyer[241] gave the Bakerian talk, in which he discussed the spectrum of the Sun and explained how there could be emission lines, observed during the eclipse, which had no corresponding Fraunhofer lines formed in the 'reversing layer'. His working hypothesis was that:

> The so-called elements not present in the reversing layer of a star will be in course of formation in the coronal atmosphere and in course of destruction as their vapour densities carry them down.

They would thus be effectively invisible. But 'helium' was not mentioned!

In later years Lockyer referred to helium indirectly. For example, in 1878,[242] he concluded that:

> The substances which give us the non-reversal line in the chromosphere […] termed the coronal line, are other forms of hydrogen.

He decided to devote a special paper to the subject.

Still in 1877, Draper[243] wrote:

> The case of the D_3 line strengthens the argument in favor of the apparent exemption of certain substances from the common law of the relation of emission and absorption, for while there can be no doubt of the existence of an ignited gas in the chromosphere giving this line, there is no corresponding dark line in the spectrum of the solar disc.

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[239] Frankland, E. and Lockyer, N.J., Proc. R. Soc. **17**, 288 (1869); ibid. **18**, 79 (1869). Lockyer was hesitant about announcing the discovery. Frankland strongly disapproved. But Kelvin did so at the 1871 British Association meeting. In 1886, Copeland, the Astronomer Royal for Scotland, discovered a single helium line in the Orion nebula.

[240] Lockyer, T.M. and Lockyer, W.L., *Life and Work of Sir Norman Lockyer*, Macmillan, London, 1928.

[241] Lockyer, J.N., Phil. Trans. R. Soc. Lond. **164**, 479 (1874).

[242] Lockyer, J.N., Proc. R. Soc. Lond. **28**, 157 (1878–1879).

[243] Draper, H., Proc. Am. Phil. Soc. **17**, no. 100, 74 (1877).

Kirchhoff's partial explanation of the formation of the Fraunhofer lines confused observers. In 1893, there was a solar eclipse which Lockyer observed. Alas, Lockyer, the scientist, reported to the Royal Society only in 1896 that:

> D_3 was absent [...] and the reason given suggested that its recorded appearance in 1882 was simply a photographic effect.

Was Lockyer ready to withdraw his claim? Definitely not. But a later attempt by Herbert Turner (1861–1930)[244] to check Lockyer's claims during the total solar eclipse of 29 August failed as well!

Luigi Palmieri (1807–1896), a well-known vulcanologist, reported that, while investigating an eruption of mount Vesuvius in 1881,[245] he found the D_3 line which Lockyer had identified as helium in the spectroscopic analysis of samples of ejected matter from the volcano. Perplexingly, Palmieri did not save his samples or collect the emitted gas, thus forestalling verification of his claim. Today we know that helium is released in vulcanic eruptions. This is a testimony to radioactive decay taking place in the Earth's solid outer layers. But when Palmieri announced his discovery, it went more or less unnoticed.

In March 1895, William Ramsay (1852–1916) published in Nature[246] the results of his analysis of the spectrum of gases emanating from a uranium mineral called clevite, and discovered an unfamiliar yellow line, as well as:

> [...] four specially characteristic lines in the helium which are absent from that of argon: they are a brilliant red, the D_3 line of a brilliant yellow, a peacock-green line, and a brilliant violet line.

Ramsay did not provide the wavelengths of the spectral lines, but sent gas samples to both Lockyer and Crookes. Within a week, Crookes confirmed that the gas was the same as the one Lockyer had observed on the Sun. The Sun, however, showed just a single line! It took a quarter of a century for Lockyer to celebrate his hard-won victory over those who had mocked him for such a long time. Ramsay's announcement in the journal was followed by a note from Lockyer.[247]

In 1892, before the identification of helium was confirmed, the French Academy minted a medal with the faces of Lockyer and Janssen, who were still alive, to commemorate this outstanding discovery. The French Astronomical Society was more conservative and it was only in 1960 that it established the *Jules Janssen prize*.

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[244] Turner, H.H., Phil. Trans. R. Soc. Lond. **180**, 385 (1886).

[245] Palmieri, L., Rendiconto dell'Academia delle Scienze Fisiche e Matematiche **20**, 150 (1881).

[246] Ramsay, W., Nature **52**, 55 (1895).

[247] Lockyer, J.N., Nature **52**, 55 (1895). Although this was Lockyer's great victory, which came after years of laughter at his expense, his comments were very reserved. Dignity prevailed. Lockyer was then the chief editor of Nature.