

## Are the Elements Elementary? Nineteenth-Century Chemical and Spectroscopical Answers

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We analyze the role and influence of a tradition of research linked to the concept of “primary matter” in nineteenth-century studies on the nature of the elements. The suggestion of William Prout (1785–1850) in 1816 that the atomic weights of pure chemical elements are whole numbers and multiples of the atomic weight of hydrogen, taken as unity, was met with serious confutations, which in turn prompted several attempts to save Prout’s hypothesis. We discuss these attempts in detail and the objections raised against them, for instance by Dmitry Ivanovich Mendeleev (1834–1907). We pay particular attention to the use of spectroscopy as a method for proving the existence of elementary forms of matter inside atoms. Leaders in this field of research were two English scientists, the astrophysicist Norman Lockyer (1836–1920) and the chemist William Crookes (1832–1919). Both of their approaches involved the idea of primary matter. However, while Crookes’s approach proved to be incorrect, Lockyer’s ideas survived for several years and supported the discovery of the electron by J.J. Thomson (1856–1940).

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### Are the Elements Elementary?

In 1897 J.J. Thomson (1856–1940), who nine years later was awarded the Nobel Prize in Physics for his work on the conduction of electricity through gases, introduced a new concept of matter:

on this view we have in the cathode rays *matter in a new state*, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state: a state in which all matter—that is, matter derived from different sources such as hydrogen, oxygen, etc.—is of one and the same kind; this matter being the substance from which all the chemical elements are built up.<sup>1</sup>

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Thomson arrived at this idea from his studies on the electrical discharge in gases, and it gained its strength from his series of reliable measurements on the characteristics of his new subatomic component. This idea, however, had its roots in the assumption that the atom is not the ultimate constituent of matter, that is, *that the elements are not elementary*. This view had circulated throughout the nineteenth century.<sup>2</sup> As Thomson wrote:

The assumption of a state of matter more finely subdivided than the atom of an element is a somewhat startling one; but a hypothesis that would involve somewhat similar consequences, viz. that the so-called elements are compounds of some primordial elements, has been put forward from time to time by various chemists. Thus Prout believed that the atoms of elements were built up of atoms of hydrogen, and Mr Norman Lockyer has advanced weighty arguments, founded on spectroscopic considerations, in favour of the composite nature of the elements.<sup>3</sup>

Besides William Prout and Norman Lockyer, other researchers faced this issue by following either chemical or spectroscopical reasoning. In this paper we trace the development of these two ways of reasoning up to 1897, when they were absorbed into Thomson's new model of the atom and the "primary matter" thereby acquired the material entity of the "corpuscle" or "electron."

## The Chemical Way to the Compound Nature of the Atom

### *Prout: A Case for the Primary Matter*

In 1816 the English chemist William Prout (1785–1850) announced that he had demonstrated mathematically that the atomic weights of chemical elements are integer multiples of the weight of a primary matter (*πρωτη νλη*). Prout (figure 1) asserted that "we may almost consider the *πρωτη νλη* of the ancients to be realized in hydrogen,"<sup>4</sup> an opinion, he added, that was "not altogether new." Similar speculations had indeed been advanced earlier by the English chemists Humphry Davy, Thomas Thomson, and John Miers,<sup>5</sup> and the German chemist Ludwig Meinecke, almost simultaneously and perhaps independently of Prout, suggested that the chemical elements were polymers of hydrogen or mixtures of hydrogen with some other form of primary matter.<sup>6</sup> The English chemist T. Edward Thorpe much later explicitly referred to the idea that the weights of chemical elements were integer multiples of a primary matter as the "hypothesis of Prout and Meinecke."<sup>7</sup>

In the decades after Prout advanced his hypothesis it met with experimental difficulties. Particularly noteworthy was the case of chlorine whose atomic weight of 35.5 appeared to conflict with Prout's hypothesis.<sup>8</sup> As the English chemist Thomas Graham remarked, "It appears to be definitely settled that the equivalents of the elements are not, without exception, multiples of the equivalent of hydrogen. The number of chlorine [35.5] is conclusive against that hypothesis."<sup>9</sup> Many scientists in fact were convinced that Prout's hypothesis was inadequate. This conclusion reached a climax in 1860 with its "refutation" by the Belgian chemist Jean Stas (1813–1891) based on his measurements of eight of the better calculated atomic weights.<sup>10</sup> Stas also emphasized



**Fig. 1.** William Prout (1785–1850). © Royal College of Physicians of London. Reproduced by permission.

another difficulty for the primary-matter supporters, namely, that the same number for the atomic weight of a given element was obtained by different methods of investigation. Thus, Thorpe noted in a Graham Lecture that he delivered at the Andersonian Institution in Glasgow on March 16, 1887, that “not many years ago” Stas’s work was considered to have “for ever demolished the doctrine of the primordial *ylé*,” and hence that Roger Bacon’s aphorism, that “barley is a horse by possibility, and wheat is a possible man, and man is possible wheat,” was “an idle saying.”<sup>11</sup>

Two factors stood in opposition to Stas’s supposed refutation of Prout’s hypothesis. The first was the metaphysical idea that Nature should be reducible to a few primary principles. As the English chemist M.M. Pattison Muir noted in 1878, “this idea ... is very apt to lead us to adopt the hypothesis of the non-elementary nature of the elements without sufficient evidence. The idea that all the elements are really compounds of one primary form of matter is a most fascinating idea, it seems to be so much in keeping with the simplicity of nature; it is so symmetrical, it surely must be true.”<sup>12</sup> Second, many scientists had the distinct impression that the atomic weights of several elements were in fact quite close to integer multiples of the atomic weight of hydrogen.<sup>13</sup> They therefore tried to reconcile the apparent discrepancies without renouncing

Prout's hypothesis. Theoretically, there were three possibilities: (a) to amend Prout's hypothesis; (b) to question the recalcitrant facts; or (c) to question some aspects of the theoretical background knowledge. All three possibilities were pursued.

