M. CAREY LEA, THE FATHER OF MECHANOCHEMISTRY

Laszlo Takacs, University of Maryland, Baltimore County

Introduction

Most historical reviews of mechanochemistry mention the papers of Matthew Carey Lea as the first systematic investigations on the chemical effects of mechanical action. Yet, very little is known about the person, his motivation and the details of his results. The original literature is not easily accessible and the two existing biographies (1, 2) focus on his results in photochemistry and the study of "allotropic silver," but overlook the importance of his mechanochemical experiments. The objective of this paper is to address these shortcomings through examination of Lea's work in mechanochemistry, by exploring how his ideas developed from observing the pressure sensitivity of photographic plates to the systematic investigations on the mechanochemical decomposition of compounds 26 years later.


M. Carey Lea.

Mechanochemistry is the study of chemical changes induced by pressure, shear, impact or friction (3). Some mechanochemical effects, such as the use of impact to initiate explosives and the grinding of salts to accelerate dissolution, are considered common knowledge, while others, like the reduction of carbon dioxide by gold under mechanical action, are quite unexpected (4). Mechanochemical reactions are often induced in ball mills, where the compression and shear between the colliding milling balls are used to drive chemical transformations in a mixture of reactant powders. Combination reactions, such as the formation of metal sulfides from a mixture of metal and sulfur powders, displacement reactions between a metal oxide and a more reactive metal and a variety of other inorganic and organic reactions have been induced by ball milling (5). Mechanochemical methods can be utilized in the processing of silicates (6) and minerals (7) and mechanical alloying is basically mechanochemical processing applied to metallurgical systems (8).

Most chemical reactions follow the same path whether induced by mechanical action or heat. For example, if CuO is ball milled with an appropriate amount of Fe powder, Cu metal and Fe_3O_4 are obtained. The same reaction can be induced by heating the powder mixture to high temperature. One could argue that the only direct result of the mechanical action is the generation of heat and if any chemical change is observed, it is due to a secondary thermochemical process. This phenomenon was questioned by Lea, however, with his recognition of the first indications that mechanochemical reactions can be fundamentally different from thermochemical ones, which he reported at the end of the 19th century (9-12). His most important observation was that silver halides decompose by trituration in a mortar, although they melt when heated. This is the result that established mechanochemistry as a separate branch of chemistry.

Carey Lea was about seventy years old when he performed these famous experiments on the mechanochemical decomposition of compounds. That work, however, was not without precedent. He discovered the effect of mechanical pressure on photographic plates already in 1866 and used it shortly thereafter to produce developable images that resembled the images produced by light (13). The similarity between the effects of pressure and light was extended into a parallelism relating the chemical effects of different energy forms, including heat, light, and chemical and mechanical energy. This parallelism provided the framework for Lea's systematic studies on the chemical changes of silver halides and "allotropic silver" (14-16). He found that the application of a small amount of energy always produced an impression that could be brought out with a photographic developer, while a larger amount of energy usually resulted in an immediately visible color change. He found only one exception, namely that mechanical energy generated by the rounded end of a glass rod was not capable of reducing silver halides without the aid of a developer. Lea suspected that more intense mechanical action was needed and decided to use grinding in a mortar as the source of mechanical energy. The results were positive, providing the motivation for the systematic investigation of mechanochemical decomposition (9-12).

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 exceptional intellectual background. His father, Isaac Lea (1792-1886), was a distinguished naturalist, an expert on contemporary and fossil shells; his collected works fill thirteen large volumes. Isaac Lea was the descendant of an influential Quaker family, the great-great-grandson of John Lea, who emigrated to America with William Penn in 1699. Carey Lea's mother was Frances Anne Carey (1799-1873), a strong and intellectual woman, who gave ample attention to the education of her children. She was the daughter of Matthew Carey (1759-1839), an Irish patriot, who fled to America from political persecution in 1784 and became an eminent writer and the founder of a major publishing house. After marrying Frances Anne Carey in 1821, Isaac Lea joined the publishing business and became a partner. The other partner at the time was his brother-in-law, Henry Charles Carey (1793-1879), who was also a reputable economist.

Matthew Carey Lea was the second son of the family, the eldest son (also called Matthew) having died in infancy. His younger brother and best friend, Henry Charles Lea, (1825-1909) continued the family's publishing business. He was also an eminent writer on philosophical and historical subjects and an expert on the history of inquisition. Early in his life, he also published a few papers on chemistry in the *American Journal of Science*. The youngest child of the family was Frances Lea (1834-1894), who dedicated much of her life to caring for her ill mother.

Because Carey Lea suffered from weak health from his early childhood, he was not sent to boarding school but received his education at home from a private tutor. He and his brother formed the "class" of Eugenius Nulty, a teacher with broad background in both the sciences and the humanities. After a short excursion into law—he was admitted to the Philadelphia bar in 1847—Lea studied chemistry at the consulting laboratory of Prof. James C. Booth. His later experiments were performed in the private laboratory of his home in the Chestnut Hill district of Philadelphia.

