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M. Carey Lea, the first mechanochemist

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The experiments of M. Carey Lea (1823–1897) are usually considered the first systematic investigations on the chemical effects of mechanical action. This paper collects the most important facts about Lea's life and discusses his research from the point of view of mechanochemistry. Lea was born into a family of considerable privilege and exceptional achievements. He suffered from weak health throughout his life. Consequently, he was educated at home by a tutor and later worked in the private laboratory of his home in Philadelphia. Lea was primarily a photochemist, his first mechanochemical observation in 1866 concerned the pressure sensitivity of photographic plates. Later in his life, he investigated the effect of various kinds of energy—heat, light, mechanical action—on allotropic (colloidal) silver and silver halides. The "parallelism" of the results motivated Lea to study the mechanochemical decomposition of dozens of stable compounds between 1892 and 1894. He observed the decomposition of silver and mercuric chlorides by trituration in a mortar, although the same compounds are known to melt or sublime undecomposed when heated. Lea was elected member of the National Academy of Sciences in 1892.

1. Introduction

Establishing mechanochemistry as a separate branch of chemistry is usually attributed to Matthew Carey Lea, who demonstrated at the end of the 19th century that certain compounds react differently under the influence of mechanical action and heat. His best known examples are silver halides and mercuric chloride, compounds he could decompose by trituration in a mortar, but melt or sublime undecomposed when heated. These results are known to most mechanochemists as they are frequently mentioned in monographs and review articles [1–5].

In spite of the importance of his work, very little is known about Lea's life, his motivation, and the details of his investigations. The two existing biographies [6, 7] provide excerpts from his articles without much interpretation and emphasize his results related to the chemistry of photography and the study of "allotropic silver". Their authors did not realize the ground-breaking importance of Lea's studies on the chemical effects of mechanical action.

Carey Lea was almost seventy years old when he decided to study the chemical effects of mechanical action. Consequently, his motivation and methods originated from a long series of earlier studies. The first related observation was made in 1866 and concerned the pressure sensitivity of photographic plates. Lea was able to use pressure to produce developable images that resembled the images created by light [8]. The observed similarity between the effects of pressure, light and other energy forms provided the framework for Lea's systematic studies on the chemical changes of silver halides and "allotropic"—colloidal—silver. He found that the application of a small amount of energy always produced a latent change that could be made visible with the aid of a photographic developer, while a larger amount of energy usually resulted in an immediately visible color change. The encouraging results provided the impetus for the systematic investigation of several compounds under the influence of large static pressure, sheer provided by a mortar and pestle, and less intense pressure and sheer delivered by marking a treated cardboard with the rounded end of a glass rod.

It is expected that a sense of common historical roots increases the cohesion of a research community. Recent efforts to explore and record the history of mechanochemistry [9, 10] are very helpful in that respect. The present article on M. Carey Lea is intended for readers familiar with mechanochemistry; an earlier version for a broader audience was published recently [11].

2. The life of M. Carey Lea (1823–1897)

Matthew Carey Lea was born in Philadelphia, August 18, 1823, to a family of considerable privilege and extraordinary achievements in a variety of fields [6].

His father, Isaac Lea (1792–1886), was the descendant of an influential Quaker merchant family, the great-great-grandson of John Lea, who emigrated to America with William Penn in 1699 [12]. Isaac Lea became a distinguished naturalist, mineralogist and an expert on contemporary and fossil shells. He was a respected scientist who served as president of the Academy of Natural Sciences and of the American