The first took the form of reducing the size of the elementary unit, which of course made Prout's hypothesis intrinsically unfalsifiable. Prout himself proposed this option.<sup>14</sup> Then the French chemists J.C.G. Marignac in 1843, T.J. Pelouze in 1845, and E.J. Maumené in 1846 suggested that the elementary unit should be one-half the atomic weight of hydrogen.<sup>15</sup> Their countryman J.B.A. Dumas suggested in 1859 that it should be one-half or one-fourth of the atomic weight of hydrogen, and the following year Marignac accepted a similar idea.<sup>16</sup> Two decades later, in 1882, the German chemist M. Zängerle suggested that the elementary unit should be chosen to be one thousandths of the atomic weight of hydrogen.<sup>17</sup> Others argued that there were a number of elementary bodies. As Pattison Muir wrote in 1878:

Are the elements really elementary? Stas's researches do not answer this question. We may put the general question in two forms. Are the elements compounds, in varying proportions, of a few simple bodies? Or, are the elements compounds, in varying proportions, of *one* primary form of matter?<sup>18</sup>

The second possibility for saving Prout's hypothesis was to challenge its apparent confutations by questioning the techniques used at the time for chemical purification. Since these techniques were not refined enough to eliminate small perturbative factors, Prout's hypothesis could be regarded as a kind of limiting law, just as was the case for Robert Boyle's and Edmé Marriotte's law for ideal gases. Marignac also accepted this as a possibility, writing that there was no evidence that "the differences observed between his [Stas's] results and those required by Prout's law cannot be explained by the imperfect nature of the experimental methods."<sup>19</sup> And the American chemist John W. Mallet, in an article of 1880 on the atomic weight of aluminum, wrote:

It must be remembered that the most careful work which has been done by Stas and others only proves by the close agreement of the results that fortuitous errors have been reduced within narrow limits. It does not prove that all sources of constant error have been avoided, and, indeed, this never can be absolutely proved, as we never can be sure that our knowledge of the substances we are dealing with is complete. Of course, one distinct exception to the assumed law would disprove it, if the exception were itself fully proved, but this is not the case.<sup>20</sup>

Several years later, in 1886, the same possibility was supported by the English chemist William Crookes, the founder and editor of *Chemical News* and a well-known supporter of Prout's hypothesis, who noted that, "Not a few chemists of admitted eminence consider that we have here [in Prout's hypothesis] an expression of the truth, masked by residual or collateral phenomena which we have not yet succeeded in eliminating."<sup>21</sup>

The third possibility was that the clash between the observations and Prout's hypothesis could be traced to possible uncertainties in the theoretical background knowledge. One of its components was the law of conservation of mass, which Marignac in 1860 doubted could be extended to the atomic world. As he wrote:



**Fig. 2.** Dmitry Ivanovich Mendeleev (1834–1907). *Source:* Daniel Q. Posin, *Mendeleev: The Story of a Great Scientist* (New York and Toronto: Whittlesey House, 1948), frontispiece.

Could we not suppose that the cause ... which underlies the arrangements of the atoms of the prime matter to form our chemical atoms, by impressing on each of these groups a special character and particular properties, might at the same time influence the manner in which these groups of prime atoms obey the law of universal attraction, *in such a way that the weight of each group might not be exactly the sum of the weights of the prime atoms composing it?*<sup>22</sup>

#### *Mendeleev: A Case against Primary Matter*

Dmitry Ivanovich Mendeleev (1834–1907), the discoverer of the periodic law, adopted a point of view similar to Marignac's in a paper of 1871 that he published in Liebig's *Annalen*.<sup>23</sup> Mendeleev (figure 2) began by arguing that Stas's measurements *proved* that the atomic weights of elements could be different non-integral multiples of the atomic weight of hydrogen, so that no definite multiples could be assigned to them. He assumed that the matter making up the elements is completely homogeneous, and he observed that if  $n$  ponderable particles were joined to form one atom of another element, it would not necessarily be  $n$  times as heavy as one of its constituent particles.

According to him, the cause of weight was a particular kind of movement of the constituent matter, so that there was no reason to deny the possibility of transforming these movements into chemical energy, or into some other form of movement. Thus, if one element changed into another one, then this transformation could be accompanied by a diminution or increase in weight. As Mendeleev explained, "In expressing this idea here I wish to say *only* that there is some possibility of the opinions of chemists on the composed nature of elements becoming uniform without adopting Prout's hypothesis."<sup>24</sup> According to Mendeleev, the idea of primary matter should be distinguished from Prout's hypothesis, so that falsification of the latter did not necessitate abandonment of the former, which could be preserved by giving up the law of conservation of mass.

A few years later, Mendeleev changed his position markedly. Some historians of science attribute this to the influence of spectroscopic studies on him during the second half of the nineteenth century,<sup>25</sup> while others focus on "external" factors.<sup>26</sup> In any case, on the occasion of the twentieth anniversary of his formulation of the periodic law, Mendeleev attacked the concept of primary matter by depicting it as an "old Pythagorean idea" wholly independent of the periodic classification of the elements. His target was the "illustrious Berthelot." According to Mendeleev, Marcellin Berthelot, in his book of 1885, *Les origines de l'Alchimie*, had confused the fundamental basis of the periodicity of the elements with Prout's, the alchemists', and Democritus's ideas about a primary matter. Instead, "the periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of an unique matter."<sup>27</sup> Mendeleev charged that the primary-matter supporters took over an ancient Greek conception without explaining the historical context in which it originated. How, for example, could the Greek belief in the existence of many gods be reconciled with the existence of an unique primary matter?

Mendeleev instead rejected the quest for a unity of matter for one for a unity of laws, thus embracing the reductionistic tradition in science.\*

When we try to explain the origin of the idea of an unique primary matter, we easily trace that in the absence of inductions from experiment it derives its origins from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around us. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, *our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material*, because they were not able to evolve the conception of any other possible unity in order to connect the multivarious relations of matter. Responding to the same legitimate scientific tendency, *natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter*, and the convincing conclusions of modern science com-

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\* Mendeleev's rejection of the unity of matter in favor of the unity of laws is dealt with in Bernardette Bensaude-Vincent, "Mendeleev's periodic system of chemical elements," *British Journal for the History of Science* **19** (1986), 3–17.

pel everyone to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere.<sup>28</sup>

In subsequent years, Mendeleev remained antagonistic to the idea of a primary matter. He refused to accept the discovery of the electron, and he rejected explanations of radioactivity that required the disintegration of atoms and transformation of elements.\* He believed that these discoveries could destroy the foundations of the periodic law. He asserted that in chemistry one adopted “the conception of many elements, all submitted to the discipline of a general law,” which offered “an escape from the Indian Nirvana – the absorption in the universal, replacing it by the individualized [substance].”<sup>29</sup> Mendeleev’s individuals were the “chemical elements,” whose distinctive mark was their atomic weights. Thus, measurements of atomic weights like Stas’s *could* refute Prout’s hypothesis.

As noted above, the second possibility adopted by supporters of a primary matter was to reject the apparent contradictory evidence by questioning the techniques used at the time for chemical purification. Another possibility for saving an amended version of Prout’s hypothesis, which was well known to Mendeleev, was to focus on the intrinsic limitations of chemical techniques. One could employ instead “a new and powerful weapon,”<sup>30</sup> or paraphrasing Galileo, search for a “senso superiore e più eccellente.”<sup>31</sup> This “superior and more excellent sensor” proved to be the spectroscope (figure 3).

