

# Independent Discoveries following Different Paths: The Case of the Law of Spectral Reversal (1848-59)<sup>1</sup>

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Publicado in: Cattani, M.S.D.; Crispino, L.C.B.; Gomes, M.O.C. & Santoro, A.F.S. (orgs.) (2009), *Trends in Physics: Festschrift in Homage to Prof. José Maria Filardo Bassalo*. São Paulo: Livraria da Física, pp. 259-82. ISBN: 978-85-7861-021-0. Crispino, L.C.B. (org.), *Festschrift em Homenagem José Maria Filardo Bassalo*, Belém, 2008.

## 1. Introduction

History of science could have been different. For example, if Sadi Carnot had published his 1826 calculation of the mechanical equivalent of heat before dying, then the principle of conservation of energy could have been anticipated perhaps by 20 years.

When studying a field of the history of science, the historian sometimes gives an opinion about “what could have taken place, if something had not happened”. Such assertions are called “counterfactual” statements. The present work is part of a project (initiated in Pessoa, 2001) that tries to explore the possible paths (factual and counterfactual) available for the evolution of science.

The historian is usually suspicious of speculations about histories that did not happen. However, it is not difficult to recognize that the notion of *cause* can usually be translated into a set of counterfactual statements, and vice-versa. One may even define “cause” in the following way: “A is cause of B, if A and B occurred, and the absence of A would affect the probability of occurrence of B”. In experimentally reproducible systems, such as those set up in laboratories of natural science, one may study in a controlled way the effect of the absence or presence of a cause or condition, and in this way stipulate the causal structures involved.

But in the case of historical disciplines, such as biological evolution or the history of science, one cannot control the individual causes in order to have a secure notion of the possible histories. In the case of history of science, however, a certain familiarity that we have with the way the mind of a scientist works, together with the advantage of hindsight that the present stage of science offers of past science, allows one to have an *intuition* of simple counterfactual scenarios with a modest degree of confidence, in the same way that we one can tentatively discern the causes involved in an historical episode.

The proposal of the project, of which this work is part, is to develop an approach, within the philosophy of science, that may assist the intuitive task of postulating counterfactual histories. This is done by expressing the evolution of science by means of *probabilistic causal models*, which involve units of scientific knowledge that may be called “advances”, “contributions” or “achievements” (Pessoa, 2001, 2005). Examples of an *advance* are the calculation of the mechanical equivalent of heat, the construction of the electrochemical pile, and an empirical law such as the law of spectral reversal, subject of the present study. One assumption of the present approach is that, for small variations in the history of science (such as the publication of the aforementioned calculation of Carnot), the advances maintain their identity (i.e., they don’t change in an essential way).

The general aim of the method is to acquire an idea of what are the historical possibilities for the evolution of science, so that one may try to explain *why* science evolved in a certain way and not in another.

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<sup>1</sup> Extended translation of the paper: “Descobertas Independentes por Caminhos Diferentes: O Caso da Lei da Reversão Espectral (1848-59)”, in Martins, R.A.; Silva, C.C.; Ferreira, J.M.H. & Martins, L.A.P. (eds.), *Filosofia e História da Ciência no Cone Sul. Seleção de trabalhos do 5º Encontro*. Campinas: AFHIC, 2008, pp. 347-55.

As an example of how the explanation of an episode in the history of science may be expressed by a causal model, we examined previously (Pessoa, 2006) the case of the beginning of the science of magnetism that occurred in China and in Europe, in which the *same* path was taken independently in two different contexts, until a bottleneck was not crossed in Europe, which resulted in the stagnation of the field. In contrast to this, in this paper we consider the situation in which two *different* paths lead to the same advance, which acted as a bottleneck to the beginning of the old quantum theory.

## 2. The Law of Spectral Reversion

Independent discoveries are quite common in the history of science, although we tend to attribute all the merit to the scientist that arrived at it first or to the one that is culturally closer to us. Quite common are also those independent paths that are abandoned after the announcement of the sought for discovery is made by other scientists.

Let us consider the independent discovery of the law that a medium absorbs the same wavelengths of visible light or of thermal radiation that it emits. This fact is sometimes called the “law of spectral reversion” (Cornu, 1872), because when the experimental conditions of a gas are varied, an emission line may revert into an absorption line (Fig. 2). The law states that, for each wavelength, absorption and emission are proportional, i.e., that if a body absorbs well (or poorly) in a certain wavelength, it will radiate well (or poorly) in this *same* wavelength (assuming the same temperatures).

Nowadays this property is better known as “Kirchhoff’s radiation law”, since Gustav Robert Kirchhoff announced it in October, 1859, providing a mathematical proof in December of that year and, in a more general form, in January of 1860 (see Siegel, 1976, pp. 577-83). Stating it more precisely, this law says that, considering electromagnetic radiation of a single wavelength  $\lambda$ , emitted at a same temperature  $T$ , for any two bodies 1 and 2 (made of any material), the ratio between the rates of emission  $E$  and absorption  $A$  are the same:

$$\frac{E_1(\lambda, T)}{A_1(\lambda, T)} = \frac{E_2(\lambda, T)}{A_2(\lambda, T)} . \quad (1)$$

Another way of announcing this, due to Kirchhoff, is to establish a “universal function”  $e(\lambda, T)$ , which has the same value for any body in the Universe, where  $e$  may be interpreted as the emissivity  $E$  of a “blackbody”, defined as that which absorbs all incident radiation, that is, for which  $A = 1$ . Kirchhoff’s work led to many experimental and theoretical developments which culminated with the beginning of quantum theory, or more specifically, with the announcement of the law of blackbody spectral radiation by Max Planck in October, 1900, followed by the explanation presented by him in December of that year, which postulated the existence of “quanta” of energy at the molecular level of the radiating bodies.

It is interesting, however, that the law announced by Kirchhoff in October, 1859, had already been published, in a less general form, by the Scottish experimental physicist Balfour Stewart, in March, 1858. His statement was less general, since it only referred to thermal (infrared) radiation, and only in March, 1860, would he extend his law to visible light. Furthermore, his mathematical derivation of the law was inferior to that presented by Kirchhoff 1½ years later (see Siegel, 1976, pp. 583-7). One can therefore understand that Kirchhoff’s work would have a greater impact in the following generations, but this does not remove the merits and priority of the Scot, justifying that this advance may be referred to as the “Stewart-Kirchhoff law”. A study of the ensuing controversy over priority, involving British and German scientists, is presented by Daniel Siegel (1976, pp. 587-600).

