

The Role of Instruments in Three Chemical' Revolutions

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Abstract This paper attempts to show one of the ways history of chemistry can be teachable for chemistry teachers, it means something more than an undifferentiated mass of names and dates, establishing a temporal framework based on chemical entities that all students use. Represents a difficult equilibrium between over-simplification versus over-elaboration. Hence, following the initial proposal of Jensen (*J Chem Educ* 75:679–687, 817–828, 961–969, 1998), reconstructs the history of one of chemistry' dimensions (composition-structure) in terms of three revolutionary moments. These moments are considered in terms of the Kuhnian notion of 'exemplar,' rather than 'paradigm.' This approach enables the incorporation of instruments, as well as concepts into the revolutionary process and provides a more adequate representation of such periods of development and consolidation. These three revolutions are called by the chemical structural entities that emerged from the same: atoms (1766–1808); molecules and isomers (1831–1860); electrons and isotopes (1897–1923).

1 Introduction

Science originated from the fusion of two old traditions, the tradition of philosophical thinking that began in ancient Greece and the tradition of skilled crafts that began even earlier and flourished in medieval Europe. Philosophy supplied the concepts for science, and skilled crafts supplied the tools. Until the end of the nineteenth century, science and craft industries developed along separate paths. They frequently borrowed tools from each other, but each maintained an independent existence. It was only in the twenty century that science and craft industries became inseparable linked.

F. Dyson (1999)

Chemistry teachers generally ignore the fact that chemistry is, among all other sciences, the most productive one in terms of knowledge and material products'. (Tague et al. 1981). Today more than 3 million chemists worldwide publish about 850,000 papers annually. They synthesize new substances. In 1800 these numbered in the hundreds. Nowadays there are more than 71 million—the vast majority of which are not found in nature (Schummer

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2006)—and the rate of production continues to accelerate. Once the majority of chemistry teachers all over the world used textbooks as the main (sometimes the only) source of information (it means the contents of the books expanded in an idealized attempt to cope with the increase in information, and references to the history of chemistry disappeared), we became, paradoxically and without wanting to... history teachers!¹

Generally speaking, when we teach chemistry scientific content is taught, but Schwab's (1962) interpretation of science teaching as a dogma or as "a rhetoric of conclusions" remains. Therefore, if scientific competence and procedures are not worked out, we cannot say that scientists are being trained. On this matter there are different positions (Allchin 2004; Chamizo 2007; de Berg 2010); but, to sum up, it is possible to recognize that scientific teaching requires more 'context' (Gilbert 2006) and reflection.

Unlike the various Positivist approaches that dominated philosophy of science until the twentieth century, Thomas Kuhn's ideas about scientific revolutions, introducing history in philosophy of science have been widely discussed and for many scholars accepted in general terms (*Historical Studies in the Natural Sciences*, 42, No 5, 2012; Kindi and Arabatzis 2012). For Kuhn, scientific revolutions are "taken to be those non-cumulative developmental episodes in which an older paradigm is replaced in whole or in part by an incompatible new one" (Kuhn 1970, p. 92). This change requires a reconstruction of the historical commitments of a particular scientific community. The commitments shared by groups or communities are characterized by the use of the word 'paradigm', which means a "criterion for choosing problems that, while the paradigm is taken for granted, can be assumed to have solutions" (Kuhn 1970, p. 37). Over the same historical period different scientific communities share the same paradigm and research and teaching based on this paradigm are known as "normal science".² When there is a scientific revolution the community changes its paradigm, thereby changing the activities related to 'normal science'. Normal or paradigmatic science is employed by a specific community in its daily activities, based on their previous achievements, and is what is taught in textbooks. Scientific progress in normal science is cumulative or gradual. Revolutionary science develops when a crisis occurs in normal science. The result of a revolutionary process in science is the emergence of a new paradigm, which displaces the previous one, and has traditionally been identified with changing theories. Therefore, the communities that assume different paradigms find significant difficulties in communicating with each other. Competing paradigms lack a common measure because they use different concepts and methods to address different problems—they are in Kuhn's terminology, incommensurable.

This paper attempts to show how chemistry teachers, using history of chemistry, could teach chemistry. It means something more than an undifferentiated mass of names and dates. Represents a difficult equilibrium between over-simplification versus over-elaboration and seeks to recognize the way that consolidates, in the teaching of chemistry, different entities such as atoms, molecules or electrons. Hence, following the initial proposal of Jensen (1998), reconstructs the history of one of chemistry's dimensions

¹ However there are many difficulties in teaching history of chemistry. Recently, Höttecke and Celestino Silva (2011) have discussed four of them: teachers' skills, epistemological and didactical attitudes and beliefs; the institutional framework of science teaching; and the nature of available textbooks.

² That means: "research firmly based upon one or more past scientific achievements, achievements that some particular scientific community acknowledges for a time as supplying the foundation for a further practice. Today such achievements are recounted through seldom in their original form, by science textbooks, elementary and advanced" (Kuhn 1970, p. 10).

(composition-structure)³ in terms of three revolutionary moments. These moments are considered in terms of the Kuhnian notion of ‘exemplar,’ rather than ‘paradigm.’⁴ This approach enables the incorporation of instruments, as well as concepts into the revolutionary process and provides a more adequate representation of such periods of development and consolidation. Moreover, accepting the premise of the ‘scientific revolutions’ recognizes better the continuity of scientific endeavour once the transitions are closer and less sharp. For educational and realism⁵ reasons these three revolutions are named after by the chemical structural entities that emerged from them: Atoms (1766–1808); Molecules and Isomers (1831–1861); Electrons and Isotopes (1897–1923). As any chemistry teacher knows, it is from these structural entities, that chemistry is taught worldwide today.

2 Scientific Revolutions: Concepts and Instruments

Indeed the traditional emphasis that historians of science have put on theory as the motor of scientific development tends to obscure the roles of instrumentation that are at the root of progress in chemical analysis. Consequently, the instrument has acquired the appearance of a tool manufactured expressly for the chemical investigator intent on making an ultimate breakthrough. This imagery is related to the commonplace subordination of technology to science in much of the existent literature on the subject.

Y. Rabkin (1993)

Kuhn’s ‘paradigms’, ‘incommensurability’ and ‘revolutions’ have been deeply studied and challenged⁶ as has his lack of interest in technology.⁷ However, ever since, James B. Conant in his 1957 foreword to Kuhn’s *Copernican Revolution* (cited by Nye 2012, p. 558) identified Kuhn’s enterprise as pedagogically exemplary in showing students how science develops through an intensive study of certain episodes, rather than by plodding through a general survey course, they have become practically ubiquitous in any discussion of the development of the sciences.

In the Postscript to the 1970 edition of *The Structure of Scientific Revolutions*, Kuhn, indicated that he had conflated two conceptually distinct connotations of paradigms-‘exemplars’ and ‘disciplinary matrices’:⁸

³ In accordance with Jensen: “In short, it is an inventory of the parts used to assemble the molecule. Information relating to the kind of atoms is obtained via a qualitative analysis of a material and that relating to the number of atoms via a quantitative analysis of the material” (Jensen 1998, p. 680). Besides this, there are two more dimensions: energy and time, which will occasion from a second article.

⁴ For some scholars, exemplar and disciplinary matrix are more important concepts than paradigm (Nickles 2012; Nye 2012).

⁵ About this Bensaude-Vincent said: “Hacking’s distinction between ‘realism about theories’ and ‘realism about entities’ could thus apply to chemistry. To be sure chemists are realists. They believe in the reality of the entities, which allows them to operate in the outside world or to be affected by it” (Bensaude-Vincent 2008, p. 52).

⁶ See for example: Cohen (1985), Gutting (1980), Kindi (2012), Lakatos and Musgrave (1970), Rouse (1998) and Toulmin (1972).

⁷ “Indeed technology is almost unique among disciplines in having been the subject of only the occasional Kuhnian analysis. There are, I believe, three reasons why this has been so: first, the assumption that technological knowledge is quintessentially tacit; second, the identification of technological knowledge with applied science; and third, the selection of analytical units for the history and present structure of technology that, however useful, for some purposes, do little to throw the cognitive aspect of technology into prominence. During the past decades or so, a number of different developments in the study of technology have been made these barriers less formidable than previously” (Laudan 1984, p. 6).

⁸ The disciplinary matrix contains; symbolic generalizations, methodology, values and exemplars (Marcum 2012).

(...) [b]ecause the term [paradigm] has assumed a life of its own... I shall here substitute 'exemplars.' By it I mean, initially, the concrete problem-solutions that students encounter from the start of their scientific education, whether in laboratories, on examinations, or at the ends of chapters in science texts....All physicists, for example, begin by learning the same exemplars: problems such as the inclined plane, the conical pendulum, and Keplerian orbits; instruments such as the vernier, the calorimeter and the Wheatstone bridge (Kuhn 1970, p. 187).

Thus the term 'exemplar' represents a specific historical community's collection of solved problems and is generally found in its professional literature, and especially in its textbooks. It is narrower than paradigm⁹ and avoids some of the ambiguities that the latter has acquired. Making explicit the role of instruments in normal science reduces the gap between normal and revolutionary science. This has an important consequence, because exemplars, being more flexible and also more practically accurate than paradigms, not only recognize the conceptual or theoretical changes within a discipline, but also indicate that they are accompanied by the design,¹⁰ construction and use of certain instruments. Here is important to recognize the words of Gary Gutting, one of Kuhn's critics:

One instance is technological practices that exist independent of theoretical science (arts and crafts). In contrast to the common view that such practices are entirely unscientific, being at best instances of knowing how rather than knowing what, an analysis in terms of exemplars suggest that both the skilled artisan or craftsman and the pure scientist are in essence people how know how to adapt and extend previously exemplary achievements to new cases (Gutting 1984, p. 56).