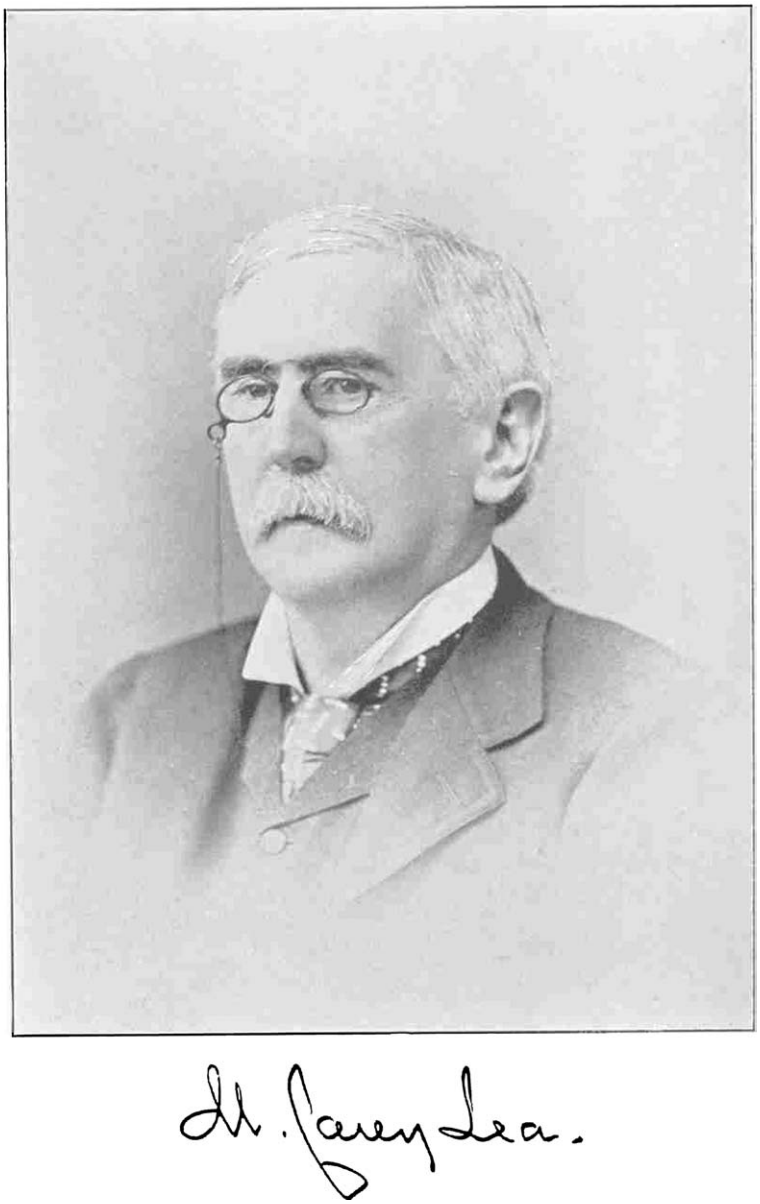

Figure 1 M. Carey Lea (1823–97).

Association for the Advancement of Science, among many other functions [13]. Between 1822 and 1851, he was also one of the partners in the family's publishing business. He donated a collection of 1316 gems to the Smithsonian Institution's Museum of Natural History, that forms the core of the museum's gem collection [14].

Carey Lea's mother was Frances Anne Carey (1799–1873), an intellectual woman, who paid ample attention to the education of her children. She was the daughter of Matthew Carey (1759–1839), a Catholic Irish patriot, energetic and opinionated, who had to flee to America from political persecution. In 1785, he established the longest running publishing company in the United States [15]. He was also a prominent political writer on both Irish and American issues. Carey had nine children, among them Henry Charles Carey (1793–1879), who carried on the family's publishing business. Later he became a noted economist, who authored the "Principles of Political Economy," a comprehensive book translated to several languages, including German and Hungarian. He had no children of his own, but played an important role in the life of his nephews.

Matthew Carey Lea was the second son of the family. The first son (also called Matthew) died as an infant. His younger brother and best friend, Henry Charles Lea (1825–1909) [16] continued the publishing business and specialized it in scientific and medical books. He also became an eminent writer on political and historical subjects, primarily known as an expert on the history of inquisition. The youngest child of the family was Frances Lea (1834–1894), who dedicated much of her life to caring for her ill mother.

M. Carey Lea suffered from weak health from his early childhood. Therefore, instead of attending boarding school as was customary at the time, he and his similarly frail brother were educated at home by a private tutor [16]. Their teacher, Eugenius Nulty, approached the sciences through a series of small projects. He initiated each subject with a clearly posed question, and study and experimentation was aimed at finding a solution to that question. Once the answer was formulated, they considered the matter closed and moved to a new, although often related subject. The influence of this working style has an identifiable effect on Lea's later approach to research.

Lea studied law initially and he was admitted to the Philadelphia bar in 1847, but due to his weak health, he never practiced [6]. Instead, he decided to study chemistry at the consulting laboratory of Prof. James C. Booth, where he learned the principles and practice of laboratory work. It was during this time that a laboratory accident damaged one of his eyes. His later experiments were performed in the private laboratory of his home in the Chestnut Hill district of Philadelphia. He was pursuing chemistry for the pleasure of discovery. His wealth was amply sufficient to support his family and his research.