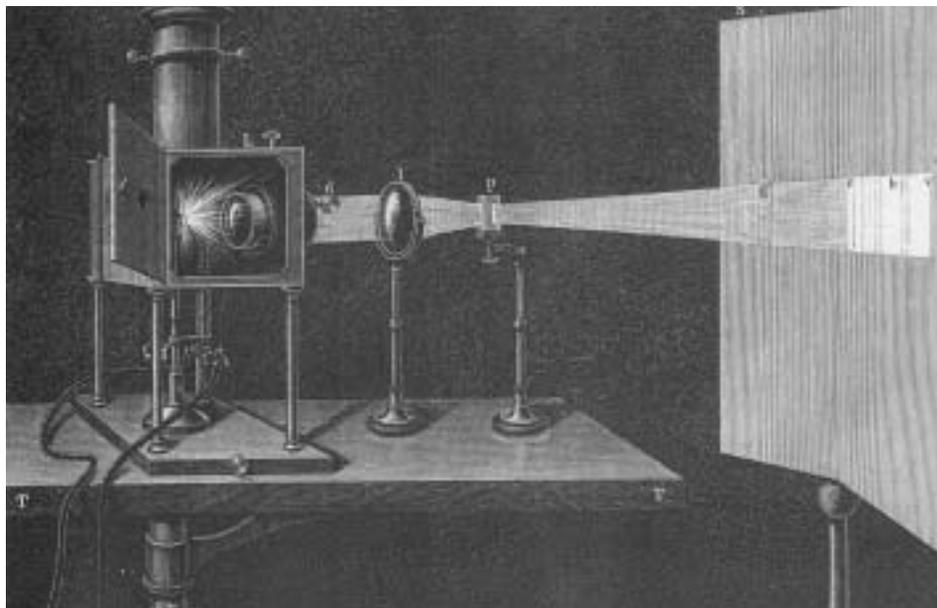
## The Spectroscopic Way To the Compound Nature of the Atom

### *Lockyer’s Involvement*

Gustav Kirchhoff’s discovery in 1859 that emission and absorption spectra are identical turned the spectroscope into a powerful instrument for chemical analysis and stellar classification. In 1860–1861 he and his Heidelberg colleague, Robert W. Bunsen, discovered two new elements, cesium and rubidium, spectroscopically. The spectroscopic discovery of other new elements followed: thallium by Crookes in 1861, indium by Ferdinand Reich and his assistant Hieronymus Richter in 1863, helium (in the solar spectrum) by Lockyer in 1866, and gallium by Paul Émile Lecoq de Boisbaudran in 1875. Earlier, in 1864, William Huggins had succeeded in identifying the main lines in the

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\* Although in Mendeleev’s conception there was no place for the transmutation of elements, he nonetheless tried to account for the emerging field of radioactivity through the idea of the ether. According to Mendeleev, the ether, conceived of as a noble gas, was attracted by the main radioactive elements, just as the sun attracts planets and cosmic dust. As Michael Gordin explained, “at some critical point, too much ether penetrates the uranium and certain chemical processes, of whose exact nature we are ignorant, cause quantities of ether to be ejected from the sample.... What is ejected is the ether, and not a ‘decayed part’ of the primary atom, its almost infinitesimal lightness explained why the ‘decay products’ were not yet weighed. Thus there is no transmutation, no primary matter from which all elements are constructed, and the periodic table is preserved in its epistemological integrity.” See Michael Gordin, “Making Newtons: Mendeleev, Metrology, and the Chemical Ether,” *Ambix* 45 (1998), 96–115; on 100.



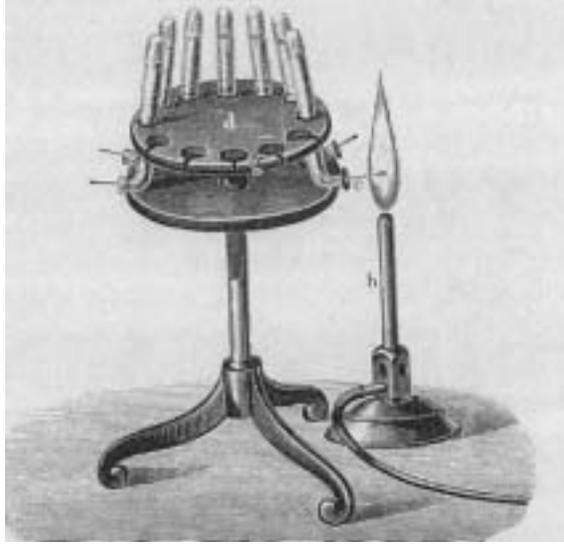
**Fig. 3.** Experimental apparatus for the observation of spectra. Here the calcium spectrum is dispersed by the prism *P* and projected onto the screen *S*. Source: H. Schellen, *Die Spectralanalyse in ihrer Anwendung auf die Stoffe der Erde und die Natur der Himmelskörper* (Braunschweig: F. Vieweg und Sohn, 1883), p. 99.

solar spectrum. But there were problems as well, such as the presence of impurities in the samples and the apparent mutability of some spectra.

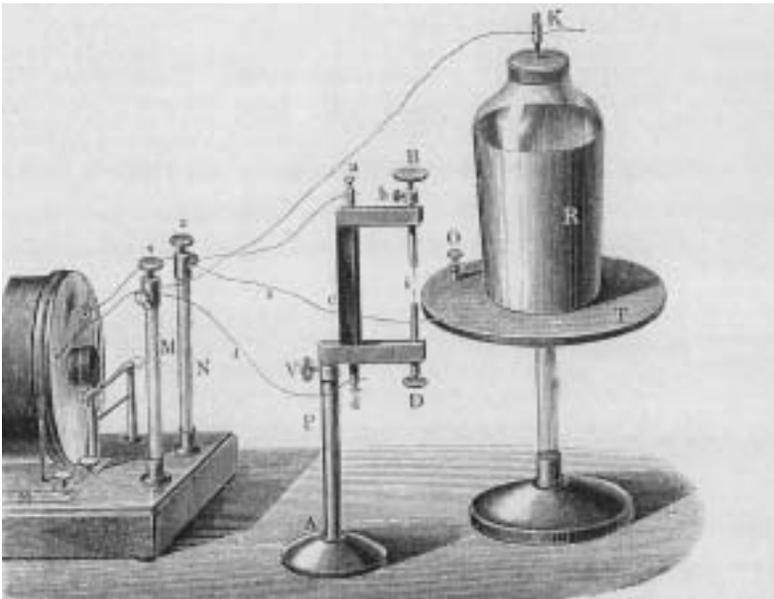
New phenomena also came to light. Laboratory spectra of various salts differed when excited by a flame (figure 4), which gave rise to band spectra, or by an electric arc or spark (figure 5), which produced line spectra. This distinction was explained independently in 1862 by the German chemist Eilhard Mitscherlich and the English chemists Henry E. Roscoe and Robert B. Clifton,<sup>32</sup> who noted that band spectra were produced by molecules at the low flame temperatures, while line spectra were produced by their constituent atoms after the molecules had been dissociated at the high arc or spark temperatures.