Furthermore, Davis Baird claims that: "instruments are not in the intellectual basement; they occupy the same floor as our greatest theoretical contributions to understand the world" (Baird 2004, p xvii). The use of new instruments¹¹ opens new territories sometimes without having any underlying theory.

Although new histories of chemistry¹² have been published,¹³ none of them consider the nature of revolutions in the history of chemistry, let alone the two interconnected dimensions of such revolutions: conceptual and instrumental, recognized by exemplars, and avoided by paradigms. This connection between words and things, concepts and instruments can acknowledge, more clearly and comprehensively, the activities that constitute a specific scientific community, in a particular historical moment (Rouse 1998).

The recognition and use of new structural entities are some of the 'products' of a chemical revolution. Their introduction into new textbooks establishes a new normal science "chemical era".

⁹ The original Kuhn paradigm has two meanings: wide as disciplinary matrix and narrow as exemplar (Kindi 2012).

¹⁰ Dyson (1999) recognized that astronomers and biologist have different attitudes towards their instruments. Astronomers traditionally invented and built their own instruments...and biologist buy them.

¹¹ In their *Instruments of Science. An Historical Encyclopedia*, Bud and Warner indicated: "Scientific instruments are central to the practice of science. All too often they have been taken for granted. Nonetheless, while most would agree that telescopes and microscopes are scientific instruments, it has proved as difficult to establish a general definition of the category, as it has been to define science itself" (Bud and Warner 1998, p. ix).

¹² As Jensen recognized: "Histories of chemistry are legion. In his 1974 bibliographic study, Jost Weyer listed no fewer than 71 general histories of chemistry written between 1561 and 1970, of which 29, or roughly 40 %, have appeared in English. Prior to Lavoisier's chemical revolution, these histories made little attempt to divide events into significant historical periods or eras" (Jensen 1998, p. 961).

¹³ Few examples from different countries only in this century and about chemistry, not sub disciplines (Aragón 2009; Bensaude-Vincent and Simon 2008; Cardone 2008; Cerruti 2003; Habashi 2002; Hargittai 2000; Klein and Lefèvre 2007; Lestel 2007; Maar 2008; Nilsen and Strbánová 2008; Rogers 2006).

Allowing for specific historiographical variations among historians, the above considerations suggest that there are at least four acceptable answers to the question “What is a scientific revolution?” According to what has been said previously, these are:

1. A radical reinterpretation of existing thought.
2. The resolution of a long-standing debate, the solution of which revolutionizes the kind of problems scientists are able to successfully attack on a routine basis.
3. The use of new instruments changes the way in which its practitioners look and work in the world.¹⁴
4. The opening of a new level of theoretical understanding that subsumes older theories as special cases.

It has been established that the beginning of the first revolution occurred with the emergence of Pneumatic Chemistry and the development of various instruments for isolation and study of various types of ‘airs’, i.e., the isolation of what we now recognize as gases. Besides, as Maurice Crosland indicated:

The Chemical Revolution of the late eighteenth century consisted essentially of combustion being explained by the addition of oxygen rather than by the removal of phlogiston. This has been seen as the “paradigm shift” of a scientific revolution in the familiar Kuhnian sense. Yet Lavoisier helped to change chemistry in several other ways as well, particularly by the introduction of a new chemical language (Crosland 2009, p. 93).

Because the culmination of this revolution in chemistry is marked by the incorporation of atoms (Siegfried and Dobbs 1968; Siegfried 1988)¹⁵ as a structural entity, answers 1 and 3 are, along with the systematic use by all European chemists of the pneumatic trough and Lavoisier’s use of balance, the best characterization of the first chemical revolution. The beginning of the second revolution is identified with the isomers definition of Berzelius and the generalized use, in all Europe, of Liebig’s Kaliapparat for determining “molecular” composition, which also changed the way the central focus of chemistry community giving rise to the new subdiscipline of organic chemistry. Pasteur separation of optical isomers and his use of polarimetry in 1848 also facilitated that change. By way of contrast, as also noted by Jensen: “Cannizzaro’s solution to the atomic weight problem did not subsume any earlier theories as special cases nor did it produce any radical reinterpretation of existing facts. Rather it allowed chemists to operationally choose from among several competing speculative views of molecular composition and structure and so resolved a longstanding debate” (Jensen 1998, p. 965). In other words, answer 2 and 3 are the best characterization of the second chemical revolution. Finally the third revolution is characterized by answers 3 and 4. The fact that Dalton’s solid atoms actually consisted of even

¹⁴ Hasok Chang strongly supports pluralism in science. For him “In place of monism (the notion that science is the search for the truth about nature) I offer pluralism as an ideal of science. I would define pluralism in science as the doctrine of advocating the cultivation of multiple systems of practice in any given field of science. By a “system of practice” I mean a coherent and interacting set of epistemic activities performed with a view to achieve certain aims” (Chang 2012, p. 260). In agreement with this approach, here answer 3 must be always considered, but not exclusively.

¹⁵ Robert Siegfried indicated: “Faced with the task of placing the Chemical Revolution in the context of the general history of chemistry, we must reconcile two unarguable truths. The first is the historical reality of the traditional revolution centered on Antoine-Laurent Lavoisier’s overthrow of the phlogiston theory. This view arose in its own time, and subsequent studies have continued to reinforce it. The second truth is that modern chemistry is founded not on the precepts of Lavoisier’s antiphlogistic chemistry, but on John Dalton’s atomic theory. Composition is the fundamental chemical property that the atomic theory symbolizes so powerfully through its ubiquitous symbols and formulas, and Dalton’s work constitutes its first successful representation” (Siegfried 1988, p. 34).

smaller particles (electrons, protons and neutrons) and that they could have more than one specific mass (isotopes) give rise to a new way of thinking and working in both chemistry and physics, and was the result of major experimental discoveries predicated on the use of new instruments, such as the cathode rays tube and the mass spectrometer. The mixed nature of this revolution is reflected in the fact that several of its major protagonists were deserving of Nobel Prizes in both physics and chemistry.

In addition to the role of new instruments in generating significant changes in research and in the formation of new kinds of specialization, the role of the textbook in signalling the end of scientific revolutions was also clearly identified by Kuhn himself. At the end of his career he recognized a different meaning of incommensurability, indicating that the emergence of new sub-disciplines within a discipline as a result of a scientific revolution, and accepted by new textbooks, separated scientific communities (Kuhn 1991). As recently indicated Bernadette Bensaude-Vincent:

Whereas historians of science ignored textbooks because of the gulf between producing science and communicating science, a number of philosophers of science have emphasized their importance due to this gulf... Thomas Kuhn also recognized the importance of textbooks for the stabilization and perpetuation of paradigms. Textbooks are fundamentally conservative as they are meant for training students in solving the puzzles raised within the paradigm rather than inventing new problems. Kuhn argued that they assume their conservative function through various ways. They present only established and incontrovertible knowledge, the stable results of past revolutions (Bensaude-Vincent 2006, p. 669).

Thus in this paper, as well as the theoretical entities, are enhanced some of the books that registered that a revolution was underway or already happened.

Despite the fact that this approach from scientific revolutions and exemplars, instruments and entities, could be subject of many unsolved controversies, leaves out many technical details, protagonists and the broader social context, all essential for the proper understanding of how chemistry developed, could help to teach chemistry from an historical approach.

Historical changes in chemistry through their own revolutions their fundamental structural entities and the two most important instruments¹⁶ are shown in Fig. 1.

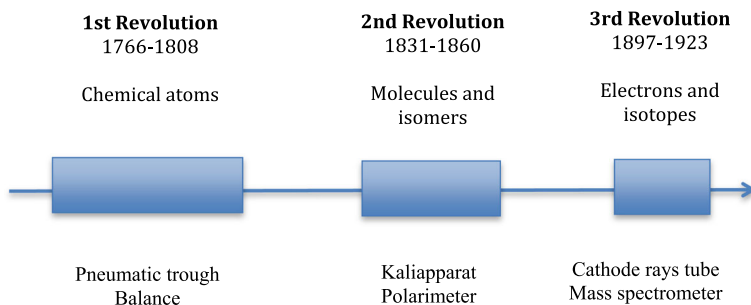


Fig. 1 Three chemical revolutions. Their structural entities, and two of the most important instruments

¹⁶ Only two instruments were selected, arbitrarily, for simplicity reasons.

3 The First Chemical Revolution: 1766–1808

Modern chemistry has three fathers: Robert Boyle, Antoine-Laurent Lavoisier and John Dalton. Their respective share of paternity is determined mainly by their relevance to the nineteenth-century development of chemical atomism.