Stewart and Kirchhoff followed quite *different* paths: Stewart did experiments in the field of thermal radiation, and Kirchhoff concentrated on visible light spectroscopy. In fact, a very similar path to that taken by Kirchhoff was previously followed by Léon Foucault (1848), who stated qualitatively the law of spectral reversion but did not go any further. In Sweden, the same spectroscopic law was discovered in 1853 by Anders Ångström, who explained it in terms of Euler's resonance theory. Our interest, in the present paper, is to describe these different paths in terms of causal models.

### 3. Visible Light Spectroscopy

In 1666, Isaac Newton used a prism to study the colored spectrum of sunlight. It would take almost a century before light from other sources was also investigated with a prism. This was done around 1752 by the Scottish Thomas Melvill, who would die a year later, only 27 years old. Melvill discovered that when different substances become incandescent, they emit light with a characteristic color which, when passed through a prism, forms a spectrum of discrete lines. The most intense line was a yellow one, present in every substance he examined (Woolf, 1964, pp. 628-30).

In 1802, William Wollaston studied the properties of refraction and dispersion of many different transparent substances, passing sunlight through a slit 1/20 of an inch wide, which was narrower than the round hole used by Newton. Examining the resulting spectrum, by placing the flint glass prism in front of his eye, he noticed a few dark lines in the otherwise continuous sunlight spectrum (Pearson & Ihde, 1951, p. 267; Woolf, 1964, pp. 621-2).

This study was conducted in a more refined way in 1814 by Joseph Fraunhofer, in Munich. As a young man, Fraunhofer developed excellent technical skills for manufacturing lenses, receiving from the Swiss Pierre Guinand his secrets for making striae-free glass, thus producing prisms and lenses of superior quality. In order to study the optical properties of different glasses used as lenses, he analyzed the refraction of the yellow line emitted by flames by means of an equipment of high sensitivity that combined a prism (made of the glass to be studied), a theodolite for measuring angles precisely, and a 25 mm telescope (Fig. 1). When he analyzed sunlight, he rediscovered the dark lines and mapped hundreds of them. He also discovered that the yellow line from incandescent sources was in fact two close lines, and that they were located exactly in the positions of two dark lines in the solar spectrum, which he had called the "D lines" (Jenkins, 1970, pp. 142-3). What was the origin of these dark lines in the solar spectrum?

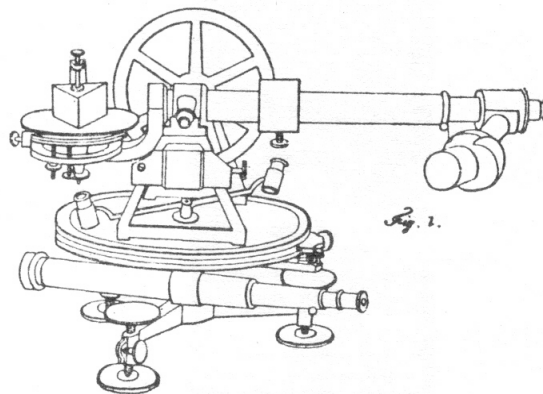


Figure 1: Spectroscopic apparatus of Fraunhofer (Woolf, 1964, p. 631).

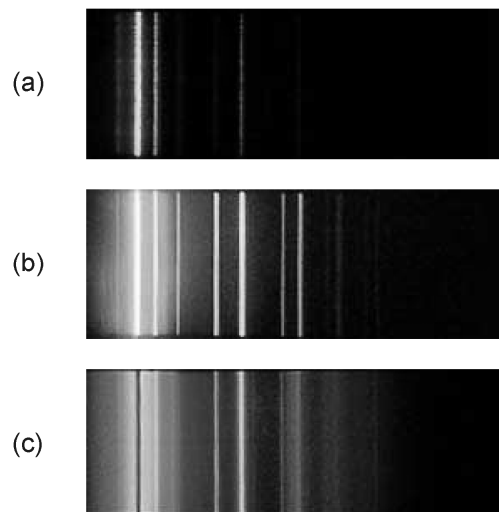
Spectral analysis of flames was further developed, after 1822, by John Herschel and Henry Fox Talbot. Another technique, introduced by Charles Wheatstone in 1834, consisted of the analysis of the spectrum of metals present in the electrodes of a carbon Voltaic arc (the carbon arc was developed by Humphry Davy, in 1821).

Taking into account the similarities between the positions of various dark lines (of the solar spectrum) and bright lines (of the spectrum of flames and voltaic arc), such as the D lines, many scientists, such as David Brewster, in the 1840's, proposed that this coincidence was a general phenomenon. Others, however, like William Swan, denied that this coincidence was general, although they admitted a few coincidences, such as the case of the D lines, which Swan himself was able to show, in 1856, as being due to the element sodium (Siegel, 1976, pp. 568-70).

This identification was delayed because of the difficulty of purifying chemical substances: minute contamination by sodium made almost all materials emit light at the D lines. A decisive step towards this confirmation was the introduction of the so-called "Bunsen burner" by the German Robert Bunsen and his English student Henry Roscoe, around 1855 (Faraday has already prepared a similar equipment in 1827, see Partington, vol. 4, 1964, p. 288). It consisted of a flame of high temperature and low luminosity that introduced a smaller background spectrum than other flames, due to the correct mixture of coal gas and air, which led to the almost complete combustion of the carbon present in the gas.

In 1848, using a voltaic arc, Léon Foucault compared the D lines luminous emissions from the arc and the dark lines in the solar spectrum. Having sunlight pass through the light emitting medium, he observed a curious phenomenon: the dark lines from the sun became even darker after passing through the emitting medium! Foucault thus concluded that the same medium that selectively *emitted* the D lines had the property of selectively *absorbing* the same lines, and this constituted the first statement of the law of spectral reversal (see Fig. 2).

Figure 2: Discharge of sodium gas lamps. (a) Low pressure gas, with the emission only of discrete lines, the stronger being the pair of D lines (not separated in the photograph). (b) Medium pressure gas, with initial broadening of lines and strong emission of the D lines. (c) High pressure gas, with the occurrence of self-reversion (darkening) of the D lines, due to the absorption, by the sodium gas surrounding the voltaic arc, of the D lines emitted in the continuous spectrum originating at the center (source of the spectra: <http://ioannis.virtualcomposer2000.com/spectroscopy/amici.html>).