But some line spectra also seemed to be mutable, since several elements seemed to produce different line spectra depending on the temperature at which they were excited. The intensities of spectral lines also varied with temperature in a complicated manner, and if the temperature of the source was sufficiently high, new spectral lines might appear. The main way to increase the temperature was to excite the spectra with an electric spark instead of an electric arc.

By an analogical argument, the English astrophysicist Norman Lockyer suggested in 1873 that the new spectral lines that appeared at higher temperatures when the source was excited with an electric spark, or in solar and stellar spectra, were caused by a dissociation of atoms:



**Fig. 4.** Eilhard Mitscherlich's apparatus for producing flame spectra. The tube is filled with a solution of the required salt, and when the wick is put into the flame a constant coloration is produced. *Source:* H. Schellen, *Die Spectralanalyse in ihrer Anwendung auf die Stoffe der Erde und die Natur der Himmelskörper* (Braunschweig: F. Vieweg und Sohn, 1883), p. 263.



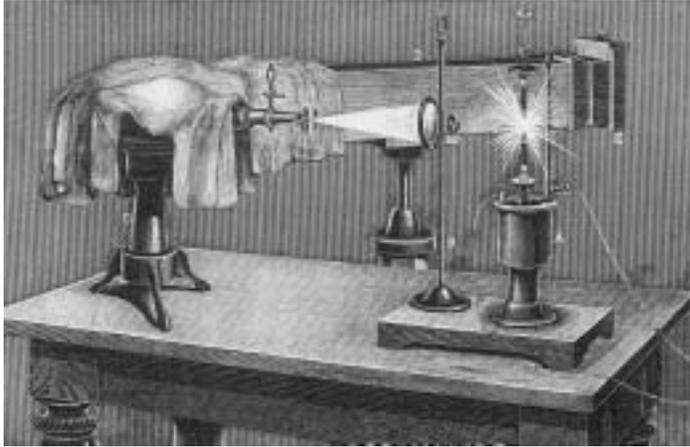
**Fig. 5.** Apparatus for the production of spark spectra. The induction coil (left) charges the Leiden jar *R*, which produces a spark across the gap *i* when it discharges. *Source:* H. Schellen, *Die Spectralanalyse in ihrer Anwendung auf die Stoffe der Erde und die Natur der Himmelskörper* (Braunschweig: F. Vieweg und Sohn, 1883), p. 267.



**Fig. 6.** Norman Lockyer (1836–1920). Reproduced by permission of the Norman Lockyer Observatory.

I have asked myself whether all the above facts cannot be grouped together in a working hypothesis which assumes that in the reversing layers of the sun and stars various degrees of “celestial dissociation” are at work, which dissociation prevents the coming together of the atoms which, at the temperature of the earth and at all artificial temperatures yet attained here, compose the metals, the metalloids, and compounds.<sup>33</sup>

Lockyer (figure 6) interpreted the observations of stellar spectra in light of the principles of uniformity and continuity, to which he frequently referred. The principle of uniformity entailed that the dissociation of elements in stars can be observed on earth, albeit only partially, at the high temperatures produced by electrical discharges. Years later, however, Lockyer wondered: “Does a temperature higher than any applied so far really act in the same way as those we have applied? Or should we expect some unforeseen break in the uniformity of natural processes?”<sup>34</sup> As for the principle of continuity, “many scientists interpreted this principle differently from Lockyer,”<sup>35</sup> although there was “surprisingly little opposition to the use of the principle of uniformity in astrochemistry,” which was “undoubtedly due to its methodological familiarity.”<sup>36</sup> Historian William H. Brock has remarked that, “By 1860, Newton’s second rule of reasoning in philosophy [Therefore to the same natural effect we must, as far as possible,



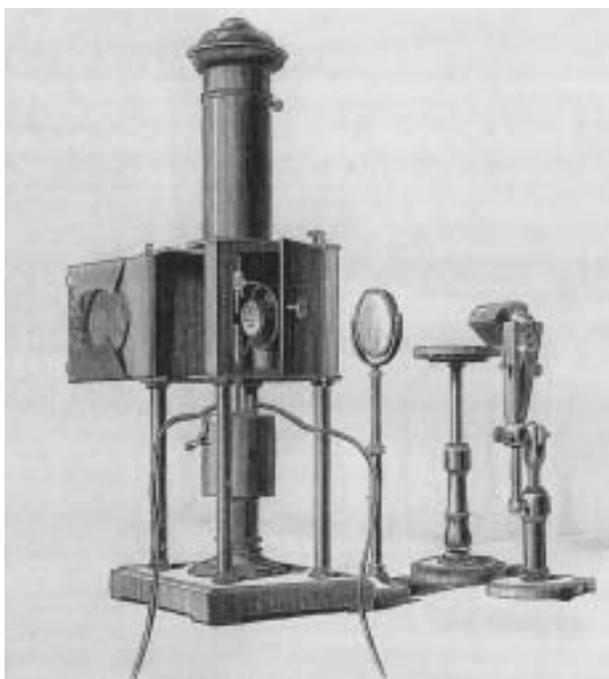
**Fig. 7.** Lockyer's apparatus for the simultaneous representation of spectra emitted by different sources of light. The image of one source is allowed to fall on half of the slit *O* and the photographic plate *E* is exposed. That half of the slit *O* is then covered up and the image of a second source is allowed to fall on the other half of the slit *O* and the photographic plate *E* is again exposed. *Source:* H. Schellen, *Die Spectralanalyse in ihrer Anwendung auf die Stoffe der Erde und die Natur der Himmelskörper* (Braunschweig: F. Vieweg und Sohn, 1883), p. 432.

assign the same causes\*] had become an unquestioned assumption in scientific discourse.”<sup>37</sup>

Lockyer also addressed the problem of coincident lines, lines of equal wavelength in the spectra of different elements (figure 7), in connection with the question of impurities. Were coincident lines due to the presence of the same element in two different samples, in one case as an impurity, or did they result from the dissociation of one element into another one? The latter possibility arose because the spectra of the two elements would differ owing to the differences in their masses, although certain lines in the two spectra could coincide, an idea that he developed further in 1878–1879 when he formulated his theory of “basic lines.”

Lockyer dealt with the problem of impurities from a spectroscopic point of view. His electric-arc observations, which he made by inserting a convex lens between the substances in question and the spectroscope (figure 8), had revealed both long and short lines. But while the long lines were present throughout the entire length of the electric arc, the short lines were seen only in its middle where the temperature is higher, and were absent at its ends where the temperature is lower. Lockyer was unable to explain this difference in length between the two sets of lines, but he realized that the short lines disappeared before the long lines when the current in the electric arc was reduced. He therefore proposed a spectroscopic criterion for identifying impurities in a sample: “When, for instance, an impurity of Mn [manganese] was searched for in Fe

\* Newton's original Latin is “Ideoque effectuum naturalium ejusdem generis eadem assignandae sunt causae, quatenus fieri potest.”