Mi Gyung Kim (2003, p. 439)

Since the late antiquity and in particular since the Middle Ages, the preparation of medicines, the manufacture of soaps, pigments, glass, ceramics, explosives and metal mining were practical activities which took place in markets and public places far removed from the realm of philosophical thinking. Skilled artisans, who learnt their trade by apprenticeship imbued with different religious ideas, developed these activities. However, eventually the most important characteristics of a scientific laboratory could be recognized: their isolation from everyday life and the presence of apparatus and instruments. This was accomplished first with chemical laboratories that preceded physics laboratories by almost two centuries. As indicated by Maurice Crosland:

To be dignified by the title ‘laboratory’, a dedicated space, whether a room, cellar, or whole building, has to be fitted up especially for the purposes of practical science...Given this more rigorous definition of a laboratory, the first laboratories were the laboratories of the alchemists... The basic facility required for practical chemistry was a source of heat. In alchemical laboratories, there would be one or more furnaces, ideally together with a fuel store, a water supply, preferably complemented by a sink, flasks, retorts, and other apparatus, and a variety of labelled chemical reagents. As we have previously indicated, it was usual for alchemical laboratories to have a number of different types of furnace, providing ascending degrees of heat, ranging perhaps from a gentle fire with a water bath to a reverberatory furnace. Distillation would usually be carried out at an intermediate temperature, although, of course, the concept of temperature really had to wait until the eighteenth century (Crosland 2005, pp. 238–239).

As shown in many books of “History of Chemistry”, this discipline comes from three parallel experimental traditions that gradually converge. Metallurgy, medicine, and alchemy were melted at the end of the eighteenth century in what we nowadays call chemistry. Nevertheless, the widespread perception that the synthesis of Lavoisier solved most of the problems of these experimental traditions eliminating the mysterious and metaphysical phlogiston becomes fragile, given the accumulation of more and new historical evidence to the contrary.

In recent times there has been an intense discussion¹⁷ about the first chemical revolution that for some scholars, including Kuhn himself, is the only one. Thus John McEvoy analysed the different interpretations that Lavoisier and Priestley had of their results with the use of the balance indicated:

The difference between Priestley and Lavoisier lay not in the mere use of gravimetric experiments (methodology) but in the epistemological purpose of their use. Both men were interested in the quantitative aspects of chemical phenomena, but they used them to serve different cognitive purposes, shaped by different epistemological presuppositions...Lavoisier’s conception of the active knowing mind, progressing through successive formulations, modifications, and corrections of “hypothesis” to “knowledge of the real laws of nature,” emphasized the epistemological importance of theoretical activity in a manner that was at odds with Priestley’s emphasis on the patient accumulation of “new facts” and the inductive emergence of a “general theory” (McEvoy 1988, pp. 205–206).

Chang’s recent research (2012) reconsiders phlogiston, challenging the legacy of Lavoisier. For him:

¹⁷ See for example: Allchin (1997), Blumenthal (2013), Chang (2012), Crosland (2009), Hoyningen-Huene (2008), Kim (2003), McEvoy (1988, 2010) and Siegfried (2002).

1. The isolation of the gas that Lavoisier called oxygen had previously been made.
2. Despite its name, oxygen was not a constituent of all acids.
3. The Phlogiston paradigm founder, Georg Stahl recognized combustion and calcination as phenomena of the same type.
4. Henry Cavendish anticipated Lavoisier's discovery of the composition of water.
5. Lavoisier's emphasis on precise weight measurements was not entirely new.
6. Lavoisier certainly did promote the quasi-operationalist concept of chemical element as an 'undecomposed body' but some phlogistonists used it long before him.

Admitting this Lavoisier is today still considered a key figure in the First Chemical Revolution merging *two largely separate and distinct chemical traditions* of Continental analytical chemistry and British pneumatic chemistry (Guerlac 1961, p. xvii). As Frederic Holmes recognized after his research in the evolution of Lavoisier's chemical apparatus:

The revolutionary effect of his work lies not in any single aspect of his thought, his laboratory methods, his rhetoric, or his ability to organize the ranks of his followers, but in the way they fitted together to form a whole more powerful than its parts. Only by following the trail of his activity through its full development can we understand in depth why he, more than any other individual, reshaped the chemistry of his time (Holmes 2000, p. 150).

Jensen arbitrarily stated (1998) that this revolution stretched from 1770 to 1790 and identified several factors that contributed to it.¹⁸ He also recognized, as an important indicator of this Revolution, the percentage of the French chemical literature dealing with phlogiston (decreases) versus oxygen (increasing) as a function of time. A similar analysis of the chemical literature shows that in Sweden, Spain and the Netherlands Lavoisier's paradigm was accepted without much opposition (Lundgren and Bensaude-Vincent 2000). This was not the case in France, Scotland or England (McEvoy 2010).

This article considers ideas that precede the text of Kuhn on scientific revolutions, from the historian Marie Boas-Hall. According to her:

It has always seemed puzzling to me that Lavoisier's work on the role of oxygen in combustion dramatic and important as it was, could, together with a new system of chemical nomenclature, have permitted the complete reform of chemistry. As usually happens when one examines a dramatic event in the history of science, it turns out not to have been so simple. Seventeenth-century chemist had tried to have both a rational system of nomenclature and a rational theory of combustion; had tried, and had failed. Their failure was inevitable without knowledge of pneumatic chemistry. But when one examines their attempts, it is plain that more than pneumatic chemistry was lacking. Much was required, including a different climate of opinion and an improved state of chemical knowledge. One further ingredient in the success of Lavoisier was a proper understanding of the nature of the chemical elements; it is my contention here that this was a development of chemistry before Lavoisier, and that it was intimately connected with discussions of the particular structure of matter though, paradoxically, a chemical satisfying atomic theory had to wait until Dalton's work in the years following Lavoisier's (Boas-Hall 1959, p. 499).

I have here assumed, in part, the position initially proposed by Siegfried and Dobbs (1968) who considers that the "Chemical Revolution" concludes with the publication of

¹⁸ "These include new chemical theories of combustion and respiration, developed by Mayow and other mechanical physiologists at Oxford in the late seventeenth century; the pneumatic chemistry of Hales, Cavendish, Scheele, and Priestley, which led to the discovery of new gases in the 1760s; the attempts to reform chemical nomenclature and classification on the basis of empirical composition, made by such chemists as Macquer, Bergman, and Guyton in the 1760s and 1770s; the development of the caloric theory of states by Black, Crawford, Irving, Cleghorn, Watt, and Lavoisier; the experimental defence of new theories of alkalinity and causticity by Black and others, which explicitly acknowledged the role of gases in chemical reactions and made use of conservation of mass as a way of monitoring their absorption and evolution; and, lastly, various theories of calcination, including those of Rey" (Jensen 1998, p. 963).

Dalton's *New System of Chemical Philosophy*. Nevertheless, I do not agree with him that it began with the publication of Lavoisier's *Traité élémentaire de chimie*, particularly by the huge amount of knowledge that was obtained on gases, using as an instrument the pneumatic trough, Fig. 2¹⁹. This beginning can be established after Pneumatic chemistry²⁰ was firmly accepted. With a long history of slow improvements around the pneumatic trough (Jensen 2003), Henry Cavendish was the first one to collect gases with this instrument over mercury. About it Thomas Thomson in his famous *History of Chemistry* said: "Pneumatic chemistry had begun by Mr. Cavendish in his valuable paper on carbonic acid and hydrogen gases, published in the Philosophical Transactions by 1766" (Thomson 1830, p. 18). However, hydrogen (inflammable air as he called it) was observed and collected before him,²¹ Cavendish was the first one to distinguish hydrogen from other gases. He was an independent discoverer of nitrogen (Weeks 1968) and improved the eudiometer, an instrument to measure the volume of gases in a chemical reaction.²² Cavendish's skill in quantitative work was evident in his chemical research.²³ He also had an important

¹⁹ Pneuma started as a common Greek noun denoting both "wind" and "breath," apparently almost 3,000 years ago. Vestiges of that word can be found, even today, in specialized terminology such as "pneumatics" and "pneumonia," and its Latin translation as *spiritus* with its numerous derivatives pervades our daily language. As one of the four elements, air was treated as a substance expressing the qualities of moisture and heat. There was only one single air. In the seventeenth century J.B. van Helmont coined the word "gas" (from the Greek chaos) as "I call this spirit, hitherto unknown, by the new name of gas, which can neither be nor retained in vessels reduced to a visible form, unless the seed is first extinguished". In spite of working with devices which precede the pneumatic trough, neither van Helmont, nor R. Boyle, J. Mayow, S. Hales, or J. Black were clearly able to build an instrument to isolate the different gases which chemists of that time were assuming that constituted air. Cavendish was the first to use the pneumatic trough to isolate a gas, hitherto unknown. He described its use as follows: "In order to fill a bottle with the air discharged from metals or alkaline substances by solution in acids, or from animal or vegetable substances by fermentation, I make use of the contrivance represented in Fig. 1 where A represents the bottle, in which the materials for producing air are placed; having a bent glass tube C ground into it, in the manner of a stopper. E represents a vessel of water. D the bottle to receive the air, which is first filled with water, and then inverted into the vessel of water, over the end of the bent tube. F represents the string, by which the bottle is suspended" (Parascandola and Ihde 1969). He improved his instrument replacing water (where gases dissolved) by mercury. Joseph Priestley fully exploited this innovation and isolated few water-soluble gases like hydrogen chloride or ammonia. In the thought and practice of Priestley distinct chemical species, were first fully conceptualized and materialized. Cavendish's trough for collecting gas.