His frail health made Lea withdrawn and he lived his life among a small circle of friends and family. He worked in his laboratory independently, keeping contact with the scientific community via publications. Lea became a member of the Franklin Institute in 1846, used its library collection extensively, but never participated in the work of the Institute. He never gave a public lecture. Nevertheless, the breadth of his scientific achievements is enormous, as shown by the list of his "more important" papers published with his Biographical Memoirs [6]. It contains more than 100 titles, published mainly in the *American Journal of Science*. He wrote his only book on photography [17]. Lea was thoroughly familiar with the results of others and read and quoted the scientific literature published in English, French, and German.

Lea was elected member of the National Academy of Sciences in 1892, at its Regular Annual Meeting [18]. (Unfortunately, the year of Lea's membership is given as 1895 in the "Biographical Memoir" by mistake [6] and that incorrect date is reproduced in most compilations of biographies, including the American National Biography [19].) He was not present at the meeting, his paper titled "Disruption of Silver Haloid Molecule by Mechanical Force" [20] was read for him by G. F. Barker.

Lea married his cousin, Elizabeth Lea Jaudon, in 1852. (Interestingly, his brother married her sister the previous year.) Carey Lea's only son, George Henry Lea was a family genealogist. Thanks to his and an uncle's effort, the male branch of the ancestry of Carey Lea is known back for 12 generations [12]. After the death of his first wife in 1881, Lea married Eva Lovering, the daughter of Harvard professor Joseph Lovering.

Matthew Carey Lea died on March 15, 1897, in the seventy fourth year of his life, from complications related to a prostate operation. Unfortunately, his notebooks were destroyed according to his will [7], limiting the information about his work to the contents of his published papers.

3. Overview of the scientific work of M. Carey Lea

The number of Lea's scientific papers versus their year of publication is shown in Fig. 2, based on the Biographical Memoir [6]. The output is quite non-uniform, years of intense work are followed by periods of inactivity, probably depending on Lea's health and events in his personal life.

His first paper on the bituminous qualities of Pennsylvania coal was written when he was only 17. It is a very promising work from a boy of that age. The subject was suggested by Lea's father, whose investment in coal fields contributed significantly to the financial stability of the family [16]. The measurements were carried out in Prof. Booth's laboratory. Lea studied law during the following years and returned to chemistry only after spending some time in Europe. He published his next paper on picric acid in 1858, followed by a flood of articles on a number of subjects related to both inorganic and organic chemistry.

He found the main research interest of his life, the chemistry of photography, in the mid 1860th. In addition to publishing several scientific papers on the subject, he wrote about 300 articles and correspondences for photographic magazines during this time. His book, published in 1868, became a standard reference on

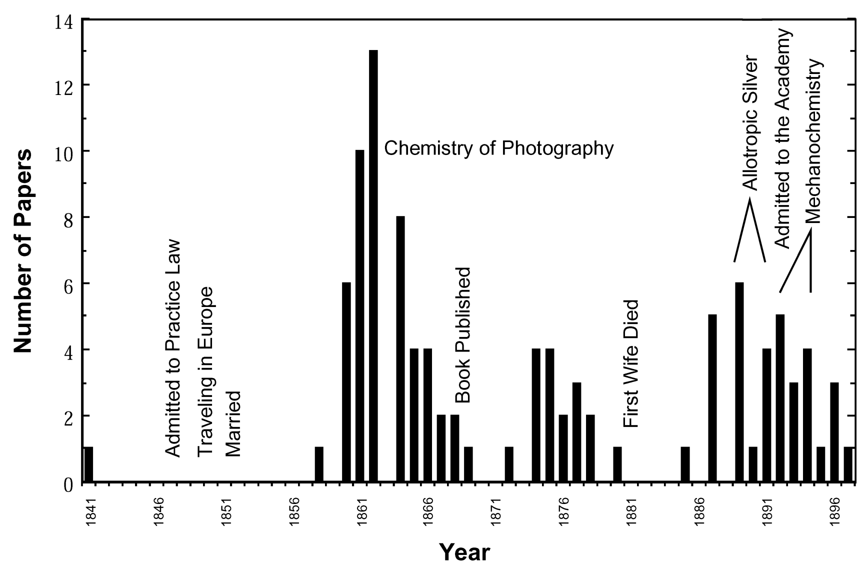

Figure 2 The number of Lea's scientific papers as a function of the year of publication. The histogram includes only the papers listed in the Biographical Memoir [6]. Some important events of Lea's life and the periods dedicated to his main research areas are also indicated.