Few chemists knew Lea personally. His weak health and a laboratory accident that damaged one of his eyes made him an elusive figure. He worked quietly and independently in his laboratory, keeping contact with the rest of the scientific community through publications. The breadth of his scientific achievements is clearly shown by the list of the more important papers included in his Biographical Memoirs (1). It contains more than 100 titles, published mainly in the *American Journal of Science*. In addition to his scientific papers, he published close to 300 technical articles and correspondences in the *British Journal of Photography*. He wrote his only book on photography, a comprehensive manual that includes chapters on optics and practical picture-taking techniques, as well as photochemistry, laboratory techniques, and safety (18). Lea was thoroughly familiar with the results of others and read and quoted the scientific literature published in English, French, and German.

For someone so active and eminent in science, he belonged to few scientific institutions. He was not associated with any university department. As a member of the Franklin Institute from 1846, he used its library collection extensively but never participated actively in the work of the Institute. In 1895* he was elected a member of the National Academy of Sciences.

In 1852 Lea married his cousin, Elizabeth Lea Jaudon, with whom he had his only son, George Henry Lea. After the death of Elizabeth in 1881, he 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 in accordance with his desire (2), seriously limiting the information available about his work. His scientific books and apparatus were donated to the Franklin Institute, together with a substantial fund in perpetuity for the purchase of books and journals.

The Observation of Mechanochemical Effects in Photochemistry

Although Carey Lea's most lasting contributions are in mechanochemistry, during his lifetime he was primarily known as an expert on the chemistry of photography. In the list of his most important scientific papers, the first photography-related article is dated 1864 (1). The following five years of his life brought incredible activity on the subject: Besides eight scientific works published mostly in the *American Journal of Science*, Lea wrote extensively for the technical magazines of photography. In 1865-66 alone he published 140 papers and correspondences in *The British Journal of Photography*. They cover every subject related to photography from optics, laboratory techniques, and practical hints to applications, legal matters and even a few related anecdotes. Some papers describe scientific experiments related to the chemical foundations of photography.

The most important, yet the most evasive and controversial question of photographic chemistry during this period regards the nature of the latent image. According to modern theory, its formation involves photoionization, defects acting as traps, local electric fields, diffusion, nucleation, etc. (19). Some details of the theory are still ambiguous today. In the 1860s anything beyond empirical studies and speculation was beyond the power of science. Two theories, "chemical" and "physical," competed with each other. The proponents of the chemical theory believed that the exposure of a silver halide to light resulted in an incipient reduction to a subhalide or even metallic silver and that the reduction of the remaining silver halide was catalyzed by the minute reduced fraction during development. Lea fiercely opposed this view, at least in the case of pure silver iodide. In 1866 he wrote (20):

> 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.

Lea based his opinion partly on chemical evidence (20):

> ...even when the action of light is prolonged to many thousand times the period sufficient for the production of a developable image, still no chemical alteration can be detected in the exposed iodid.

Generalizing 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 perfectly sufficient to carry the latent image.

Although Lea considered such chemical evidence a decisive proof of the physical theory, he offered an even more conclusive one, through an argument based on mechanical action (13):

> ...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 it extraordinarily hard to countervail.

The language of the statement clearly reflects his excitement over this idea. Curiously enough, Lea, who later performed the first systematic studies on mechanochemistry, considered the production of a developable latent image by pure mechanical force a very strong argument for the physical theory, because—as he stated very explicitly—a *mechanical* cause certainly could not produce any *chemical* impression. As he wrote in the same paper (13), "Here is no possibility of reduction, no possible production of metallic silver, or of subiodid, no possible elimination of iodine ..." In order to test his idea, he 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. Clearly, the image originated from the different pressures under the carved-out or raised letters and the rest of the surface. Of course, there is another possible explanation: pressure may actually produce a chemical change that is amplified by development; but in 1866 Carey Lea did not even consider this possibility.

Photographic chemistry remained the main topic of Lea's research for the next two decades, although his work on the topic was not as intense as it was during 1864-66 (1). As his objection to the chemical theory of the latent image faded, he began to attribute the latent image to the formation of "photosalts," combinations of a silver halide and a small amount of sub-halide. His last paper on photographic chemistry was published in 1889. Dry plates and films were produced on an industrial scale by then, and Lea in his small private laboratory could not compete with the resources of the emerging photographic industry.