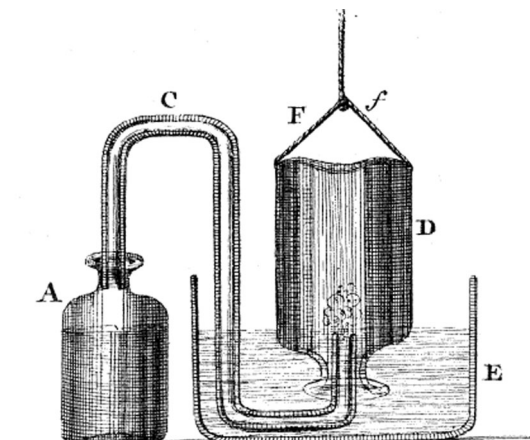
²⁰ About this Jungnickel and McCormmach stated: "Had there been no "chemical revolution," the progressive development of techniques in chemistry in the eighteenth century would have taken place all the same. But there was a chemical revolution—an assertion which is accepted by most historians of chemistry even if they disagree about what the revolution was, what its boundaries were, and what place the overthrow of phlogiston had in it—and consequently the historical interest in Cavendish has been largely in relation with this event. (Jungnickel and McCormmach 1999, p. 370).

²¹ For example in 1751 the paper by M.V. Lomonosov "On the luster of metals" indicated: "On solution of any non-precious metal, specifically iron, in acid spirit there emerges from the mouth of the vessel an inflammable vapour which is nothing else than phlogiston". Cavendish performed similar experiments and isolated hydrogen however he had the wrong conclusion that hydrogen came from the metal rather than from the acid. He also first identified hydrogen with phlogiston.

²² In the Bud and Warner's *Instruments of Science. An historical Encyclopedia* eudiometer entry said: "...Based on Joseph Priestley's nitrous air test which he first described in his Experiments and Observations of Different Kinds of Air (1774) natural philosophers such as Felice Fontana and Marcilio Landrini designed a variety of instruments in which a test air might be combined with nitrous air (now known as nitric oxide) over water or mercury, and the consequent diminution of its volume measured". A deep study of this instrument can be found in Levere (2000) and a constructivist approach in Schaffer (1990).

²³ "In any experiment he usually began with carefully measured quantities of substances, which he then combined and performed various operations on, and the products he obtained he would again weight" (Jungnickel and McCormmach 1999, p. 198).

Fig. 2 Cavendish's pneumatic trough. From H. Cavendish *Philosophical Transactions of the Royal Society*, 1766, 56, p. 141, Fig. 1



controversy with Lavoisier. In a paper in the *Philosophical Transactions* in 1784, “Experiments on Air”, Cavendish reported his experiments on the water deposited by the explosion of common air with inflammable air. Lavoisier claimed that he himself had discovered how water was formed—in fact, it was he who coined the word “hydrogen,” which means, “water former”. For many historians the cause of the controversy was “the casual way scientific information was communicated in the eighteenth century” (Jungnickel and McCormach 1999, p. 380).

As mentioned above, the expansion of the “Chemical Revolution” from Lavoisier to Dalton was proposed originally by Boas-Hall (1959) after her analysis of eighteen-century explanations of the structure of matter, which was accepted only by few scholars.²⁴ She recognized that in the period between Boyle and Lavoisier most chemists explained chemical change in terms of chemical principles and elements. During this revolutionary period, the Scottish chemist Joseph Black, discoverer of carbon dioxide,²⁵ summarized the long trend away from metaphysical towards an operational concept of the element:

...These four supposed elements were accordingly considered, until very lately, as the primary elements of natural bodies...[...]. On the contrary, there were many reasons for doubting, even at that time, that these four supposed elements were in reality simple, elementary, and unchangeable substances; and now, we have direct evidence from experiments, and most of them are not. Atmospheric air has been demonstrated to be a compound mass of more than two or three different kinds of matter. Water is also believed now to be a compound body. And of the purest and most simple earthy matter, six or more different kinds are now reckoned, which we cannot reduce to greater simplicity by our operations (Black 1803, pp. 342–343).

In 1808 Dalton published his *New System of Chemistry*. Here the modern atomic model with associated relative atomic weights was used to explain results on the absorption of

²⁴ Besides Siegfried, one of those David Oldroyd claimed: “The major part of the chemical revolution was the change in matter theory, with its accompanying methodological shift. By comparison, the change of the theory of combustion was perhaps, in the long run, a matter of subsidiary importance” (Oldroyd 1973, p. 52).

²⁵ Black’s investigations using a balance, at mid-eighteenth century, proved that limestone (calcium carbonate) changed into quicklime (calcium oxide) when ‘fixed air’ (carbon dioxide) was removed, and that could be obtained from limestone quicklime by reversal of this process. He obtained similar conclusions working with other carbonates.

gases into water²⁶ and more else (Viana and Porto 2010). Thereafter, the problems that chemists of his time had to face, particularly for the determination of atomic weights (which did in a remarkable way Berzelius, producing his own atomic weights table) became normal science. The operational relationship between atoms and elements was built.²⁷

With the first revolution (Table 1), the pneumatic trough and the balance (Fig. 3²⁸) became everyday laboratory instruments. The first one opened a new world of substances and the second one, the possibility to measure accurately. Through his admittedly inconsistent definition of an element as the last unit of empirical analysis in his *Elementary Treatise of Chemistry*, Lavoisier achieved his ambition of “reform and improve the chemical nomenclature” and began what we identify as modern chemistry.²⁹ Dalton's *New System of Chemistry* delimited and clarified what became normal science. With the first revolution the first paradigm was built. Diversity began to move to unity. At least in chemistry, atoms, its structural entity, became ubiquitous.

²⁶ For example the British chemist H.E. Roscoe stated in 1895: “Before John Dalton's discovery of the laws of chemical combination, and without his atomic theory to explain these laws, chemistry as an exact science did not exist...Dalton may truly be said to be the founder of modern chemistry” (Thackray 1972, p. 27). Also Siegfried identified: “It was a time of tremendous discovery; by 1809 thirteen new metals had been added to the seventeen recognized as simple by Lavoisier in 1789... Typically the men making these discoveries expressed their concern for the multiplicity of fundamental bodies they were themselves increasing” (Siegfried and Dobbs 1968, p. 284).

²⁷ Chang stated: “I do believe that there was an analytical system-type that clearly dominated chemistry for two centuries, from the middle of the eighteenth century well into the twentieth century. In the context of my earlier and on going work trying to recast our view of the Chemical Revolution, I have called this system-type “compositionism”, with a view to explain the Chemical Revolution as a ripple riding on the larger wave of the ascendancy of compositionism.... On the basis of that presumption, chemists have engaged in the activity of explaining chemical reactions as the rearrangement of distinct and stable building-blocks, which retain their identity throughout even when their properties are not manifest in a state of combination” (Chang 2011, p. 255).

²⁸ The word balance comes from the Latin (bi-lanx, meaning two dishes). It referred some specimens of this instrument used more than three thousand years ago. One of its earliest depictions appears in a fifteenth century alchemical laboratory (Stock 1969). Pharmacists, jewellers and metallurgists used them for centuries with acceptable accuracy. Other chemists, as Black, Cavendish and Lomonosov, preceded Lavoisier in the use of the balance weighting reactants and products [For example about the work of the 17th century Belgian chymist Joan Baptista Van Helmont, Newman and Principe indicated: “What Van Helmont has in mind is that the weight of ingredients going into a reaction must come out in the products, regardless of any transformation that have taken place” (Newman and Principe 2005, p. 81)]. However, with its systematic use, he placed it, as the symbol of the new chemistry. He also indicated the importance of access to instruments of much greater sensitivity and accuracy [About the history of analytical balances see Ihde (1964)]. Over the years the balance, as the other instruments used by Lavoisier, went from common instruments (i.e. accessible to the rest of the chemical community) to specialized instruments, specifically designed to solving the experimental problems he was studying. An important issue is that balance's equilibrium referred to a method (balance sheet, Poirier 2005) and a principle (the law of conservation of matter, Holmes 1994). About that Perrin indicated: In his early chemical papers, too, he employed quantitative methods. For example, his use of an analytical balance to investigate the alleged conversion of water into earth is a prime example of what has been called his “balance sheet” approach...Although his technique was not without precedent, no chemist before him had pursued quantitative methods so systematically or so effectively (Perrin 1988).

²⁹ This new chemistry was clearly characterized by Golinski: “In the years after his death Lavoisier's followers set in train the adoption of new practices in chemical instruction and research. The new theory and new nomenclature were accompanied by new instruments and methods. These were embodied in pedagogical programmes and became definitive of higher standards of expertise among chemist” (Golinski 2002, p. 203).