photography and was reprinted in 1871 [17]. The temporary silence around 1870 could be the result of exhaustion from this frantic activity, but photochemistry remained Lea's main area of interest until the late 1880th and his research methods and materials often derive from his experience in photochemistry, even when the subject seems unrelated. He studied the effect of light on silver and mercury halides, investigated the influence of modifiers on spectral sensitivity and improved the development process. He speculated on the nature of the latent image, the hardest, yet most central problem of photographic chemistry.

The golden and—from the point of view of today's science—most valuable years of Lea's research career were dedicated mainly to "allotropic" silver and the chemical effects of mechanical energy. These subjects will be discussed in more detail in the next sections.

Lea published on a broad variety of subjects even during the period when photochemistry dominated his work. A critical review of all his papers is beyond the scope of this article, but a few topics are mentioned here to exemplify the breadth of his scientific interest. He studied the properties of the platinum-group metals; prepared and investigated $AgHgClI_2$ and other silver salts. In organic chemistry, he worked with picric acid, ethyl and methyl bases, and developed organic coloring agents. He designed laboratory instruments and developed or refined test reactions and analytical techniques. Lea was also searching for broad organizing principles and recommended an alternative to Mendeleyev's periodic table that considered color in addition to atomic weight as a characteristic property.

When assessing Lea's work, one must keep in mind that he was a "classical" chemist, who used only test reactions, visual inspection, color and solubility differences for his investigations; his only analytical instrument was the balance. He worked alone, without close interaction with other scientists. His health was weak, he often worked on the verge of a breakdown. With these circumstances in mind, the achievements of Carey Lea are truly remarkable.

4. Mechanical effects on photographic plates and allotropic silver

Mechanical action entered Lea's research related to a dispute on the nature of the latent photographic image. In the 1860s, two theories, the "chemical" and "physical" ones, competed with each other. The proponents of the chemical theory believed that exposure of a silver halide to light resulted in an incipient reduction to a subhalide or even metallic silver. During development, the reduction of the remaining silver halide was catalyzed by the minute reduced fraction. Lea fiercely opposed this view, at least in the case of pure silver iodide. He wrote in 1866: "Does chemical decomposition necessarily accompany the production of an impression upon iodid of silver? In my opinion *it does not*. I hold that: When perfectly pure iodid of silver, isolated, is exposed to light, it receives a physical impression only" [21]. He based his opinion on chemical evidence: Even small traces of iodine can be detected by the starch reaction, but no iodine was observed even after exposing AgI to thousands of times the period sufficient to produce a developable image. Lea generalized this observation to photographic plates based on other silver halides, supporting the "physical" theory of the latent image. He insisted that, although some sort of chemical change during exposure of a photographic plate was possible, it was not necessary, a physical impression was sufficient to carry the latent image.

Although Lea considered the above chemical evidence a decisive proof of the physical theory, he offered an even more direct one, that used an argument based on mechanical action [22]. He wrote: ". . . no confirmation of the physical theory could be more striking than that which would result, if it could plainly be shown that a purely physical cause, independently of light, was competent to control development; and that if this cause was not merely physical as distinguished from chemical, but also purely *mechanical* in its nature, there would result an inference which the advocates of the chemical theory would find . . . extraordinarily hard to countervail." Carey Lea considered the production of a developable latent image by pure mechanical force a very strong argument for the physical theory, because a *mechanical* cause certainly could not produce any *chemical* impression. "Here is no possibility of reduction, no possible production of metallic silver, or of subiodide, no possible elimination of iodine . . . " [22]. In order to test this idea, Lea selected a ruler with carved-out letters and an embossed card with raised lettering, pressed them against sensitized photographic plates in the dark, and brought out an image of the lettering by developing the plates. He could also "draw" developable patterns on sensitized photographic plates with the rounded end of a glass rod. It was clear to Lea that the images originated from pressure differences, not from a chemical impression. Of course, pressure may actually produce a chemical change that is amplified by development. In 1866, Lea did not even consider this possibility. But independent of the interpretation, these are Lea's first observations of a mechanochemical effect. Years later, his objection to the chemical theory of the latent image faded and he began attributing the latent image to the formation of "photosalts," combinations of a silver halide and a small amount of sub-halide.