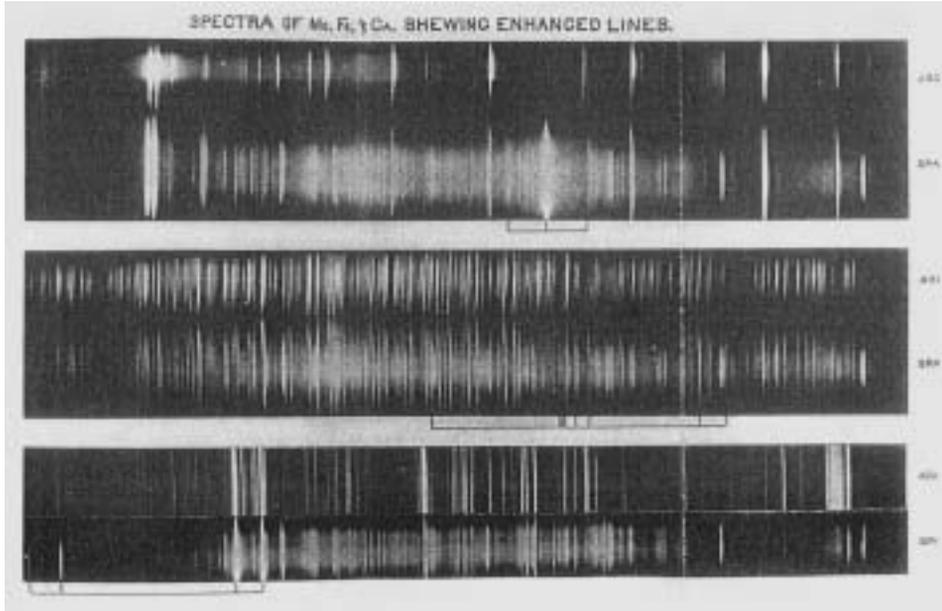


**Fig. 8.** Apparatus for observing short and long spectral lines. The light from an arc or spark passes through a horizontal slit. Some spectral lines then appear only in the center of the image of the slit while others extend far outward. *Source:* Georges Salet, *Traité élémentaire de Spectroscopie* (Paris: G. Masson, 1888), p. 130.

[iron], if the longest line of Mn was absent, the short lines must also be absent on the hypothesis that the elements are elementary; if the longest line were present, then the impurity was traced down to the shortest line present.”<sup>38</sup>

According to Lockyer, simple forms of matter were common to the different chemical elements. He believed that the presence of coincident short lines in different spectra (the “basic lines”) was evidence of such simple forms. Furthermore, the hotter the source, the simpler the spectrum became as these coincident lines appeared. In his view, there were two distinct classes of coincident lines in the spectra of metals: (1) coincident lines due to impurities, and (2) coincident lines due to dissociated elements. “Hence,” he wrote, “it was allowable to term the coincident lines of the second order [or class] ‘basic lines,’ since they might point to the existence of a base common to the substances in the spectra of which they appeared.”<sup>39</sup>

Lockyer retained his hypothesis of basic lines more and less unchanged until 1896. In the meantime, however, the empirical data on which it rested proved to be less than accurate. The coincident lines he assumed to be common to the various elements in the solar spectrum turned out to be accidental coincidences owing in part to poor resolution of the spectroscope that was used.<sup>40</sup> An important role also was played by the presence of impurities. For example, G.D. Liveing and J. Dewar showed in 1880 that Lockyer’s magnesium samples were not pure but consisted of a compound of magne-



**Fig. 9.** Arc and spark spectra of magnesium, iron, and calcium showing enhanced lines in the spark spectra. *Source:* Lockyer, “Chemistry of the Hottest Stars” (ref. 44), plate 1.

sium and hydrogen.<sup>41</sup> Lockyer also thought that each elementary substance could be separated into as many simpler substances as there are lines in the element’s spectrum. That meant, for example, that the “molecular” structure of iron would have to be complex enough to include at least 1,200 different simpler substances—a result that seemed unacceptable.<sup>42</sup>

Toward the end of 1896, Lockyer advanced a new dissociation criterion. By comparing arc spectra with spark spectra, he discovered that the higher-temperature spark spectra contained lines that are absent in the arc spectra. Furthermore, there were lines in the higher-temperature spark spectra that looked “enhanced” compared to those in the arc spectra.<sup>43</sup> Collectively, Lockyer called both sets of lines “enhanced lines” (figure 9). In this way, he was able to account for several previously unidentified lines in stellar spectra,<sup>44</sup> and to explain differences between the solar chromospheric spectrum and Fraunhofer’s visible solar spectrum.<sup>45</sup>

This result affords a valuable confirmation of my view, that the arc spectrum of the metallic elements is produced by molecules of different complexities, and it also indicates that the temperature of the hottest stars is sufficient to produce simplifications beyond those which have so far been produced in our laboratories.<sup>46</sup>

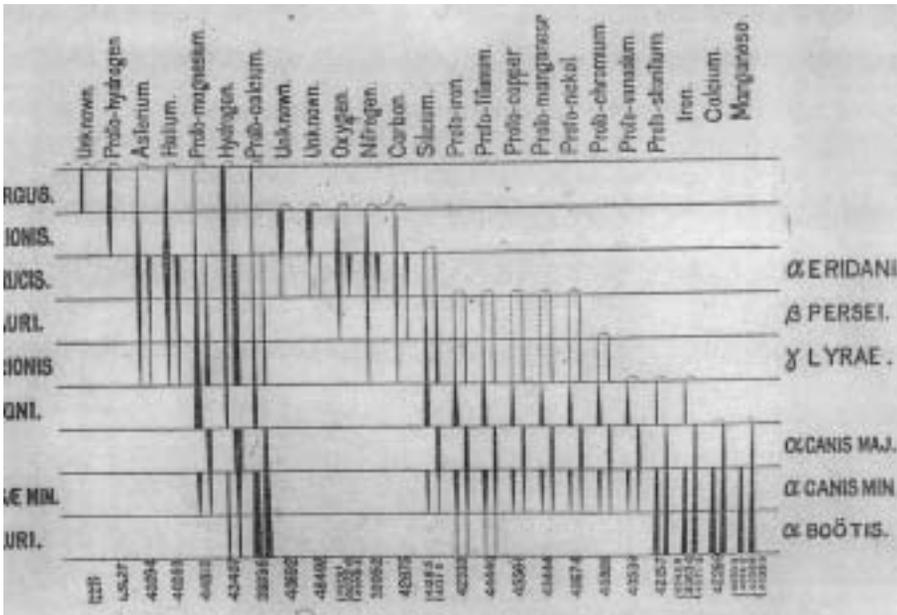
Thus, the role of temperature as the cause of dissociation remained the same, but Lockyer now took the source of the enhanced lines in the higher-temperature spark spectra to be the “proto-element,” while the “element” was responsible for the lines in the arc

spectra. The proto-element then became the link in a chain of “inorganic evolution”<sup>\*</sup> that led from the heavy metals to the light gases through a thermal-dissociation process. As support for his theory, Lockyer displayed a diagram from which he made predictions that were unforeseen by other theories.<sup>47</sup> Thus, by employing a thermometric classification that extended into the ultraviolet region, he discovered that the higher-temperature stellar spectra consisted mainly of spectral lines from light gases (hydrogen, helium), while the lower-temperature stellar spectra consisted of lines from heavy metals. In the intermediate-temperature region, the enhanced lines were particularly prominent (figure 10). Lockyer repeatedly insisted on the basis of his molecular-dissociation theory of spectra that the source of the enhanced lines was the “proto-element,” which was similar to the “element” (from a spectroscopic point of view), but had a mass intermediate between the masses of the light gases and those of the heavy metals.