Fig. 3 Lavoisier's balance. Precision balance built by Mégnié to Lavoisier. Weight capacity 600 g; sensibility 5 mg (Delacroix and Porte 1975)

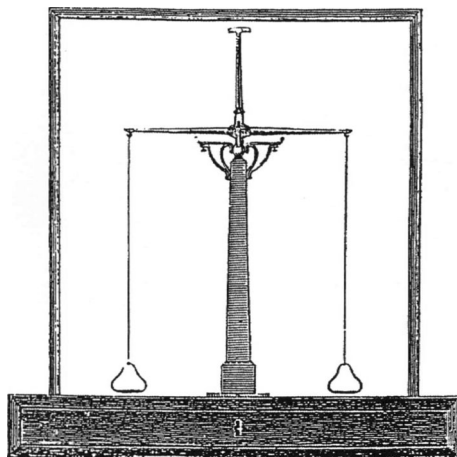


Table 1 Atom revolution

	EXEMPLAR	
	INSTRUMENTS	CONCEPTS
Instruments	Pneumatic trough and balance	
Concepts		Language, Quantitative Chemistry, Chemical Atom
Books	<i>Elementary Treatise of Chemistry, New System of Chemistry</i>	
Protagonists	Cavendish, Priestley, Lavoisier, Dalton	

Main figures related to instruments and concepts of the first chemical revolution (1766–1808)

4 The Second Chemical Revolution: 1831–1860

It becomes readily apparent that the discipline of chemistry was in a state of extreme chaos at mid-century and was, in fact, ripe for reform. The older chemists like Berzelius, Liebig, Dumas, Gmelin, and Mitscherlich were giving ground to a new generation of chemists. Some, particularly Laurent and Gerhardt, were openly contemptuous of authority. Others like Kekulé were respectful of the past, but not prevented by it from examining unique new concepts. It was this atmosphere that the Karlsruhe Congress was called
A. Ihde (1961)

The beginning of the second revolution can be recognized with the 1831 publication of Berzelius,³⁰ the leading chemist of the day, of the definition of isomers followed few years later by the monograph of Justus Liebig, *Instructions for the Chemical Analysis of Organic Bodies*. Here he explained how one of the instrument that characterizes this revolution had to be used, the Kaliapparat. Pasteur separation, in 1848, of optical isomers and his use of the polarimeter (the second instrument of this revolution) recognized few years ago as the

³⁰ Berzelius research, perhaps more than anyone fulfil Dalton's chemical atomism and in an indirect way (through his controversies with Whöler or Dumas) and his isomers definition "catalyse" the rise of organic chemistry. Hence it is possible to consider him as one of the protagonist of the chemistry second revolution.

chemical most beautiful experiment (Freemantle 2003) helps to change the central focus of chemistry community giving rise to the new subdiscipline of organic chemistry. The end of the second revolution coincides with the end of the Karlsruhe Congress in 1860. The brief text of Stanislaw Cannizaro *Sketch of a Course of Chemical Philosophy* distributed there marks a turning point in the difficulties that chemists had to recognize between atoms and molecules. After the second revolution³¹ the chemical community adopted the new concepts of valence, molecular structure (that can explain isomerism) and periodicity.

The chemistry historian Alan Rocke has performed a lot of research in this period and called it “the quiet revolution”

I use this phrase (the quiet revolution in chemistry) here to signify a series of changes during the 1850s that centered both on reforms of atomic weights and molecular formulas, and on the subdiscipline of organic chemistry. The essential elements of this extended event, prepared since the 1830s by the work of Justus Liebig (1803–1873), Jean-Baptiste Dumas (1800–1884), and Auguste Laurent (1807–1853), and in the 1840s by Charles Gerhardt (1816–1856) as well, were the decline of Berzelius electrochemical theory, the development of “type” theories based on substitution reactions, the establishment of consistent (“two-volume”) molecular magnitudes spanning organic as well as inorganic chemistry, the return to conventional equivalents to a modified version of Berzelius atomic weights, and, finally the rise of a theory of the “atomicity of the elements”, which comprised in part and led to in full what became knowledge as valence and structure theory...Is the word revolution appropriate to describe these changes? Others have merely referred to various new theories and conventions introducing during this period, culminating in the first chemical conference, the Karlsruhe Congress of 1860. Within a few years after the Congress most European chemists has accepted most of the elements of the Laurent-Gerhardt agenda, and structure theory began to develop dramatically, specially in Germany...Considering only impressionistically, there are a number of justifications for emphasizing the magnitude of the changes. Many quantitative indicator of the very size and importance of the profession –number of chemists, number of paper published, total compounds known, technological applications and the explosive growth on chemical industries, an so on- suggest an inflection point shortly after the middle of the century (Rocke 1993, pp. 90–91).

The acceptance of Dalton’s atomic model was not immediate and widespread. Research done by Joseph L. Gay-Lussac and André M. Ampere raised serious objections and for this reason it was forgotten for many years. That happened mainly because Jöns Jacob Berzelius, the highest personality of chemistry in the first half of the nineteenth century, accepted Dalton’s atomic model. From Stockholm, and through his “Jahresbericht” (Ostwald 1955), Berzelius defined a large part of the chemical “normal” research agenda. It set, as accurately as possible, the atomic weight of the different elements.³² Thus he discovered silicon, selenium, thorium and cerium, built his own table of atomic weights, and explained how atoms are bound together.³³ By 1830 most of the Swedish and German chemists, like Justus Liebig or Friedrich Whöler, used the atomic weights given by Berzelius.

³¹ For Jensen (1998) the second revolution spans in a 20-year period from 1855 to 1875. Since the first revolution, Dalton’s rules for assigning formulas proved to be operationally imperfect and various competing atomic and so-called equivalent weight scales were developed. Jensen used the percentage by decade of the American chemical literature dealing with mineral analysis and inorganic chemistry versus organic chemistry and also the American chemistry textbooks using affinity theory versus valence as an organizational principle as the evidence that identifies the end of this revolution.

³² Berzelius himself stated: “I came to think that Dalton’s numbers lacked that accuracy which is necessary for the practical application of his theory. I realized that above all it is necessary to determine with the maximum accuracy weights of the majority of elements; otherwise it can hardly be expected that the dawn of chemical theory will develop into long-awaited day. At the time this was the most important task of chemical research and I devoted myself to this entirely” (Siegfried 2002, p. 255).

³³ After he identified that in chemistry there had been two main material structures: one corresponded to the vital matter, organic chemistry; and the other one to the inanimate matter, inorganic chemistry. This line of research (based on his own electronegativity concept) brought great difficulties, for their inability to explain the atomic combination in organic compounds.

The development of experimental chemistry teaching can be attributed to Justus Liebig, a German Gay-Lussac's student in Paris. With Gay-Lussac, Liebig improved an instrument to measure the gases evolved in organic compounds analysis. In his laboratory in Giessen, Liebig structured the following pattern of work: he suggested to the student a minor problem of a major issue on which Liebig himself was working, which should be solved using experimental methods and procedures that Liebig had already developed (Holmes 1989). Following an original procedure of Berzelius, he invented a new instrument for chemical analysis. Instead of measuring gas volume, he measured weight changes of specific compounds. In 1831 Liebig wrote to Berzelius:

After I had begun to concern myself preferentially with organic analysis, I quickly came to the conclusion that only your method of determining carbon by the weight of carbonic acid promised entirely secure results in all circumstances, and since then all my efforts have been devoted to making this process more easily accessible; this was the way my apparatus came to be (Cited in Rocke 2000, p. 283).

There is an agreement among nineteenth century historians of chemistry that the routine use of this instrument made "possible in a few hours analyses that had hitherto taken days and weeks," enabled "large numbers of young persons of moderate talent" to do significant investigations, "and reduced the analyses to the assembly-line work" (Holmes 1989, p. 132). Liebig himself argued for the superiority of his new instrument partly by demonstrating the large number of accurate analysis that could be performed by his students' semiskilled hands. At this time the main aim of organic analysis was to establish the number of atoms of each element contained in the compound analysed. Liebig's students could publish their own results in different journal articles with analyses using the Kaliapparat. In 1835 Berzelius wrote to Wohler, "We are using Liebig's apparatus daily. It is a splendid apparatus. Through small, minor modifications we have come so far that the results that one can attain cannot possibly be incorrect". As Frederic Holmes said: "The use of Liebig's apparatus apparently also spread rapidly among less-prominent organic chemists. This movement toward a standardization of the basic analytical procedures narrowed the area for disagreement among organic chemists in their debates over organic composition" (Holmes 1989, p. 142).

In 1837 Liebig wrote a booklet entitled *Instructions to the Analysis of Organic Bodies* where he described the instrument (Fig. 4³⁴) and the method devised, both already used by almost all of the organic chemists community. The American Chemical Society that

³⁴ The instrument comprises the horizontal combustion tube *a* (inserted in a charcoal trough) in which a mixture of copper oxide and the sample to be analysed is burned; a tube *b* containing fused calcium chloride to absorb water; a "five-bulb" apparatus (the Kaliapparat itself) in which carbonic acid gas is completely absorbed as it bubbles through concentrated caustic alkali solution; and a suction tube B.

The German word Kaliapparat, refers to the instrument that contains a solution of kali (or caustic potash, i.e. potassium hydroxide) to absorb carbon dioxide, generated by the combustion of the organic sample. The Kaliapparat eliminated the need for a pneumatic trough and allowed for the entire process to take place at atmospheric pressure, making it easier to determine the amount of carbon in a sample by weight. The tube could be heated more strongly ensuring complete combustion. Two other simple improvements in the instrument were: (a) To ensure that all of the products of combustion passed through the tubes in which the water and carbonic acid were collected, Liebig "drew the closed end of the combustion tube to a fine point. After the combustion was completed, he could break off the point and suck the residual gases through the tubes with his mouth" (Holmes 1989, p. 139). (b) The use of cork stopper to connect the combustion tube with the calcium chloride tube. Liebig stated: "It must be emphasized here particularly, that we are against the method of connection of Berzelius because with that method organic analysis loses in most hands the accuracy and reliability that the method described can give, and because it takes away the simplicity of the work along with that of the apparatus, and makes it accessible only to a relatively smaller number of experimenters". (Holmes 1989, p. 157).