This same phenomenon of darkening of the solar D lines was observed by William Thomson (future Lord Kelvin) in 1854, but he considered that the darkening of the D lines was a psychological effect, like an optical illusion, as described in a letter to George Stokes (Siegel, 1976, pp. 571-2).

In Stockholm, in February, 1853, Ångström clearly stated the law of spectral reversion, after comparing the solar spectrum with that of metals in a voltaic arc. He based his conclusion on Euler's theory of resonance (Maier, 1970, p. 166). Later, Stokes would also justify this law as being a special case of the phenomenon of resonance, explaining that any mechanical system, which has a natural frequency of oscillation, when perturbed will emit mechanical oscillations at this same frequency, and if submitted to incoming vibrations, will mainly absorb at this same frequency (Dampier, 1929, p. 241). This is the origin of the conception that an atom contains mechanical oscillators which emit light of same frequency, an idea that would only be abandoned after Bohr's atomic theory.

Kirchhoff repeated the experiment in 1859, without knowing the details of Foucault's publication, and was also surprised by the darkening of the solar lines. However, contrary to the Frenchman, he took a further step. He used the continuous spectrum of lime light (developed by Goldsworthy Gurney, in 1823, and Thomas Drummond, in 1826; see Partington, vol. 3, 1962, p. 725), and tried to observe dark lines by passing the lamp light through a sodium flame: he noticed that this only worked with a cooler flame, obtained by mixing alcohol and water. This suggested to him that temperature had an important role in this kind of phenomenon. Inspired by known results (see the following section) for the total emission of radiation (that is, for all wavelengths), but incorporating the first law of thermodynamics (conservation of energy), he derived the law that a medium absorbs the same wavelengths of light or thermal radiation that it emits, i.e., he obtained his universal function  $e(\lambda, T)$ , as mentioned in the previous section.

Besides Foucault, Ångström and Kirchhoff, other scientists that came close to the law of spectral reversion, besides Thomson and Stokes, were William Hallows Miller and John Tyndall (Pearson & Ihde, 1951, p. 270).

#### **4. Researches on Thermal Radiation**

In 1791, the Swiss Pierre Prévost used the notion of caloric (the imponderable fluid of heat, postulated by Lavoisier and others, around 1777) to formulate his "exchange theory". In a situation of equilibrium, all the bodies of an isolated system have the same temperature (satisfying the 2nd law of thermodynamics, which at the time had not yet been formulated); on the other hand, there is a conservation of caloric (expressing the 1st law of thermodynamics, which would only be formulated after 1842). Prévost therefore concluded that a body which absorbs a lot of caloric must emit a lot of caloric. This is in fact what was observed by John Leslie, in 1804, verifying that a good absorber, such as lampblack, is also a good emitter of radiant heat, while a bad absorber, such as polished metal, is also a bad emitter.

Measurements of the thermal radiation emitted and absorbed were made with thermometers, and that was how the great astronomer William Herschel (father of John) discovered in 1800 the existence of infrared radiation. He was studying the Sun, using filters of different colors to darken the solar image. He noticed that when he used some darker filters, he could still experience a sensation of heat, while with other filters that transmitted more light, the sensation of heat was smaller. Passing sunlight through a prism, he measured with his thermometers the rise in temperature as a function of the distance in relation to the visible spectrum (Woolf, 1964, pp. 622-5).

In 1833, with a differential thermometer, William Ritchie verified the equality of total emission and absorption (and not only their proportionality, as Leslie had done), for the same material (Kangro, 1976, p. 7).

The study of infrared radiation increased in the 1830's, after the development of the thermopile by the Italians Leopoldo Nobili and Macedonio Melloni. The principle used in this detector is the "thermocouple", which consists of two metal strips joined at one of their ends, while their loose ends lie at different temperatures, resulting in an electric current proportional to the difference in temperature. Such phenomenon of thermoelectricity was discovered in Berlin by the Estonian Thomas Seebeck in 1821, while measuring, with a rudimentary galvanometer, a current in a ring composed of two metallic semicircles, made of bismuth and copper, with one of junctions being heated. Experimental setups in which the thermoelectric couples were mounted in series, alternating the warm and cold junctions, were introduced by Ørsted and Fourier in 1823. These setups were improved by Nobili, in 1829, connecting the system to an astatic galvanometer, which he had developed in 1825, and which achieved higher sensibility by canceling the effect of the Earth's magnetic field by means of a second magnetized needle. The resulting "thermomultiplier" was extremely sensitive to temperature differences between objects in touch with the thermocouples. In the following year, Melloni suggested to Nobili that the detector be adapted to measure radiation, resulting in an instrument which avoided two problems of the thermometer: its slow and small response, and the absorption of radiation by the glass bulb. The resulting thermopile detector (Fig. 3) of Nobili & Melloni (1931) was sensitive to the presence of a person located 10 meters away (Barr, 1960, pp. 45-6).

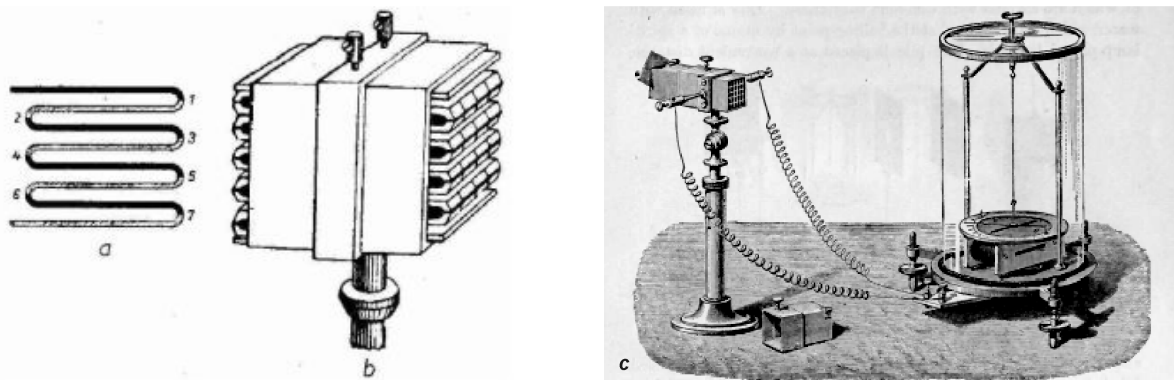


Figure 3: (a, b) Detail of the thermoelectric junctions of a thermopile made of the metals antimony and bismuth, as drawn by Nobili, in 1835. (c) General view of the thermopile connected to an astatic galvanometer (Deschanel, 1886, p. 441).