Transformations of Allotropic Silver

Probably Lea's best-known discovery is that of "allotropic silver" (21). He took up the study of the reduction products of silver 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. Depending on the proportions of the reactants and on the method of purification, three forms of allotropic silver were found: A, soluble; B, insoluble, derived from A; and C, gold-colored. All these forms of silver were sensitive to light (22). Some allotropic silver samples prepared by Lea are preserved in the Library of the Franklin Institute, (23). What Lea considered solutions of allotropic silver were in fact colloids, and the dried forms would be classified as porous nanocrystalline materials today. Nevertheless, his recipe is still useful to make silver sols for physical investigation (24).

Allotropic silver, however, was particularly interesting to Lea because of its light sensitivity. Exposure to light for an extended amount of time converted gold-colored silver into an intermediate form and finally to ordinary white silver. Lea also made an observation that was directly related to mechanochemistry (25):

> 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 and had preserved the gold color perfectly. 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 being tightly packed with cotton wool, on a 2,400-mile train trip. The sample arrived back unaltered, while the control samples that were left loose in partially filled tubes became white.

Lea investigated the properties and transformations of allotropic silver in significant detail over the next two years. 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 (26). This question was discussed systematically in a series of three articles published in 1891 (14-16). In the first paper Lea described the properties and reactions of gold-colored allotropic silver (14). He also 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." When allotropic silver is converted into a more stable form, it becomes less dispersed, as indicated by the lower reactivity and larger density. This observation led 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* (15)." If taken literally, this statement is naive, but one can focus on the logic of Lea's reasoning. He claimed that silver in its compounds must exist in the atomic form. 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—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 only one exception to the above parallelism between allotropic silver and silver halides. Mechanical stress, namely sheering and pressure applied with the rounded end of a glass rod, was capable of fully transforming allotropic silver into regular silver, but it only produced a developable impression in halides. No visible reduction could be effected this way. Lea decided to investigate whether this asymmetry was indeed valid, expecting the contrary. The resulting investigation is his first systematic study on the chemical effect of mechanical action (9).

The Four Papers on Mechanochemistry

In 1892 Lea proved conclusively that any form of energy, including mechanical, was indeed capable of disrupting silver halide molecules (9). The paper presenting the results was read before the National Academy by George F. Barker. This is a very important work, rich in ideas and ground-breaking results. The chloride, bromide, and iodide of silver were investigated, and to all were applied both static pressure and shearing stress. He applied 100,000 pounds to the square inch (about 6,900 times atmospheric pressure) to halide powders wrapped in platinum foil, the pressure being maintained for 24 hours. The coloration of the powders clearly indicated that some decomposition of the halide had taken place. The decomposition of the iodide was surprising for Lea, because it did not decompose upon exposure to light.

Lea next used trituration in a porcelain mortar to deliver large amounts of shear. Initially he was skeptical about decomposing the silver halides by the relatively weak forces during trituration. Therefore, he added tannin as a weak reducing agent to the silver chloride before grinding it in a mortar. The reaction was so quick that he decided to use an additive, namely sodium carbonate, which was capable of taking up acid but lacked reducing power of its own. The characteristic coloration was observed again, indicating that reduction took place. Finally, he repeated the experiment without any additive, to explore whether silver chloride could not be disrupted by stress alone (9):

> 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.

For Lea, the main objective of this series of experiments was to prove that "..every form of energy is not only capable of producing an invisible image, that is, of loosening the bonds which unite the atoms, but is also capable, if applied more strongly, of totally disrupting the molecule." For today's mechanochemists, the relevance of the experiments is much broader. Even the abandoned trials and the decomposition experiments in the presence of other reactants are quite interesting, although they are never mentioned in later references to Lea's works. In a discussion on the role of heat, he noted that it could be important when generated by friction, but "in the case of simple pressure heat certainly plays no part (9)." This is not quite so. Although the mechanical work done by the press on the powder is indeed negligible, the experiment is carried out under isothermic rather than adiabatic conditions. Nevertheless, the role of heat, if any, is certainly different in the cases of static pressure and trituration; yet the halides were decomposed by both.

The paper described above (9) is the prelude to the purely mechanochemical investigations published in a series of three articles during 1893-94 (10-12). The main theme of these papers is 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 (10). In an examination of the possible decomposition of 15 materials, 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 effects or no darkening at all.

The second part of the series is the most important of Lea's writings on mechanochemistry (11). He begins with a review of the existing literature, concluding that, "Of the relations which exist between two forms of energy, mechanical and chemical, very little if anything is known." He quotes Ostwald (27), who introduced the term "mechanochemistry" by analogy to thermochemistry and photochemistry, but stated that "almost nothing" was known about it. A lengthy quotation from Horstmann exemplifies the general view of chemists at the end of the 19th century. It concludes by stating that "...it cannot be admitted that actual chemical changes can be brought about by mechanical impulse." Carey Lea set out to prove the contrary.