During his lifetime, Lea's best-known discovery was that of "allotropic silver" [23]. He decided to study the reduction products of silver salts in connection with the investigation of the photosalts in 1886. The reduction of silver citrate by ferrous citrate provided several new forms of silver in a reproducible manner; all these forms of silver were sensitive to light [24]. Some allotropic silver samples prepared by Lea are preserved in the Library of the Franklin Institute, Philadelphia [25]. What Lea considered solutions of allotropic silver are in fact colloids, but that became clear only many years later. In fact, his results were still mentioned in the presentation speech when the Nobel prize was awarded to Zsigmondy in 1925 "for his demonstration of the heterogeneous nature of colloids", among them allotropic silver, by the use of the ultramicroscope [26].

Allotropic silver was interesting for Lea because of its light sensitivity, but it also responded to mechanical agitation. As he described [27]: "I brought with me to my summer home a number of specimens in tubes . . . On opening the box no tubes of gold colored silver were to be found, all had changed to white. But the same box contained pieces of paper and of glass on which the same material had been extended; these were wholly unchanged . . . Apparently, the explanation was this, the mere vibration caused by the jarring of a journey of 600 miles by rail and steamboat had had no effect in changing the molecular form, but the material contained in the partly filled tubes had been also subjected to friction of pieces moved over each other, and this had caused the change." To confirm this interpretation, he sent a tube, partly filled with gold colored silver but rendered motionless by tightly filling the space with cotton wool, on a 2400 miles long train trip. The sample arrived back unaltered, while the control samples that were left loose in partially filled tubes became white.

Carey Lea investigated the properties and transformations of allotropic silver in significant detail. Some properties, such as light sensitivity and the formation of allotropic silver from partially reduced halides or oxides, suggested structural similarities between the subsalts of silver and allotropic silver [28]. This question was discussed systematically in a series of three articles published in 1891 [29–31]. Lea attempted "to prove that all forms of energy act upon allotropic silver, converting it either into ordinary silver or into the intermediate form. Mechanical force (sheering stress) . . . converts it directly into ordinary silver" [29]. When allotropic silver is converted into a more stable form, it becomes less dispersed, as indicated by lower reactivity and larger density. This observation lead to the working hypothesis on the nature of allotropic, intermediate, and ordinary silver "that they may represent the three possible molecular forms of silver, viz: atomic, molecular and polymerized" [30]. If taken literally, this statement is quite naive, but it is important for the understanding of Lea's reasoning: Silver in its compounds must exist in the atomic form, just as in allotropic silver. Consequently, a parallelism is anticipated between the transformations of allotropic silver and the reduction of silver halides. Experiments confirm the existence of such a parallelism. The application of a small amount of energy to a silver halide—in the form of heat, light, mechanical force, electricity (high tension spark), and chemism—produces a latent change that can be brought out by the application of a developer. A larger amount of energy usually brings about full decomposition, as indicated by color change.

There was one exception to this parallelism: mechanical stress in the form of sheer and pressure applied with the rounded end of a glass rod to a treated piece of cardboard, was capable of fully transforming allotropic silver into regular silver, but it only produced a developable impression in halides. No visible reduction could be affected this way. Lea decided to investigate this problem, suspecting that the only reason for the negative result was the insufficient intensity of the mechanical energy.

5. Mechanochemical investigations

In 1892, Carey Lea demonstrated that any form of energy, including mechanical, was indeed capable of disrupting silver halide molecules [20]. The paper describing the results is the one that was read before the National Academy of Science when Lea was elected to membership. This is a very important work, rich in ideas and ground breaking results. The chloride, the bromide, and—for sake of completeness—the iodide of silver were investigated and both static pressure and shearing stress were applied.

Static pressure of one hundred thousand pounds per square inch (about 6900 times atmospheric pressure) was applied by a mechanical press to halide powders wrapped into platinum foil. The coloration of the powders clearly indicated that some decomposition of the halide took place. The decomposition of the iodide was surprising to Lea, as the iodide did not decompose upon the action of light.