With the thermopile detector, Melloni (1834) showed that thermal radiation had different "descriptions", analogous to the colors of visible light, with different wavelengths, and James Forbes (1836), of the University of Edinburgh, showed that thermal radiation also has polarization states. In 1835, André-Marie Ampère defended the view that thermal radiation and visible light have the same undulatory nature, differing only with respect to their wavelengths. This conclusion only became consensual after the observation of interference fringes in infrared radiation by Armand Hippolyte Fizeau & Léon Foucault, in 1847 (Barr, 1960, p.48).

It was in Forbes' laboratory that Balfour Stewart carried out his studies on radiation, published in March, 1858. He prepared samples of different materials, such as rock salt, glass, mica, and also lampblack. This latter material, being the best absorber of thermal radiation, should, according to Leslie's observations, also be the best emitter, and thus was used as a reference standard. The samples, when heated to 100°C, served as emitters of radiation, and

the same samples could be used as filters, when placed before the thermopile radiation detector. Stewart noticed that a rock salt filter absorbed 25% of the radiation emitted by lampblack, but absorbed 68% when the emitter was also rock salt. In other words, rock salt emits radiation of a peculiar “quality”, and is quite opaque for that same quality of radiation. This also happened for other materials. From this observation, he concluded that “every body [...] is more opaque with regard to heat radiated by a thin slice of its own substance, than it is with regard to ordinary heat”. The novelty of Stewart’s statement was that he restricted Ritchie’s conclusion, that “absorption is equal to emission”, to each wavelength of radiation. Although he wasn’t able to observe this directly, he inferred it from the concept of “quality” of radiation (Siegel, 1976, pp. 575-7).

Using the exchange theory, Stewart then derived this result in a theoretical way. When Kirchhoff published the derivation of the same law, in December, 1859, and learned of Stewart’s similar conclusions, he criticized him (with good reasons) for lack of rigor in his derivation and for not having done a thorough experiment. Stewart would only extend his results to visible light in a paper published in February, 1860.

## **5. Counterfactual Questions**

We have seen that the law of spectral reversal appeared in two independent paths, both with a strong empirical component, but involving different domains of physical reality: spectroscopy of visible light and infrared radiation.

Why did the two results appear more or less at the same time? Was it a coincidence, or did both fields mature together due to the same set of causes? In other words, if we imagine a set of possible histories developing, say since 1750, in what fraction of these worlds would a similar coincidence occur, in what fraction would the path involving optical spectroscopy arrive first at the law of spectral reversion, and in what fraction would the path involving thermal radiation arrive first?

Since both paths are strongly empirical, dependent on experiments, an answer to the above questions could only be given after a study of the rate in which experimental techniques and instruments were developed in each path. Both fields were involved with the question of the nature of solar radiation, but each was based on different sets of instruments. The optical techniques included the improvement of the manufacture of prisms and lenses, while the infrared techniques included thermal detectors, such as the thermopile, and the preparation of materials that acted as emitters and filters, such as rock salt. One striking difference between these two sets is the use of voltaic currents in the detectors of thermal radiation, and their absence in optical spectroscopy. This indicates that the discovery of the electrochemical pile by Volta has an essential role in one of the paths, but not in the other. Let us investigate these issues in more detail.

## **6. Rate of Advances in Optical Spectroscopy**

Contrary to the case of thermal radiation, which we will examine in the next section, the rate of advances in the field of optical spectroscopy was not dictated by the electrical techniques (except for the use of the Voltaic arc), since the basic apparatus used in this field were prisms, lenses, diffraction gratings and flames, together with precise determinations of angles and positions. The difference in relation to the field of thermal radiation was that the basic detectors were the human eye and (later) photographic plates, and not thermoelectric detectors requiring electrical amplification.

Because of this, one may say that the main advances, in the path to the discovery of the law of spectral reversion in optics, could have occurred before the date that they in fact took place, since the technology required was in general available. The exception to this were the technical innovations introduced by Fraunhofer, especially more homogeneous prisms, which improved significantly the resolution of optical spectroscopy.

The work of Thomas Melvill on the chemical analysis of flames (advance A1), in 1752, did not involve any technique that was not previously available at the time of Newton. These discoveries could have been made by a scientist as bright as Melvill as early as 1700, while the fact that it was not repeated before the 19th century suggests that it could have been made for the first time only around 1800. In this year, William Herschel, while studying the Sun, discovered infrared radiation, which stimulated many other researchers, such as Wollaston, who identified for the first time the dark lines in the solar spectrum. It is not an exaggeration to speculate that Melvill could have made this discovery, if it weren't for his untimely death at the age of 27, when, according to the historian Harry Woolf (1964, p. 628), he "was clearly on the road to major discovery in science".

In Fig. 4a, we chose to begin the causal model in 1750, so that this initial dispersion (standard deviation) of  $\pm 50$  years, estimated above for the beginning of chemical analysis, was not included in our analysis. In this year of 1750, we imagine that one hundred slightly different copies of the Universe were generated (see Pessoa, 2008, for more details on this fantasy), and we assume that in each of them Melvill made his discovery of 1752. We suppose, however, that in 1750 the microorganism that led to the death of Melvill had still not encountered him. What would be the probability that a promising scientist would die at an early age? Maybe not more than 20%, at that time. Adopting this estimate, then in 80% of the worlds Melvill would have continued his experimental investigations, and maybe in a fourth of them (to adopt a conservative estimate) he would have discovered the dark lines of the solar spectrum (advance A2). Therefore, in Fig. 4a, in one fifth of the worlds this discovery would have occurred before 1785. In these worlds, A2 would follow causally from A1, but since this would consist of an exploratory process (the discovery would take place when a scientist, fortuitously, decided to examine sunlight), we use an initially exponential distribution (for the criteria of use of this distribution, see Pessoa, 2006). What in fact happened, in our world, was that Wollaston arrived at A2 not influenced by A1, but inspired by the discovery of Herschel. We therefore assume that in most (80%) of the possible worlds the discovery of A2 took place around the year of 1802, with a dispersion of  $\pm 5$  years. The resulting distribution has a mean value of 1796, with a standard deviation of  $\pm 16$  years.