The existence of the enhanced lines thus caused Lockyer to modify his dissociation idea significantly, which was based originally on his hypothesis of basic lines. As A.J. Meadows explained, “the ‘basic lines’ approach had suggested that different elements broke down on heating to the same simpler substances. The ‘enhanced lines’ approach implied rather that each element dissociated into different, equally unique, forms of the specific element concerned.”<sup>48</sup> This, however, was not tantamount to abandoning the reductionistic approach that was inherent in the idea of primary matter. In Lockyer’s revised dissociation hypotheses, the role of the enhanced lines was just different from that of the basic lines. The enhanced lines, as evidence for the existence of proto-elements, were a link in a chain of inorganic evolution, while the basic lines pointed straight toward the “simpler forms of matter” that were common to the different chemical elements. Lockyer thus retained his idea of an “ultimate state of simplification” of matter; what he changed was its target: The evidence for primary matter now had to be sought in the stellar spectra of gases.<sup>49</sup> “How I wish we could get a bit of your hottest star in a bottle!” exclaimed Crookes to Lockyer in a letter of February 1, 1897 (figure 11).<sup>50</sup>

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\* *Inorganic Evolution* was the title of Lockyer’s book of 1900, in which he expounded his new dissociation hypothesis. Lockyer was not the first to suggest the idea of the inorganic evolution of the elements. Robert Chambers in his anonymously published book, *Vestiges of the Natural History of Creation* of 1844, argued that the organic world is controlled by the law of development, just as the inorganic is controlled by gravitation. According to Chambers, the solar system had developed from a “universal Fire Mist” into its present configuration. A century earlier, Immanuel Kant published his *Allgemeine Naturgeschichte und Theorie des Himmels, oder Versuch von der Verfassung und dem mechanischen Ursprunge des ganzen Weltgebäudes nach Newtonischen Grundsätzen abgehandelt*; translated as *Universal Natural History and Theory of the Heavens: An Essay on the Constitution and Mechanical Origin of the Whole Universe Treated According to Newtonian Principles* (Edinburgh: Scottish Academic Press, 1981), in which he suggested evolutionary ideas: “the sphere of developed nature is incessantly engaged in extending itself. Creation is not the work of a moment. When it has once made a beginning with the production of an infinity of substances and matter, it continues in operation through the whole succession of eternity with ever increasing degrees of fruitfulness” (Part Two, Section Seven, “Concerning Creation in the Total Extent of its Infinity Both in Space and Time”).



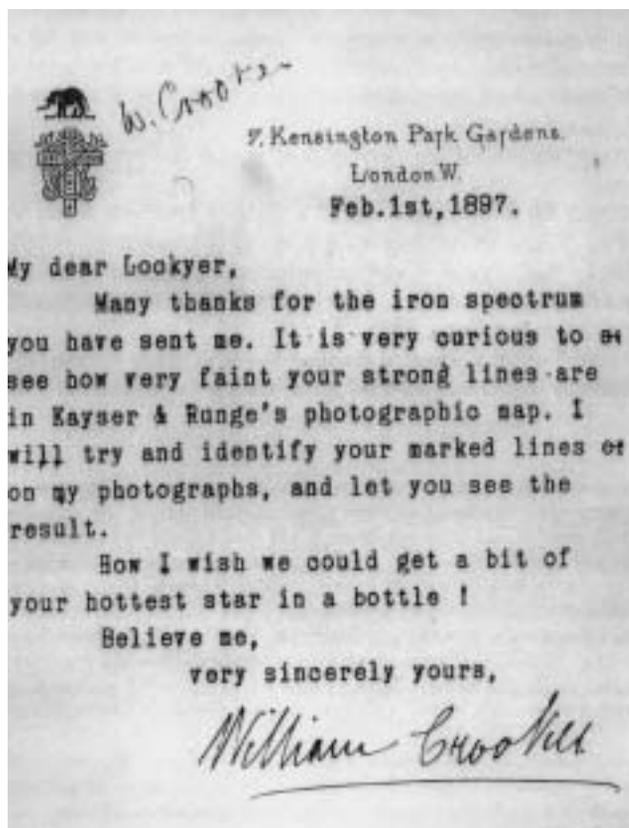
**Fig. 10.** Plot of spectral lines (horizontal axis) versus stellar temperatures (vertical axis). According to Lockyer's measurements, the spectra of the hottest stars are characterized by lines from gases (upper left); at intermediate temperatures (center) the spectra show enhanced lines from proto-titanium, proto-copper, and so forth; at lower temperatures (lower right) arc lines predominate. *Source:* Lockyer, "Order of Appearance of Chemical Substances" (ref. 47), p. 396.

### *Crookes's Involvement*

William Crookes also followed the spectroscopic way to demonstrate the complexity of atoms. Crookes (figure 12) was the discoverer of thallium and the founder and editor of *Chemical News*, but his fame rests mostly on his spectroscopic observations and studies of electrical discharge in rarefied gases, in which he traced the eponymous "dark space" and proposed the existence of "radiant matter." Less known are his researches on chemical fractionation, which focused on the analysis of the phosphorescent spectra of rare-earth elements and aimed at developing a method for finding traces of substances and in this way discovering new chemical elements.<sup>51</sup> The line and band spectra of the rare earths were complicated and puzzling, and several years passed before he experienced a breakthrough.