Lea used trituration in a porcelain mortar with a pestle to deliver large amounts of shear. Initially he was skeptical about decomposing the silver halides by the relatively weak forces during trituration, so he used a weakly reducing additive. The reaction was so quick that he repeated the experiment without any additive, to explore if silver chloride could be disrupted by stress alone. "For some time no effect was visible. After about ten minutes' action dark streaks began to appear and after about five minutes' more work a considerable portion of the chloride was darkened." Based on its color and reactivity, he identified the darkened portion as silver photochloride, i.e. a molecular combination of a chloride and a hemichloride. He obtained similar results with silver bromide [20].

These initial results were followed by systematic investigations published in a series of three articles during 1893–94 [32–34]. The main objective of these studies was the initiation of *endothermic reactions*, specifically the decomposition of compounds with negative heat of formation, by the application of mechanical force.

The effect of static pressure was investigated in the first paper [32]. The possible decomposition of fifteen materials was examined and strong darkening was observed in silver salicylate, potassium platinobromide, and mercuric oxychloride. Mercuric iodide showed considerable darkening, although no free iodine was detected. Other materials showed less pronounced effect or no darkening at all.

The second paper of the series is the most important of Lea's writings on mechanochemistry [33]. It begins with a review of the existing literature, concluding that very little if anything is known about the relations between the mechanical and chemical forms of energy. The paper quotes Ostwald [35], who introduced the term "mechanochemistry" in analogy to thermochemistry and photochemistry, but stated that "almost nothing" was known about it. Lea used a lengthy quotation from Horstmann to exemplify the general view of chemists at the end of the 19th century. It concludes with stating that ". . . it cannot be admitted that actual chemical changes can be brought about by mechanical impulse" [36]. Of course, Lea was about to prove the contrary.

Although static pressure was capable of inducing chemical decomposition [32], the actual decomposed fraction was quite small. Lea recalled from his investigation of silver halides that shearing stress could initiate reactions much more efficiently than static pressure [20]. Therefore, he performed decomposition experiments on at least 17 materials using a mortar and pestle. The most important examples were sodium chloroaurate and the chlorides of mercury and silver [33].

Lea studied the decomposition of sodium chloroaurate, as the reaction product, metallic gold, could be separated easily and weighed, making the quantitative measurement of the reduced fraction possible. In one experiment, the trituration of 0.5 g of chloroaurate for half an hour yielded 10.5 mg of pure gold—a sizable quantity, although far from complete transformation. The reaction products of the decomposition of silver and mercuric oxide and the carbonate and sulphite of silver could also be separated and weighed. These examples are discussed in the third article of the series [34].

Mercuric chloride is a very important example, as it sublimes rather than decomposes upon the action of heat [33]. This is one of Lea's frequently cited results, the first example of a mechanochemical reaction that brings about an outcome different from the effect of heat. Incidentally, silver chloride melts undecomposed when heated, but decomposes by trituration, providing another example where the effects of heat and mechanical energy are distinctly different.

Shearing stress was also applied in a less energetic way. A piece of strong paper was treated with the material to be investigated, laid upon a piece of plate glass, and marked with the rounded end of a glass rod [33]. The appearance of darkened lines was regarded an indication of decomposition. The method was not new, it was adapted from earlier studies in photochemistry [8] and it was also used to apply shearing stress to allotropic silver [29]. In the current experiment, he applied the method to about a dozen silver, platinum, and mercury compounds. Usually positive results were obtained on the same materials that could be decomposed by trituration.

Lea considered the difference between the effects of heat and stress a very significant finding himself. After a negative attempt at reducing cupric chloride by trituration, he wrote [34]: "This reaction taken with the preceding shows how distinct is the action of mechanical energy from that of heat. For cupric chloride is reduced by heat to cuprous chloride, but shearing stress has no such action. On the other hand shearing stress reduces ferric sulphate which heat does not." This discrimination between the affects of heat and mechanical action is the idea, that made Carey Lea the true founder of mechanochemistry. He not only showed that mechanical action was capable of inducing chemical changes, even endothermic ones, but he also proved that these changes were sometimes different from those produced by heat.