Once the discoveries A1 and A2 were made, a comparison of the two phenomena could have led some scientist to notice that many of the dark lines of sunlight were in the same position as the bright lines arising in flames of chemical substances, especially the D lines (advance A3). This, however, would require a precise spectrometer, such as the one Fraunhofer built in 1814. We don't know whether Fraunhofer's experimental work could have been done by someone else in the previous decades: that would depend on technical and economical details concerning the manufacture of striae-free lenses. Thus, we will assume that the manufacture of this equipment was "ripe" at that time, and ignore any influence it could have in our estimates of probability. We therefore suppose that A3 would follow from the conjunction of A1 and A2 according to an exponential distribution (since someone familiar with the optical techniques could simply compare A1 and A2, and notice A3), with a mean value of 1814 (see Figura 4b).



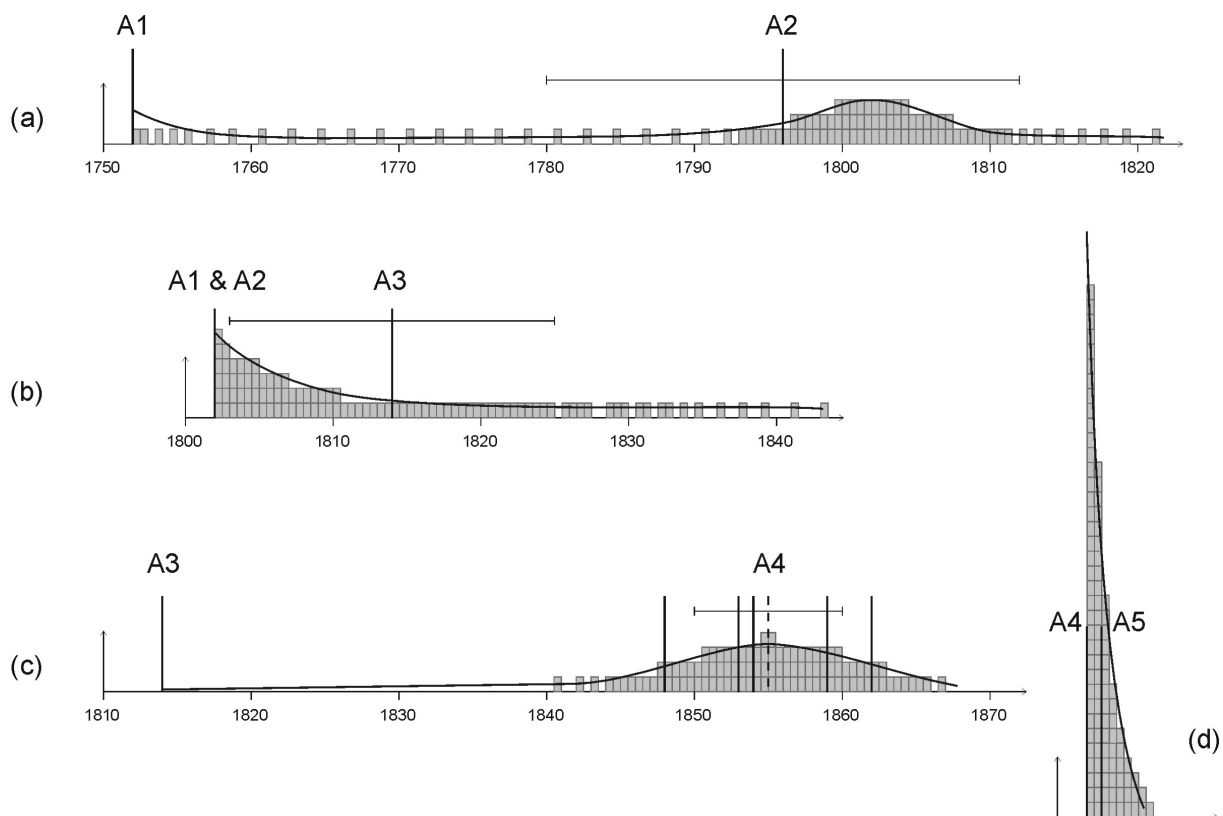


Figure 4: Estimates of the probability distribution of an advance, given a previous one, in the field of optical spectroscopy. Each one of the hundred small rectangles under each distribution curve (of area 1 under each curve) represents the appearance of the advance in a possible world. (a) Distribution, given A1 (chemical analysis of flames), of A2 (the discovery of dark lines in the solar spectrum). (b) Exponential distribution, given A1 and A2, of A3 (the discovery that the solar D lines are emitted by flames). (c) Distribution, given A3, of A4 (the observation that the solar lines darken as they pass through sodium vapor), represented by five dates, the mean value of which is indicated by the dashed line. (d) Exponential distribution, given A4, of A5 (the law of spectral reversion).

From the knowledge that there is a coincidence between the D lines in the solar spectrum and in chemical substances (advance A3), it took around 34 years for scientists to superimpose both spectra and notice that the flame or voltaic arc containing sodium could darken even more the dark lines from the Sun (advance A4). This step involved many intermediary advances, such as the researches on chemical analysis of flames, on the analysis with a voltaic arc, the recognition that the D lines arise from sodium, besides the improvement of the spectrometer and the Bunsen burner, which were not used in the observations of Foucault (1848), Ångström (1853), and Kelvin (1854), but which helped Kirchhoff (1859). Strictly speaking, Ångström's path to advance A5 did not involve A4, so the spike for 1853 in Fig. 4c should be omitted (see causal model of the situation in Fig. 7).

Given this chain of advances, one should not use an exponential distribution, but one that is similar to a gamma distribution (see Pessoa, 2006), such as the one in Fig. 4c. In this case, in order to estimate the mean value and the standard deviation of the curve, one may make use of the fact that this discovery was made independently by the four scientists. We have also introduced a fifth possible world, that in which Tyndall would have arrived at the discovery some time later (as has been suggested in the literature), say in 1862. With these

five data, the mean value is 1855 and the standard deviation  $\pm 5$  years. The gamma distribution was drawn on the basis of these two values.

With the observation of A4, Foucault and Kirchhoff immediately noticed that this implied the law of spectral reversal, or, in other words, that if a medium emits well in a certain wavelength, it will also absorb well in that wavelength (the same applying to thermal radiation) (advance A5). However, Kelvin did not take this leap, for he judged that darkening effect was psychological. In Fig. 4d, this situation is represented by an exponential distribution of narrow dispersion.