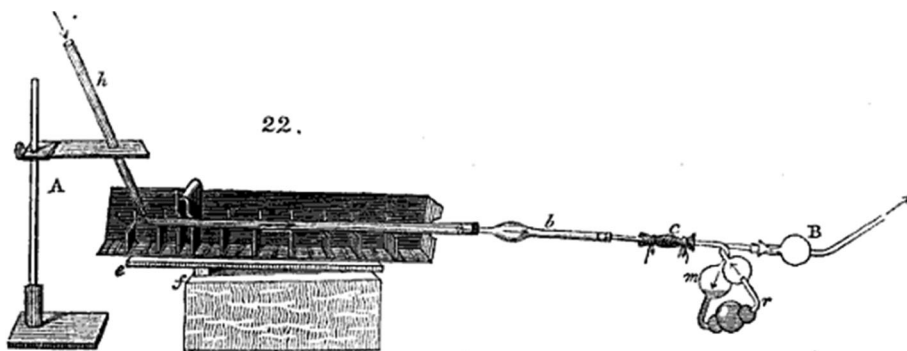


Fig. 4 Liebig's Kaliapparat

incorporated an image of this instrument in its logo recognized its importance. Rocke stated:

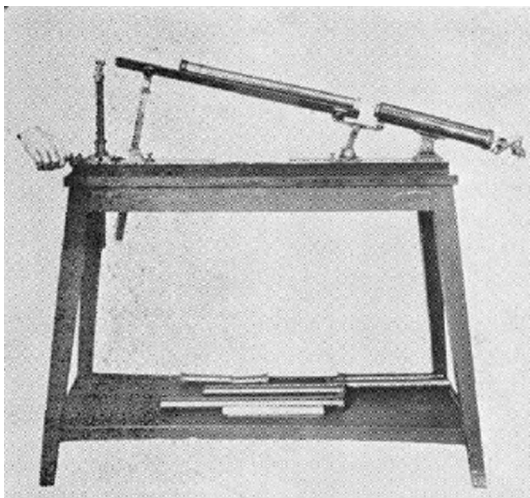
Until 1837, Liebig's method had been communicated largely by direct means, one chemist showing another the procedure in chains of transmission that led back to Liebig himself. After the publication of this monograph, anyone with minimal chemical expertise could fashion the devices and perform the operations from the detailed instructions readily available in bookstores. The essential superiority of the method and its now openly accessible details ensured that it would be employed anywhere chemistry was done. The method can be found in German as well as non-German textbooks throughout most of the rest of the century, little altered from Liebig's description of 1837 (Rocke 2000, p. 296).

Liebig's Kaliapparat represented a complete transition to gravimetry and thus to an essentially chemical methodology that started in the first chemical revolution.

Berzelius' definition of isomerism, in 1831, solved a long series of unexplained experimental results: those obtained from its own investigation into two different tin oxides that had the same composition (de Berg 2008; 2010), the Faraday isolation of benzene and acetylene or the synthesis of urea from ammonium cyanate made by Whöler. The first explanation of isomerism recognized different order of attachment of atoms in molecules, it means different constitution, and *became a fundamental tenet of organic chemistry* (Esteban 2008). More or less during the same period Jean-Baptiste Biot formulated practically all the basic laws of polarimetry. Hence with this instrument (Fig. 5³⁵) Pasteur

³⁵ Polarimeters, were one of the first instruments used to investigate structure without the destruction of the material under examination. It consists of a monochromatic light source, a polarizer, a sample cell, a second polarizer (analyser), and a light detector. The analyser is oriented 90° to the polarizer so that no light reaches the detector. With a long history (Lyle and Lyle 1964) of small improvements that began in 1678 with the identification of what Huygens called polarized light passing through the recognition of Biot, in 1815, that the polarization of the light was not only produced by some crystals but also by substances dissolved, was until 1842 when it was reported polarimeters employing white light and the combination of two Nicol prisms to provide the polarizer and analyser. The old Biot was sceptical about young Pasteur's results of molecular chirality and required to see the experiments performed for him self. Pasteur wrote as follows: He (J.B. Biot) sent for me to repeat before his eyes the several experiments. He gave me racemic acid, which he had himself previously examined and found to be quite inactive to polarized light. I prepared from it in his presence the sodium ammonium double-salt, for which he also desired himself to provide soda and ammonia. The liquid was set aside for slow evaporation in one of the rooms of his own laboratory, and when 30–40 g of crystals had separated he again summoned me to the Collège de France, so that I might collect the dextro- and laevo-rotatory crystals before his eyes, and separate them according to their crystallographic character, asking me to repeat the statement that the crystals which I should place on his right hand would

Fig. 5 Biot's polarimeter used by him, in 1848, to recognize Pasteur discovery of enantiomorphism among salts of racemic acid



was capable, in 1848, to show his separation of the optical isomers of tartaric salts, to Biot himself. In the sesquicentennial anniversary of this episode Kauffman and Myers wrote:

Pasteur's resolution immortalized his name in the annals of chemistry. His discovery that one of the forms of a salt of racemic acid consists of two optically active isomeric constituents laid the groundwork for the science of stereochemistry, the study of the spatial arrangement of atoms in molecules. He attributed their activity to what he called "molecular asymmetry" (*une dissymétrie dans les molécules*), a phrase selected as the title of the first volume of his collected works and inscribed on his mausoleum at the Institut Pasteur in Paris.

This resolution belongs to a small group of classic experiments that radically changed our view of the world and opened up new paths of research, yet are simple enough to be duplicated by a skilled undergraduate student. It has had a profound influence on research in stereochemistry, crystallography, biology, biochemistry, mineralogy, pharmaceutical chemistry, and organic and inorganic chemistry, to single out only a few of the fields that have benefited from Pasteur's genius (Kauffman and Myers 1998).

Lavoisier's elements and Dalton's atoms, electrochemistry, the separation that Berzelius himself made of organic and inorganic chemistry, equivalents, molecules, isomerism, valence and many new compounds met in the Franco-German border city of Karlsruhe in early September 1860 (Kauffman and Adloff 2010), at the First International Congress of Chemistry, convened by three renowned personalities of the time: Karl Weltzein, Friedrich A. Kekulé and Charles A. Wurtz. They sought, as Lavoisier years earlier, to reform and improve the language of chemistry. Despite the congress gathered chemists of twelve countries, among which R. Bunsen, E. Erlenmeyer, L. Meyer, A. Crum Brown, J.B.A.

Footnote 35 continued

cause the deviation to the right, and the others to the left. This done, he said that he himself would do the rest. He prepared the carefully weighed solutions, and, at the moment when he was about to examine them in the polarimeter, he again called me into the laboratory. He first put the more interesting solution, which was to cause rotation to the left, into the apparatus. Without making a reading, but already at the first sight of the colour-tints presented by the two halves of the field in the Soleil saccharimeter, he recognized that there was a strong laevorotation. Then the illustrious old man, who was visibly moved, seized me by the hand, and said 'Mon cher enfant, j'ai tant aimé les sciences dans ma vie que cela me fait battre le coeur!'. (My dear child, I have loved science so much throughout my life that this makes my heart throb) (Flack 2009).

Dumas, J. Wislicenus, D. Mendeleev stand out, they did not reach what was expected. However, the Italian Stanislao Cannizzaro rescued the ideas of his compatriot Amadeo Avogadro about the difference between atoms and molecules, and achieved in terms of Kuhn, one of the most notable accounts of scientific conversion through a scientific revolution. Lothar Meyer, years after the event, was recalling a striking event that occurred:

After the close of the congress, at the author's behest, a friend, Angelo Pavesi, distributed a short, apparently insignificant work, Cannizzaro's *Sunto* (Sketch)...reproduced here in translation. It had appeared few years earlier but had not become well known. I too, received a copy, which I pocketed in order to read it on the way home. I also read it over and over at home and was astonished at the light, which the little work shed upon the most important points of controversy. Scales as it were fell from my eyes, doubts evaporated, and a feeling of the most tranquil certainty took their place. If a few years later I was able to contribute something to clarifying the situation and calming down overheated spirits, this is in no small part thank to Cannizzaro's paper. Something similar must have happened to many other participants in the congress. The towering waves of the controversy began to smooth out (Cited in Cohen 1985, p. 472).

The Kaliapparat, an instrument developed hand in hand with chemical atomism, completed Avogadro and Cannizzaro's ideas of molecules (Table 3). The new organic chemistry, with all its isomers, was strongly incorporated in chemists' paradigm (here disciplinary matrix). Throughout the second 'quiet' revolution, scientific communities witnessed the end of the amateur chemist, giving way to the professional chemist. Chemistry was the first science in which the experimental work during its teaching became mandatory.³⁶ At that time, in many European countries compulsory education was being introduced and state schools began to be built and ruled. Cannizzaro, himself a teacher, stated in his *Sketch of a Course of Chemical Philosophy*:

Once my students have become familiar with the importance of the numbers as they are exhibited in the preceding table, it is easy to lead them to discover the law which results from their comparison. "Compare" I say to them "the various quantities of the same element contained in the molecule of the free substance and in those of all its different compounds, and you will not be able to scape the following law: *The different quantities of the same element contained in different molecules are all whole multiples of one and the same quantity, which always being entire, has the right to be called atom*" (Cannizzaro 1858, pp. 10–11).

Simultaneously that a new chemical speciality had been established, the proposal of Edward Frankland, and other chemists³⁷ of the time, to characterize the ability of combination of atoms with the name of "valence"³⁸ along with the statement of the periodic law³⁹ by two of the participants in Karlsruhe's congress completed the theoretical contributions of the second chemical revolution (Table 2). Molecules and isomers were the new structural entities adopted by the chemical community both constituted by atoms, and clearly differentiated from them.

³⁶ David Knight explained this: "It was not Göttingen or Berlin, but at the small university of Giessen that the revolution in chemistry teaching happened, when Liebig began laboratory teaching for the PhD degree [...] Only after the middle of the century did it cease to be possible to study chemistry as a spectator sport: it was the first science where practical work became compulsory [...] This was a recognition that the chemist must think with hands as well as brain" (Knight 1995, pp. 151–152).