It was impossible to divest myself of the conviction that I was looking at a series of autograph inscriptions from the molecular world, evidently of intense interest, but written in a strange and baffling tongue. All attempts to decipher the mysterious signs were, however, for a long time fruitless. I required a Rosetta stone.<sup>52</sup>

That appeared during an incomplete chemical reaction of yttrium oxide with a very dilute solution of ammonia when Crookes observed that it precipitated out only a cer-



**Fig. 11.** Crookes's letter to Lockyer, February 1, 1897. Courtesy of Professor G.A. Wilkins.

tain amount of the base. He allowed the precipitate to stand for several hours and then filtered it. After each such "fractionation," the filtrate was passed to the left and the precipitate to the right, and this operation was repeated many thousands of times. Crookes thus exploited the incompleteness of the fractional precipitation as a method of chemical separation. He found that the process had to be iterated many times "before even approximate purity is attained," and the minute quantity of the substance he obtained was "made to accumulate by a systematic process until it becomes perceptible by a chemical or physical test."<sup>53</sup>

Crookes's procedure for the fractional precipitation of yttrium generated a pyramidal structure of samples (figure 13) that emitted phosphorescent light displaying a multiplicity of line and band spectra differing both in their wavelengths and relative intensities (figure 14). Consistent with Lockyer's molecular-dissociation theory of spectra, which he also accepted, Crookes saw these spectra as evidence for the separation of yttrium into its primary components: "The final result to which I have come is that there are certainly five, and probably eight, constituents into which yttrium may be split."<sup>54</sup>



**Fig. 12.** William Crookes (1832–1919). *Source:* E.E. Fournier, *The Life of Sir William Crookes, O.M., F.R.S.* (London: T. Fisher Unwin Ltd, 1923), facing p. 312.

To explain this result, Crookes rejected the traditional concept of chemical element. His chemical-fractionation studies had widened the gap between data obtained by traditional chemical methods and by spectroscopic ones. “Our notions of a chemical element have expanded,” wrote Crookes.

Hitherto the molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the architectural design on which these atoms have been joined. We may consider that the structure of a chemical element is more complicated than has hitherto been supposed. Between the molecules we are accustomed to deal with in chemical reactions and ultimate atoms as first created, come smaller molecules or aggregates of physical atoms; these sub-molecules differ one from the other, according to the position they occupied in the yttrium edifice.<sup>55</sup>

A second possibility (a “heroic alternative”) considered by Crookes was to rank new chemical elements spectroscopically. Thus, the two German rare-earth chemists Gerhard Krüss and L.F. Nilson stated that “according to our present knowledge about the samarium and didymium compounds we cannot doubt that they are compounds *of two*

NUMBERS OF THE BOTTLES.												
-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6
						1000						
					500	1000	500					
				250	500	500	500	250				
			125	250	375	500	375	250	125			
		63	125	250	375	375	375	250	125	63		
	31	63	156	250	312	375	312	250	156	63	31	
15	31	94	156	234	312	312	312	234	156	94	31	15

**Fig. 13.** Pyramid of chemical fractionation according to Crookes's method. He started with, say, 1000 grams in the 0 bottle, then transferred the filtrate to bottle -1 and the precipitate to bottle +1. He then added another 1000 grams to the 0 bottle and repeated the operations as shown in the table. *Source:* Crookes, "Method of Chemical Fractionation" (ref. 53), p. 585.

*distinct bodies.*<sup>56</sup> The acceptance of this viewpoint of course would result in the periodic system losing its meaning, because a large number of allegedly new chemical elements, some identical in atomic weight to others,\* would be added to it.<sup>57</sup> A third possibility (though an improbable one) considered by Crookes was Lecoq de Boisbaudran's proposal that the substances emitting the phosphorescent spectra were impurities in the yttrium samples.<sup>58</sup>

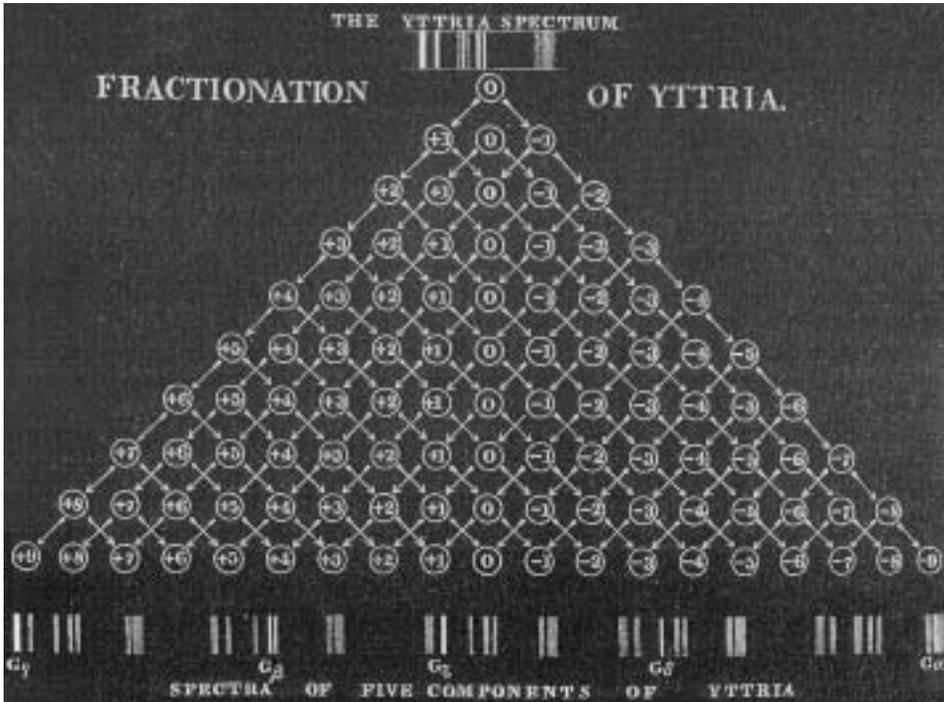
As a result of his studies, Crookes introduced the concept of "elementary group" in place of that of the traditional chemical element:

In defining an element, let us not take an external boundary, but an internal type. Let us say, *e.g.*, the smallest ponderable quantity of yttrium is an assemblage of ultimate atoms almost infinitely more like each other than they are to the atoms of any other approximating element. It does not necessarily follow that the atoms shall all be absolutely alike among themselves. The atomic weight which we ascribe to yttrium, therefore, merely represents a mean value around which the actual weights of the individual atoms of the "element" range within certain limits. But if my conjecture is tenable, could we separate atom from atom, we should find them varying within narrow limits on each side of the mean.<sup>59</sup>

Crookes called the members of the elementary group "meta-elements." Each chemical element then derived from a process akin to the cooling of an elementary "protyle,"\*\* and the defining characteristic of each chemical element was the weighted mean of the

\* The concept of isotopes was eventually introduced by Frederick Soddy in 1913 in connection with the transformation of radioactive elements.

\*\* Details regarding the protyle's etymology are traceable in Crookes's paper, "Genesis of the Elements" (ref. 55). According to Crookes: "We require a word, analogous to protoplasm, to express the idea of the original primal matter existing before the evolution of the chemical elements. The word I have ventured to use for this purpose is composed of  $\pi\rho\acute{o}$  (*earlier than*) and  $\nu\lambda\eta$  (*the stuff of which things are made*)" (p. 95).