Calculating the composition (or convolution) of these four probabilistic causal processes, the resulting distribution is indicated in Fig. 6a. It represents an estimate of the year in which the law of spectral reversal would have been discovered, through the path of optical spectroscopy, starting from the factual situation in 1750. The mean value for the year is around 1850, with a dispersion of  $\pm 20$  years.

We notice that this calculated value is below the mean value in which A5 actually occurred, although it is above the year of Foucault's discovery. This lower mean value is due to the curve in Fig. 4a, the mean value of which is below the year in which Wollaston actually made his discovery.

## 7. Rate of the Techniques in Thermal Radiation

We saw that the field of optical spectroscopy, between 1750 and 1860, did not have its rate determined by technical innovations, but by other factors we were unable to identify clearly, maybe connected to the institutionalization of scientific practice or to random causes. On the other hand, the field of infrared radiation depended heavily on the thermopile, the construction of which was based on the advances in electromagnetic instrumentation. Therefore, the rate of development of this path was dependent on the date in which the electrochemical pile was first built by Alessandro Volta and on the discovery of the conversion process between electricity and magnetism, by Hans Christian Ørsted.

In order to compare the path of thermal radiation with that of optical spectroscopy, we use the same date of 1750 as starting point. At this time, research in electrostatics was well on its way: the machine for generating electricity by friction had already been invented, as well as the Leyden jar, which stored electricity. In 1752, Johann Sulzer made the first observations that the contact of two different metals with the tongue led to a peculiar flavor (Whittaker, 1951, p. 67), but such observation was not followed through to the point of obtaining a pile which generated electricity (a possibility of low probability). The starting point of Volta's advance was the discovery of Luigi Galvani, in 1780, that the spinal marrow or other nerves of a frog, when pressed by a brass hook against an iron lattice, would lead to muscle contractions. Twenty years later, Volta arrived at his electrochemical pile.

In Fig. 5a, the possible histories of Galvani's discovery (advance B1) are represented, in lack of further information, by a Gaussian curve centered around 1780 and with a standard deviation of  $\pm 10$  years, since there was no technical obstacle for this discovery being made 10 years before. The path from this discovery to the invention of the electrochemical pile (B2) involved many intermediary steps, taken especially in Italy, by Volta and Giovanni Fabroni. Assuming that each of these steps may be represented by an exponential distribution, then the composition of many such steps would lead to a distribution that is similar to the gamma distribution of Fig. 5b (see Pessoa, 2006). The dispersion around the mean value of 1800 (the year of Volta's invention) was estimated as  $\pm 5$  years. If the French Revolution hadn't interrupted scientific research in France, it is plausible to assume that the French might have preceded Volta.

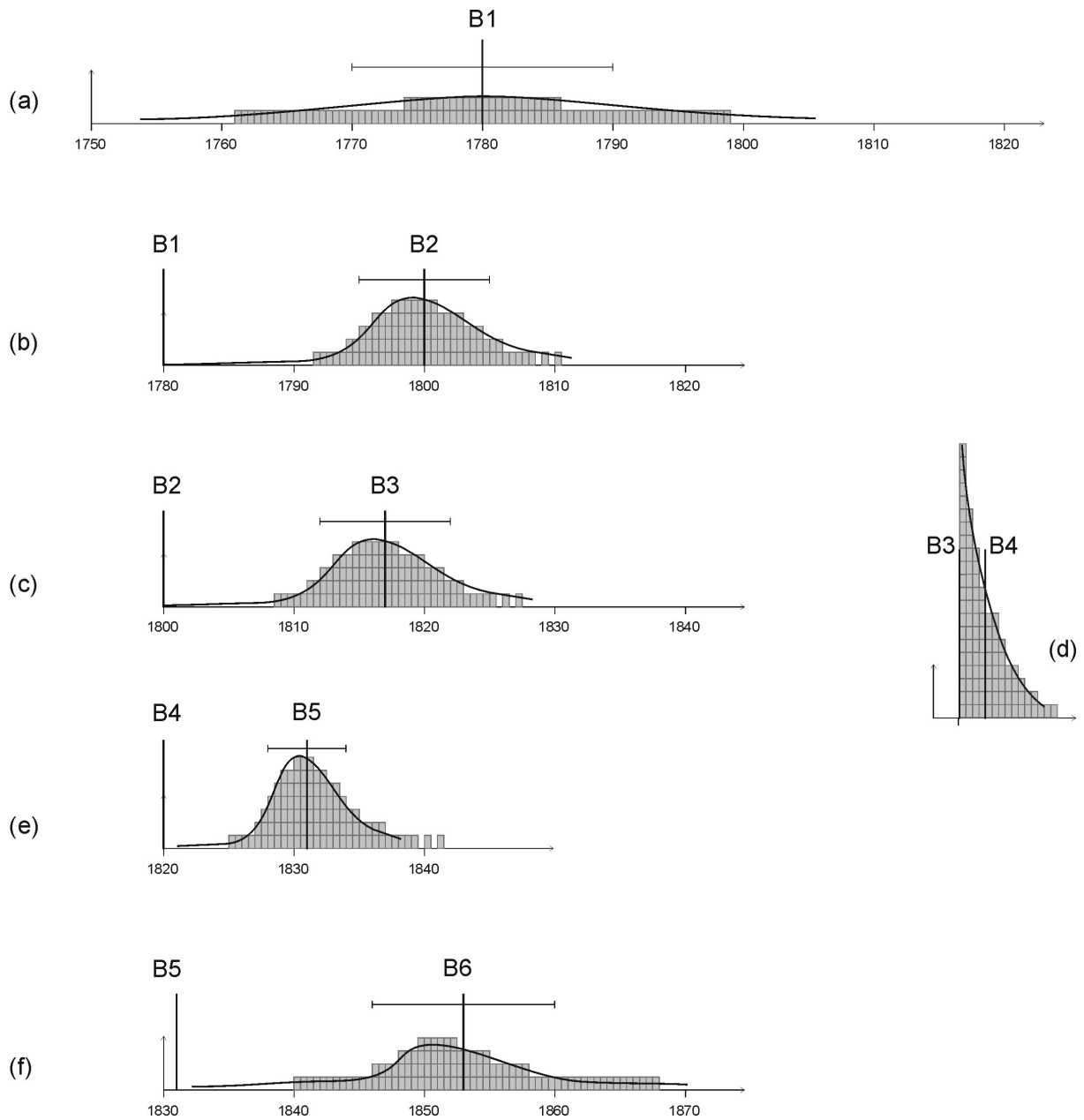


Figure 5: Estimate of the probability distribution of an advance, given a previous one, in the field of thermal radiation. (a) Initial Gaussian distribution, corresponding to advance B1 (the discovery of galvanism). (b) Gamma distribution which represents the appearance of B2 (Voltaic pile), given B1. (c) Gamma distribution of the appearance of B3 (Ørsted's experiment), given B2. (d) Exponential curve representing the discovery of thermoelectricity (B4), given B3. (e) Gamma distribution for the discovery of the thermopile (B5). (f) Gamma distribution for the appearance of B6 (law of spectral reversal in the field of thermal radiation), given B5.