Lea also investigated practical questions related to choosing the most suitable mechanochemical reactor and processing conditions. He compared the benefits and problems associated with using different mortars and pestles. Unglazed porcelain had the disadvantage that "a very appreciable amount of material is removed from the mortar and pestle" [34]. Dealing with contamination from the milling bodies is still an important issue in mechanochemistry. Lea also stated that a metal mortar was not appropriate for his experiments due to the possibility of chemical interaction [33]. He tried to use an agate mortar, but the amount of chemical change was "only one fifths to one-tenth of a porcelain mortar of the same size." Lea actually performed quantitative comparisons to establish this fact, using the decomposition of silver oxide as the test reaction. He blamed "the high polish which is very unnecessarily given to the inside of agate mortars" for the difference. Lea also mentioned that the quantity of the processed material had to be small, about a few tenth of a gram only [33], in the same way the ball-to-powder mass ratio is limited in a typical ball mill. Selecting the proper type of mechanochemical reactor is another important practical consideration, as different combinations of compression and shear may result in different reaction products. Similarly, mercuric chloride and silver tartrate responded to trituration but not to static pressure in Lea's experiments [33].

In summary, Lea performed a long series of experiments using different methods to deliver mechanical energy. He studied dozens of materials, some of them quantitatively. He discussed fundamental principles as well as technical details. He was fully aware of the significance of the results. The breath of his research was far more substantial than usually realized.

6. Final words

The question can be asked if there are any researchers, who studied the chemical effects of mechanical action prior to Lea's work. Lea himself made reference to two earlier investigators: Walter Spring in Refs. [30] and [32] and William Hallock in Ref. [32]. He wrote: "In Prof. Spring's well known investigation, combination was brought about between substances whose tendency to combine was restrained by their being in the solid form. . . . The same remark applies to some of the interesting experiments of Dr. Hallock" [32].

In 1883, Prof. Spring (University of Liége) initiated several reactions between solids by either pressure or sheer [37, 38]. These are interesting studies, that deserve more attention from the community of mechanochemists. Nevertheless, the investigated reactions were exothermic, they could just as well be initiated by heating. They did not establish the distinct nature of mechanochemical reactions, although they certainly proved that pressure could facilitate chemical reactions between solids. Spring and Lea debated the issue of priority in a set of letters to Z. anorg. Chem [39].

The other person mentioned by Lea was William Hallock, a researcher with the U. S. Geological Survey.

His primary interest was the possible liquefaction of solids under pressure and the possibility that liquefaction may also result in chemical reactions [40]. This problem is somewhat farther from the central questions of mechanochemistry. As neither Spring nor Hallock made reference to any substantial investigation by other researchers, the existence of earlier systematic studies performed by others seems unlikely.

Lea's seminal results are often recalled in a simplified form, stating only that silver and mercuric chlorides melt or sublime when heated, but decompose by trituration in a mortar. While this statement is not quite incorrect, it suggests that pieces of silver or droplets of mercury are formed in the mortar, while plumes of chlorine gas are released when grinding a silver or mercury chloride. Of course, this is not the case. As Lea stated clearly, by "decomposition" he meant the formation of a few dark streaks that was probably due to the formation of traces of "photochlorides," i.e. combinations of the chloride and a hemichloride. The bulk of the chlorides remained completely unaffected. In a recent experiment [41], AgCl was milled in a SPEX 8000 Mixer Mill under very energetic conditions. After 90 min of activation, only a small trace, much less than 1%, of free silver was found by X-ray diffraction. Even that little transformation could result from using steel milling tools, and exposure to light and X-rays could contribute to the formation of silver as well. Decomposing a significant fraction of AgCl by mechanical agitation seems very difficult.

Consequently, while it is certainly true that silver and mercuric chlorides exhibit different changes when exposed to mechanical action and heat, the decomposition by pressure and sheer provides only a very small yield. While recalling Lea's ground-breaking results is appropriate, finding simple inorganic compounds that melt when heated but decompose in the usual sense due to mechanical agitation would still be interesting.

Carey Lea is considered the father of mechanochemistry based on his ground-breaking experiments that clearly show that some materials react differently when exposed to mechanical and thermal energy. Equally important is the fact that he understood and explicitly stated the significance of the results, launching mechanochemistry as a separate branch of chemistry.

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*M. Carey Lea published his more important papers in more than one journal, e.g. in *Am. J. Sci., Phil. Mag.* and in German translation in *Z. Anorg. Chem.* This list gives references to only one version for each paper. A more complete list including the coordinates of the parallel versions and the titles of the papers was published in [11].

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