³⁷ Like A.S. Couper, A.W. Hofmann or A.W. Williamson.

³⁸ This subject has been discussed in: Russell 1971. For example he stated (Russell 1971, p. 85): Frankland's Lecture Notes (1866) assert that "this combining powers of the elementary atoms is usually termed their "atomicity" or "atom fixing power", but in the 1879 edition he adds the Word "equivalence" as a further synonym....

³⁹ See, for example: Jensen (2002), Scerri (2007) and Spronsen (1969).

Table 2 Molecules and isomers revolution

	EXEMPLAR	
	INSTRUMENTS	CONCEPTS
Instruments	Kaliapparat, polarimeter	
Concepts		Language, Molecules, Isomers, Valence, Periodicity
Books	<i>Instructions for the Chemical Analysis of Organic Bodies,</i>	<i>Sketch of a Course of Chemical Philosophy</i>
Protagonists	Berzelius, Liebig, Pasteur, Kekule, Cannizzaro, Frankland, Mendeleiev	

Main figures related to instruments and concepts of the second chemical revolution (1831–1860)

5 The Third Chemical Revolution: 1897–1923

The problem of the structure of atoms has been attacked mainly by physicists who have given little consideration to the chemical properties, which must ultimately be explained by a theory of atomic structure. The vast store of knowledge of chemical properties and relationships, such as is summarized in the periodic table, should serve as a better foundation for a theory of atomic structure than the relatively meager experimental data along purely physical lines.

I. Langmuir (1919)

The period between the second and third chemical revolution has been regarded as the “golden age of chemistry” (Knight 1995). The matter was composed of atoms (with valence) and molecules, which regularly classified as elements, could predict their behaviour. Organic chemists could copy molecules that were originally in plants and animals, and then synthesize entirely new molecules. European societies first, then the rest of the world, were flooded with new dyes, materials and medicines from the powerful German chemical industries. In this country, the number of colleges and universities with chemistry departments and their teachers, researchers and students grew significantly. Chemists gradually incorporated more instruments in their laboratories and measured more accurately. Physical chemistry and chemical physics, the new speciality of chemistry and physics was under way, as was the third chemical revolution.⁴⁰

This paper claims that instruments have been instrumental, ‘exemplars’, forging chemical revolutions. Therefore, what indicates the beginning of the third revolution is the

⁴⁰ Jensen stated that this revolution spans roughly from 1904 to 1924 and identified several factors that contributed to it: “In the recognition of the various factors contributing to the third chemical revolution we encounter an interesting pedagogical irony. Most modern chemistry textbooks include brief discussions of how each of these factors (Periodic Table, electrochemistry, radioactivity, discharge tubes, spectroscopy, quantum hypothesis) contributed to our understanding of the electrical structure of matter, with the exception of the two that are most explicitly chemical in nature—namely the periodic table and electrochemistry. Though even the most superficial acquaintance with the literature of this period shows that both of these topics played key roles in the development of the modern electronic theory of valence, they are instead presented in the textbook as deductions from—rather than as contributors to—the modern electrical theory of matter, which, in turn, is attributed solely to the work of physicists. In fact, did chemists make significant contributions to this theory via electrochemistry and the development of the periodic law, they made significant contributions, in the person of Sir William Crookes, to the study of gaseous discharge tubes, and they virtually dominated the study of radioactivity until the 1920s. After all, we need only remind ourselves that Rutherford was given, much to his chagrin, the Nobel Prize in chemistry, rather than physics, for his work on the disintegration theory of radioactivity. But here the irony often degenerates into farce, since the few textbooks that explicitly refer to Crookes by name, or to such radio chemists as Frederick Soddy or Otto Hahn, almost invariably misidentify them as physicists” (Jensen 1998).

discovery of the electron by J.J. Thomson, in 1897, using the cathode rays tubes as an instrument. The end of the third revolution was 1 year later when Francis W. Aston was awarded with the Nobel Prize in Chemistry for “his discovery, by means of his mass spectrograph, of isotopes, in a large number of non-radioactive elements, and for his enunciation of the whole-number rule” (Rogers 2006, p. 114). In 1923 the publication of G.N. Lewis’ *Valence and the Structure of Atoms and Molecules* and J.J. Thomson’s *The electron in chemistry* turned paradigmatic this entity and testified the end of the third chemical revolution.⁴¹

Though electrolytic and ionization studies during nineteenth century had provided sufficient evidence for the existence of electrically charged atoms, molecules or ions, it was not proved that the charge could be found independently of those entities. At the end of the century the investigations of the chemist and physicist William Crookes about the electrical conduction of rarefied gases, followed by the research of Eugene Goldstein and Joseph J. Thomson, gives the answer. Crookes’ tube consists of a partially evacuated glass container, with two metal electrodes, the anode and the cathode one at either end. When a high voltage is applied between the electrodes, a radiation with mass (cathode rays) travels in straight lines from the cathode to the anode, suggesting their negative charge character. In 1886 Goldstein identified another type of radiation, which he called “canal rays”, composed by positive charged particles. Canal rays produced a glow discharge and their colour changed in accordance to the nature of the gas that remains in the tube. At that moment there was a controversy about the nature of cathode rays (German physicists supported the ether theory for their origin, while the British argued for their particle nature), but it was the discovery of X-rays in 1895 that triggered Thomson’s interest in cathode rays. He conducted a series of experiments, published at length in 1897, which gained him recognition as the discoverer of the electron. However, another scientist proclaimed that honour (P. Lenard, P. Zeeman and W. Crookes). Achinstein (2001), discussing this historical moment, assigned the following components for a discovery:

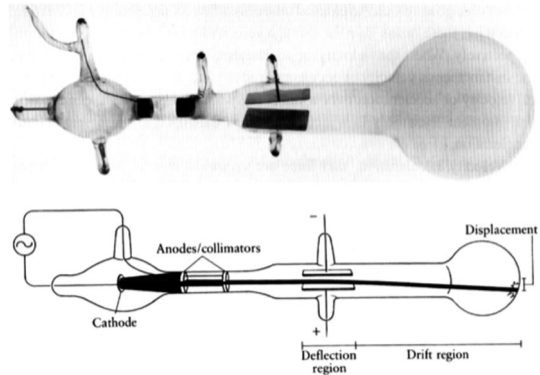
- The existence of what is discovered is needed.
- A certain state of knowledge of the discoverer is required.
- Social recognition of the discovery is demanded.

The previous criterion agrees that Thomson was the electron’ discoverer using a cathode rays tube as an instrument (Fig. 6⁴²). He chose “corpuscle” to refer to the material carrier of negative electric charge constituting cathode rays, but years later he used electron (introduced by G. Johnstone Stoney two decades earlier to refer to a putative physically fundamental unit of charge, positive and negative). Thomson points out a fundamental aspect of his experiments; namely, that cathode rays are the same whatever the gas through which the discharge passes, and concludes that cathode rays are charges of negative

⁴¹ About the importance of G.N. Lewis recently Bogaard said: There are many reasons to include G.N. Lewis within the pantheon of chemists from a century ago, but one reason in particular is to recall the role he played in musing philosophically about chemistry. At least in this sense: at a crucial time in the revolutionary changes rippling through theoretical physics, Lewis as North America’s leading “physical chemist” warned physicist that their most recent theoretical proposals—particularly the Bohr theory of the atom—would not suffice as a conceptual or causal foundation for chemistry” (Bogaard 2012, p. 133).

⁴² Above: One of the tubes with which J.J. Thomson measured the m/e ratio of the corpuscle later called electron. Below: A schematic view of the instrument. Cathode rays are emitted at the cathode. They travel in a straight line, hitting the glass wall and producing a spot of light. However, through a magnetic or electric field they are deflected, and then the electron mass/charge ratio can be measured.

Fig. 6 Thomson's instrument. Adapted from Weinberg (2003, p. 26)



electricity carried by particles of matter.⁴³ Thomson goes further and proposes an atomic model that would last until Geiger and Marsden's experiment, in 1909, which consisted in bombarding metal thin films with radioactive particles. This allowed Ernest Rutherford⁴⁴ to postulate the existence of the nucleus, and a nuclear atomic model with electrons turning around the nucleus. In 1912, Frederick Soddy,⁴⁵ coined the term isotope: "on Rutherford's theory of atomic structure, are elements with identical external electronic systems, with identical net positive charge on the nucleus, but with nuclei in which the overall number of positive and negative charges and therefore the mass is different" (Rogers 2006, p. 111). After World War I, Thomson's assistant Francis Aston, following the initial research made by Goldstein and Thomson in "canal rays" built a mass spectrograph instrument (Falconer 1988) (Fig. 7⁴⁶). As indicated above, positive "canal rays" produced a glow discharge the colour of which changes in accordance with the nature of the gas that remains in the tube. Aston investigations with neon, allowed him to identify that this element was composed of two isotopes, one of mass 20 with an abundance of nearly 90 % and another one of mass 22 with an abundance of 10 %. With this research, made in his new instrument, he extended Soddy's isotope concept to stable elements.

The electron that broke atoms unity, radioactivity that betrayed the fragility of the elements, and the nucleus and isotopes were incorporated conceptually and experimentally

⁴³ Thomson determined the relation m/e and founded that its value, 10^{-12} kg/C, is independent of the nature of the gas, and it is very small compared with the 10^{-8} kg/C of H^+ , the hydrogen ion in electrolysis, which is the smallest value of this quantity previously known. In 1906 he was awarded, with the Nobel Prize in Physics "in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases".