**Fig. 14.** Spectra of five components of yttrium oxide following chemical fractionation. The diagram shows the directions the precipitates and solutions travel. After each fractionation the filtrate is passed to the left (+1) and the precipitates to the right (-1). On examining the series of earths in the lowest line of bottles, Crookes found that their phosphorescent spectra had altered in the relative intensities of some of the spectral lines. *Source:* Crookes, “On the Fractionation of Yttria” (ref. 54 ), p. 588.

atomic weights of the meta-elements.\* This model, on the one hand, saved Prout’s hypothesis and the close proximity of atomic weights to whole numbers and, on the other hand, it explained the differences in the spectra of the rare earths derived from the chemical-fractionation process:

Another important inference which may be drawn from the facts is that the atoms of which yttrium consists, though differing, do not differ continuously, but *per*

\* As regards the magnitudes of such differences, Crookes’s position varied over the years. In his paper of 1886, “On the Nature and Origin of the so-called elements” (ref. 21), he wrote: “when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, *there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on.*” In his paper of 1887, “Genesis of the Elements” (ref. 55), the sentence in italics was rendered as follows: “*some are represented by 39.9 or 40.1, a smaller number by 39.8 or 40.2.*” In 1915 Crookes claimed that Soddy’s concept of isotopes confirmed his idea of meta-elements. Soddy himself quoted Crookes as historical support for his new conception. For a critique of this point, see DeKosky, “Spectroscopy and the elements” (ref. 67), p. 422.

*saltum*. We have evidence of this in the fact that the spectroscopic bands characteristic of each group are distinct from those of the other groups, and do not pass gradually into them.<sup>60</sup>

In 1891, during the inaugural session of the Institution of Electrical Engineers, Crookes as chairman discussed the rare-earth spectra in connection with electrical-discharge phenomena in gases. In particular, to answer the question, what “occasions the phosphorescence of yttria and other bodies in vacuo under molecular bombardment,” he suggested that one should appeal to the “electrolysis hypothesis.”<sup>61</sup> According to this hypothesis, a gas in a discharge tube undergoes a process that was analogous to the one taking place in an electrolytic solution, that is, under the influence of a strong electric field the gas molecules are dissociated into positive and negative ions. Thus, a molecule of hydrogen gas, for instance, may be composed of one group of hydrogen atoms with a certain amount of negative electricity bound to it, and another group with an equivalent of positive electricity bound to it. “These atoms are also charged with additional equivalents of positive or negative electricity.... We are not concerned with the inherent electricity – of which we are ignorant – but with the extra ... charge.”<sup>62</sup> Therefore, the “negative atoms,” which are driven away violently from the cathode by the electric field, are moved toward the anode. If they strike an obstacle, for example, a phosphorescent substance like yttrium oxide, they could transfer their negative charge to it and set it into vibration, causing it to emit visible light.

Crookes also discovered, however, that electrical-discharge phenomena, for instance the Crookes dark space and phosphorescence, occurred not only with diatomic gases like hydrogen, but also with monatomic elements like mercury.<sup>63</sup> He solved this puzzle by appealing to the meta-element concept, by conjecturing that “the atomic weight of mercury, for instance, is called 200, but the atom of mercury, as we know it, is assumed to be made up of an enormous number of sub-atoms, each of which may vary slightly round the mean number 200 as a centre.” In his illustration of the yttria spectrum, Crookes classed the sub-atoms into electro-positive and electro-negative ones, according to “one of the latest theories in chemistry.”

Calling the atom in the mean position electrically neutral, *those sub-atoms which are on one side of the mean will be charged with positive electricity, and those on the other side of the mean position will be charged with negative electricity, the whole atom being neutral.*<sup>64</sup>

Thus, Crookes’s meta-elements or sub-atoms acquired a new and distinctive characteristic in addition to their mass, namely, their electric charge. These two characteristics were closely connected. Positive and negative charges were linked to the masses of the meta-elements, their average being the mass of the traditional chemical element.

### **The Fates of Crookes’s Meta-elements and Lockyer’s Proto-elements**

In 1897 J.J. Thomson, based on his cathode-ray experiments, presented a new concept of the atom as a structure composed of charged particles of matter or “cor-

puscles” that could be separated from it. The long period of transition from the enunciation of Prout’s hypothesis to the discovery of Thomson’s corpuscle constituted a long quest to identify the primary matter. But Thomson’s cathode-ray experiments were not carried out in a conceptual vacuum; they were embedded in this long tradition of research on the concept of primary matter: Thomson’s new atom arose out of old conjectures. As Thomson himself remarked, the hypothesis that “the so-called elements are compounds of some primordial elements, has been put forward from time to time by various chemists,” and there were “weighty arguments, founded on spectroscopic considerations, in favour of the composite nature of the elements.”<sup>65</sup>

As we have seen, these spectroscopic considerations led Crookes and Lockyer to suggest, respectively, the existence of “meta-elements” and “proto-elements.” Crookes’s and Lockyer’s approaches to the complexity and dissociability of atoms derived from the same molecular-dissociation theory of spectra, whether it was concerned with phosphorescent or spark spectra. Both Crookes and Lockyer were convinced that spectroscopy could corroborate the concept of primary matter as an amended version of Prout’s hypothesis. Their belief was based on the high sensitivity of spectroscopic as compared to traditional methods of chemical analysis. The spectroscope thus assumed for Crookes and Lockyer and many of their contemporaries the role of Galileo’s “superior and more excellent sensor.” As Mendeleev noted, “as soon as the spectrum analysis appears as a new and powerful weapon of chemistry, the idea of primary matter is immediately attached to it.”<sup>66</sup>

Yet, the concepts introduced by Crookes and Lockyer suffered diametrically opposite fates. Crookes’s evidence for his meta-elements from his chemical-fractionation studies turned out to be due to impurities in his samples. Different spectroscopic studies carried out by Crookes and Lecoq de Boisbaudran after 1885 exhibited contradictory results,<sup>67</sup> and Georges Urbain showed conclusively in 1909 that pure rare-earth elements exhibit no phosphorescence, that phosphorescence always was produced by a mixture of at least two substances.<sup>68</sup> In particular, Urbain was able to reproduce Crookes’s results by mixing pure rare-earth elements with other elements in certain ratios. Thus, the spectral variations that Crookes had observed did not support his assertions about the compound nature of rare-earth elements, and his concept of meta-elements had to be abandoned.

Lockyer’s concept of proto-element, by contrast, survived and was finally replaced by that of the “ionized atom.” This was a complex conceptual development that required many years for completion. First, the correct formulas for the spectral series of hydrogen had to be found.<sup>69</sup> Second, the origin of the so-called “proto-hydrogen” lines in certain stellar spectra had to be explained and reproduced in laboratory experiments.<sup>70</sup> Finally, a new quantum-theoretical framework had to be discovered to explain atomic spectra.<sup>71</sup> This work extended over the period from 1888 to 1913, and only then was it possible to establish that Lockyer’s enhanced lines should be attributed not to a proto-element but to an ionized atom.<sup>72</sup> In general, the recognition that ionized atoms produce their own spectra opened up a new chapter in the history of spectroscopy with important consequences for the emerging quantum theory.

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