The next important discovery involving electrical phenomena was made by Ørsted, in 1820, showing that an electric current may deflect a nearby magnetic compass (B3). This discovery did not require a very intense electric current, and it is rather surprising that it didn't

happen before. Ørsted himself, in 1812, had planned to investigate the effects of galvanism on magnets. We may thus speculate that the probability distribution between B2 and B3 has a mean value different from 1820, maybe 1817. The gamma distribution with such a mean value and standard deviation of  $\pm 5$  years is sketched in Fig. 5c.

Ørsted's discovery had immediate influence over all of Europe, especially France. The exploration of new territories is typically represented by an exponential distribution, and the swiftness with which the new discoveries took place is consistent with this distribution. One of the most important developments of the Dane's discovery was the galvanometer, an instrument for measuring electric currents. In 1821, a rudimentary galvanometer allowed Seebeck to discover the phenomenon of thermoelectricity (B4). This causal influence may be represented by the exponential distribution of Fig. 5d, for which a mean value of 1822 was chosen, since Seebeck's discovery seems to have taken place in a particularly fast way.

The next advance to be considered was the construction of the radiation detector based on the thermopile (advance B5), obtained in 1831 by Nobili & Melloni, after many intermediary steps. This process is represented once more by a gamma distribution, shown in Fig. 5e, with mean value in 1831 and estimated dispersion of  $\pm 3$  years.

The thermopile (advance B5) was one of the necessary causes for Stewart's experiments, which resulted in the law of spectral reversal for thermal radiation (advance B6). The path from B5 to B6 had some intermediary stages, mentioned in section 4, but these had already been attained in 1840, after the work of Melloni and Forbes. This suggests that we may move back the mean value of the distribution between B5 and B6 by at least five years, so that the mean value would be 1853, with a standard deviation of  $\pm 7$  years, as sketched in Fig. 5f.

The composition of these six processes results in a distribution for B6, starting from 1750, with a mean value of 1853 and standard deviation of  $\pm 13$  years, illustrated in Fig. 6b.

It should be stressed that in the present analysis we have neglected the theoretical and experimental advances, related to thermal radiation, which took place before the development of the thermopile.

## 8. The Computation of Compositions of Causal Processes

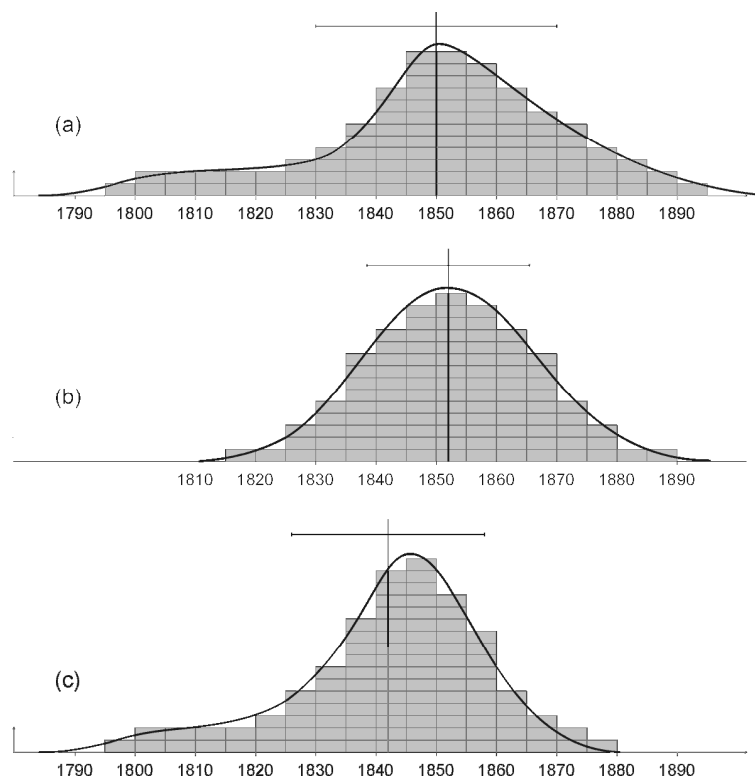
In Figs. 4 and 5, different probability distribution curves are used to describe the appearance of an advance after another. Each small rectangle represents one among a hundred possible worlds, and the actual computations of the composition of causal processes were made from each discrete sample (of one hundred worlds), which approximates the continuous curve in each figure. The shape of the distribution functions is important for attributing a probability for the occurrence of a certain advance within a certain time interval (Pessoa, 2006). However, the exact form of the distribution functions involved in a *composition* is not important for computing the overall mean value and standard deviation. The mean value of the convoluted function (obtained by composition) is the *sum* of the mean values of the component distributions. And the *square* of the standard deviation of the convoluted function is the *sum of the squares* of the standard deviations of the component distributions. These properties should allow a significant simplification in the calculation of probabilities of large networks of advances.

Fig. 6 (a and b) presents a comparison between the estimates for the appearance of the law of spectral reversal by the paths of optical spectroscopy and thermal radiation, taking 1750 as the initial date. The advances A5 and B6 are considered the same (strictly speaking, B6 refers only to thermal radiation, but we suppose that the extension to visible light is immediate). In the first path, of optical spectroscopy, the appearance of the law was found to

have as mean value  $1850 \pm 20$  years, while in the path of thermal radiation it was found to have the mean value of  $1852 \pm 13$  years.

If we imagine one hundred worlds created in 1750, our estimates would be that in around 51% of them the discovery would occur first in the field of optical spectroscopy, and in 48% of them first in the field of thermal radiation (a little less than 1% would occur in the same year). In factual history, Foucault's 1848 observation would put our world in the first class.