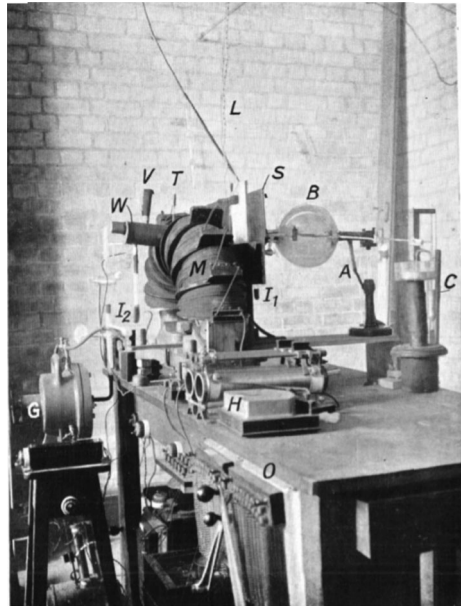
⁴⁴ Awarded with the Chemistry Nobel Prize, in 1908 "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances".

⁴⁵ Awarded with the Chemistry Nobel Prize, in 1921 "for his contribution to our knowledge of the chemistry of radioactive substances, and his investigations into the origin and nature of isotopes".

⁴⁶ The original mass-spectrograph (1919). A, Anode (connected to high potential terminal); B, Discharge tube; C, Reservoir containing gas to be analysed; M, Electromagnet; W, Camera; G, Gaede mercury (vacuum) pump.

Aston's first major contribution was to develop a new kind of instrument which he named a "mass spectrograph" and which showed two great improvements over Thomson's parabola machine. Aston replaced the capillary tube that had been used by Thomson to collimate the ion beam by a pair of slits arranged at the ends of a tube connected to the discharge-vessel...But, more importantly, he discovered a method of "focussing" his ion beam by passing it through successive electric and magnetic fields (Beynon and Morgan 1978, p. 18). With these two improvements ions having e/m ratios differing in only one part in 130 parts could be separated.

Fig. 7 Aston's mass spectrograph (Aston 1933)



in chemistry. The existence of the nucleus in the atom had been demonstrated and accepted however a dispute between the communities of chemists and physicists was established to explain the electrical nature of atoms. Two different paradigms emerged: one, from the chemists who assumed that electrons were static, and the other, from the physicists, who considered that the electrons were moving.

Kuhn himself recognized the difficulties that arose when two communities do not share the same paradigm (here we would say disciplinary matrix): “[P]aradigm debates always involve the question: Which problems is it more significant to have solved?”⁴⁷ The problems were, and still are, different for chemists and physicists. Some of them, working with atoms, thought into molecules, whereas the others, on radiation. About this Arabatzis, in the chapter of his book entitled “How the electrons spend their Leisure-Time”, stated recently:

We have seen that both chemist and physicist felt obliged to account for experimental evidence that was not produced within their discipline. This suggests that a scientific theory has to account for all the data that are deemed part of its explanatory domain. The latter may encompass experimental results from more than one discipline. The relevance of a piece of experimental evidence to the evaluation of a theory is, in turn, determined by the entities that the theory employs (Arabatzis 2006, p. 197).

That entity is the electron about which two notorious books were written. Both appeared in 1923, when the third chemical revolution ended (Table 3). The authors were two distinguished representatives of both communities. Find below the first paragraph of *The*

⁴⁷ The full paragraph says: “To the extent, as significant as it is incomplete, that two scientific schools disagree about what is a problem and what a solution, they will inevitably talk through each other when debating the relative merits of their respective paradigms. In the partially circular arguments that regularly result, each paradigm will be shown to satisfy more or less the criteria that it dictates for itself and to fall short of a few of those dictated by its opponent. [P]aradigm debates always involve the question: Which problems is it more significant to have solved?” (Kuhn 1962, p. 108–109).

Table 3 Electrons and isotopes revolution

	EXEMPLAR	
	INSTRUMENTS	CONCEPTS
Instruments	Cathode rays tube, Mass spectrograph	
Concepts		Language, electric chemistry, nuclear chemistry
Books	<i>Mass-spectra and isotopes</i>	<i>Valence and the Structure of Atoms and Molecules</i>
Protagonists	Thomson, Aston, Lewis, Soddy, Rutherford	

Main figures related to instruments and concepts of the third chemical revolution (1897–1923)

electron in chemistry of J.J. Thomson and the last paragraph of *Valence and the Structure of Atoms and Molecules* by G.N. Lewis. Chemical physics or physical chemistry communities devoted to study corpuscles were settled (Nye 1993; Schummer 1998). However their interests and different approaches remains...until today.⁴⁸

I ought to explain why it is that I, who am a physicist and not a chemist, have chosen chemistry as the subject of these lectures. I have done so because I believe that the introduction of the idea of the electron will break down, and indeed has already done so to some extent, the barrier of ignorance, which has divided the study of the properties of matter into two distinct sciences, physics and chemistry (Thomson 1923, p. 1).

Indeed in a period of transition such as the present we must more than ever focus our attention upon our actual experimental facts, and give less heed to those conventional abstractions of the mind, such as force and fields of force, energy and the conservation of energy, or even space and time. Some of these abstractions may have to be abandoned as the conventional ether was abandoned after the acceptance of relativity. Others may have to be modified, and my chief purpose in writing the present section is not so much to predict just how these modifications are to occur as it to emphasize the necessity of maintaining an openness of mind; so that, when the solution of these problems, which now seems so baffling, is ultimately offered, its acceptance will not be retarded by the conventions and inadequate mental abstractions of the past (Lewis 1923, p. 165).

Briefly and metaphorically speaking, from the atomic tree of chemistry, the result of the second revolution, sprouted a second branch, organic chemistry, with its multitude of molecules and isomers. Of the third revolution (Table 3) sprouted other branch, around atomic nuclei with different masses where their electrons ‘spend their leisure time’, corpuscular physical chemistry.

⁴⁸ For example in their history of quantum chemistry, “Philosophers of science have attempted to understand the intricate balance between the descriptive, the explanatory, and predictive power of mainly the physicists’ theories. And chemists were rather happy in trying to explain to their colleagues how they will be using the theories they were devising or “borrowing” often realizing that these were theories that the physicist would snub and most philosophers of science simply ignore. It was Lewis who, already back in 1933, contrasted the different features of theories in chemistry and physics. He presented structural organic chemistry as the paradigm of a chemical theory, as an analytical theory in the sense it was grounded on a large body of experimental material from which the chemist attempted to deduce a body of simple laws that were consistent with the known phenomena” (Gavroglu and Simoes 2012, p. 247).

6 Conclusions

I am far from alone in urging a flexible approach as regards the classic (many would say outworn) dichotomy between cognitive and social history of science. Flexibility, pluralism, and an eclectic and empirical approach is often a recipe for success in science...In the valuable perspectives provided by recent sociological studies, the power and vitality of scientific ideas and logic, the constant regulating appeal to the empirical world, and the contingent influence of individuals ought not be underestimated.

A. Rocke (1993, p. 112)

Although there are few original approximations to the way in which chemistry could be taught⁴⁹ it generally implies a unique philosophical position that hides history of chemistry. Generally this position is logical positivism,⁵⁰ the traditional historiographical approach to study history of science. The difficulties of teaching a discipline without knowing its philosophical positions have been clearly exposed by the French historian of chemistry Bernadette Bensaude-Vincent discussing on the issue here exposed:

It is well-known that French chemists were reluctant to adopt the atomic theory in the nineteenth century. Their opposition was long-standing and tenacious since the atomic hypothesis formulated in the first decade of the nineteenth century by John Dalton was banished from the teaching of chemistry until the early decades of the twentieth century. Instead of atomism, the French chemists preferred the Richter's language of equivalents because it avoided commitment to a speculative theory of indivisible elementary particles...[...]. There is a general agreement among historians of chemistry that this national feature was due to the overarching influence of positivism in France (Bensaude-Vincent 1999).

Assuming that instruments and concepts are the 'exemplars' developed by the protagonists of the history of science, the possibility of weaving a more comprehensive and detailed fabric of the past is open.⁵¹

The development of both instruments and concepts can be distinguished in the history of chemistry, and following the ideas of Kuhn and Jensen, three revolutions around different entities are recognized: chemical atoms, molecules, isomers, electrons and isotopes. Therefore, among the different ways of teaching the history of chemistry,⁵² and general chemistry as well, the one described here, which established a temporal frame of reference on the occurrence of chemical entities, that all chemistry students use, and recognized the emergence of new chemical sub-disciplines may be a new approach to the teaching of chemistry, considering its own history.

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⁴⁹ See, for example: Izquierdo-Aymerich (2012), Jensen (1998, 2003), Lazlo (2011), Talanquer (2011) and Van Aalsvoort (2004).

⁵⁰ As has been indicated by: Chamizo (2013), Erduran and Scerri (2002), Van Aalsvoort (2004) and Van Berkel et al. (2000).

⁵¹ The history of chemical instruments was generally not considered for the positivistic and postpositivistic historiographical approaches. Here only the instruments directly related with the revolutions have been described, however many others like thermometers, eudiometers, calorimeters, the Reflux, high pressure recipients (developed by Frankland in Russell 2000), the Bunsen burner, ultramicroscopes or X-rays spectrometers were very important along this period of time. Also more factors can be considered, like the builders and designers of the instruments.

⁵² For example, through some of its more important experiments (Chamizo 2009), or using old instruments (Cavicchi 2012).

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