Fig. 6c presents a distribution curve of the year that the discovery of the law of spectral reversal would first take place, if we consider *either path*. In this case of disjunction, the resultant distribution was computed from the distributions of Figs. 6a and 6b. The mean value of the resultant distribution is  $1842 \pm 16$  years.



*Figure 6: Distribution curves for the discovery of the law of spectral reversal, relative to the initial date of 1750. (a) Path of optical spectroscopy, with mean value  $1850 \pm 12$  years. (b) Path of thermal radiation, with mean value  $1852 \pm 13$  years. (c) Disjunction of the previous curves, that is, distribution of the discovery by any of the two paths, which gives the mean value  $1842 \pm 16$  years.*

A general view of the main advances involved in these two paths that led to the Stewart-Kirchhoff law is given in the causal diagram of Fig. 7.

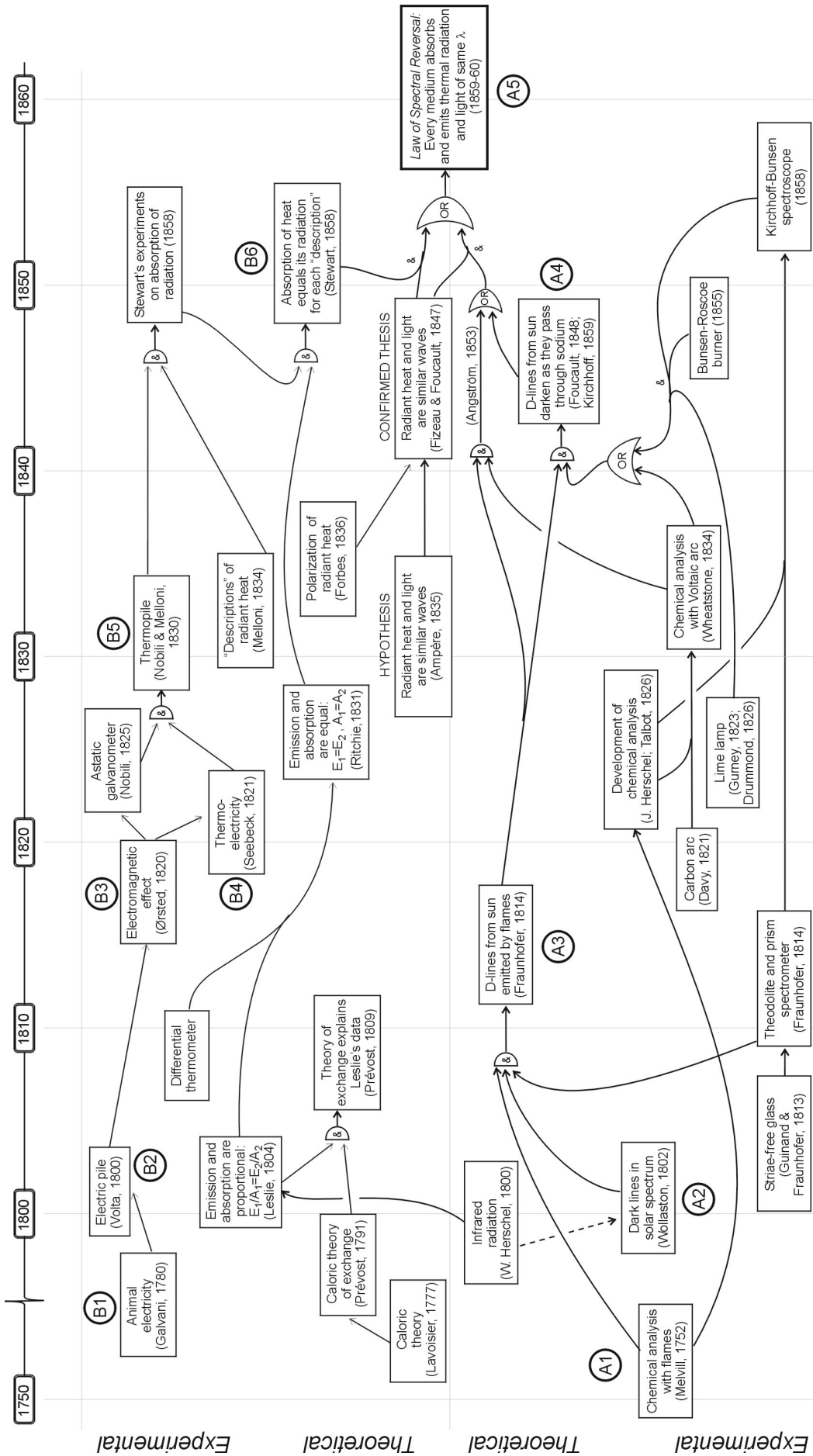


Figure 7: Causal diagram of the main advances leading to the Stewart-Kirchhoff law, following the path of thermal radiation (upper part) and of optical spectroscopy (lower part), with indication of the advances used for analysis.

## 9. Conclusion

We examined the two historical paths that independently led to the discovery of the law of spectral reversal. One difference between these two paths is that the one involving research in thermal radiation is strongly dependent on electrodynamical techniques (thermoelectric effect, astatic galvanometer), contrary to that involving optical spectroscopy. Therefore, one can say that the rate of advances in thermal radiation was dictated, until 1840, mainly by the techniques associated with scientific instruments, especially detectors.

We considered that, in most possible worlds, the path involving thermal radiation would arrive at the law of spectral radiation at a previous date than it actually did, due to an anticipation of Ørsted's discovery by an average of 3 years, and of Stewart's results by 5 years.

The rate of development of the field of optical spectroscopy was not initially influenced by technical issues, so we estimated (conservatively) that, averaging over the possible worlds, Wollaston's discovery would have occurred 6 years before the time that it actually did. After Fraunhofer's development of optical techniques, the pace of the field did not suffer further delays (in relation to the estimated mean of the possible worlds).

So we ended up estimating similar delays for both fields, which resulted in curves with similar mean values in Figs. 6a and 6b.

The methodology of causal models and counterfactual histories is still being explored, and the present study is far from being the final word on the subject. The method is based on the historian's intuitions for each individual advance, and it will probably become more useful for large networks, for which human intuitive ability is more limited. One result of the present paper, that will be useful for further work, is that one need not work with distribution functions to compute the composition of causes, since sufficient information is given by the mean value and standard deviation of each individual causal process. However, as far as we were able to investigate, the evaluation of disjunctions of causes (Fig. 6c) does not have a similar simplification.

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