Although static pressure was capable of inducing chemical decomposition (10), 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 (9). Therefore, he performed decomposition experiments on at least 17 materials with a mortar and pestle. The most important examples are sodium chloroaurate and the chlorides of mercury and silver (11).

The decomposition of sodium chloroaurate was studied, 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. Using reaction heat data from the literature, Lea estimated that the decomposition of the appropriate amount of chloroaurate required 518 gram-meters (about 5 Joules) of energy. This energy had to originate from the mechanical work of the trituration.

Mercuric chloride is a very important example for two reasons: For one, it was not decomposed by static pressure, but easily acted upon by trituration. More importantly, it sublimes rather than decomposes upon the action of heat. 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 different, 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 (11). The appearance of darkened lines was regarded an indication of decomposition. The idea was adapted from earlier studies in photochemistry (13). As Lea wrote, "More than twenty years ago I was able to show that marks made in this way on a sensitive photographic film could be developed, as an invisible image had been impressed. That, however, is a somewhat different matter from actual and visible decomposition following each stroke of the rod..." He also used the same method to apply shearing stress to allotropic silver, spread over boards of paper (14). 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. Silver chloride was an exception that did not show distinct marks from the pressure of the glass rod, although it did respond to trituration.

Some quantitative examples are given in the last paper of the series (12). Silver oxide is soluble in ammonia but silver is not. Using this difference in solubility, Lea could separate the two substances after trituration in order to weigh the decomposed fraction. He also studied mercuric oxide. It could be separated from its decomposition products because mercuric oxide dissolves in dilute hydrochloric acid, but mercury does not. Consequently, quantitative measurements of the decomposed fraction were possible. Similar experiments were performed on silver carbonate and sulphite, auric oxide, and potassium permanganate. The iron in potassium ferricyanide and ferric ammonia alum could be reduced to the ferrous state by trituration.

Lea himself considered the difference between the effects of heat and stress a very significant finding. After a failed attempt at reducing cupric chloride by trituration, he wrote (12):

> 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.

His understanding of the clear difference between the effects of heat and mechanical action justifies identifying Carey Lea as the true founder of mechanochemistry. Not only did he show 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.

Choosing the most suitable mechanochemical reactor and processing conditions is an important problem for today's mechanochemists. Besides his important fundamental observations, Lea also investigated the practical question regarding benefits and problems associated with the choice of different mortars and pestles. Unglazed porcelain had the disadvantage that "a very appreciable amount of material is removed from the mortar and pestle. (12)." Minimizing 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 because of the possibility of chemical interaction (11). He tried to use an agate mortar, but the amount of chemical change was "only one fifth to one-tenth of a porcelain mortar of the same size." Quantitative comparisons on the decomposition of silver oxide were performed to establish this fact. Lea blamed "the high polish which is very unnecessarily given to the inside of agate mortars" for the difference. He favored porcelain mortars, but the abraded material had to be separated from the product (12). Lea also mentioned that the quantity of the processed material should be small, only about a few tenths of a gram (11). The analogous problem is well known to modern mechanochemists, who usually limit the mass of the powder to less than one fifth of the total mass of the balls. Selecting the proper type of mechanochemical reactor is another important practical problem, because different combinations of compression and shear may result in different reaction products, just like mercuric chloride and silver tartrate responded to trituration but not to static pressure in Lea's experiments (11).

Questions on Priority

As Barker describes, Carey Lea "was naturally retiring in his disposition and, owing, no doubt, to his continued ill health, lived the life almost of a recluse (1)." Yet, he was aware of the value of his work and made sure that his achievements would become widely known. He published his most important findings in more than one journal, first in both *The British Journal of Photography* and *The Philadelphia Photographer* (13) and later in the *American Journal of Science* and the *Philosophical Magazine* (9-12, 14-16). Papers 10-12 on mechanochemistry (and a few articles on other subjects) were also published in German translation in the *Zeitschrift für Anorganische Chemie*. The papers make reference to earlier publications in the same journal but not to the parallel versions in other periodicals. This is sometimes confusing, as references to two papers published at about the same time in two different journals may refer to the same article; but, given the large number of publications, that is not necessarily the case. The list of references at the end of this paper is grouped together according to different versions of the same paper as a means of clarification. Summaries and full copies of Carey Lea's papers appeared regularly in other journals, such as the *Chemical News* and the *Journal of the Franklin Institute*.

Lea's experiments in 1892-94 are usually cited as the first systematic investigations related to mechanochemistry (9-12). They certainly provide an overwhelming array of new ideas and conclusive experiments, far beyond anything published earlier by others. However, some attempts to investigate the chemical effects of mechanical action preceded the works of Lea.

The earliest known mention of a mechanochemical process is that by Theophrastus of Eresus on the preparation of mercury from cinnabar by trituration (28). Although that remark extends the history of mechanochemistry into antiquity, it is only a single sentence on a single reaction, far from a systematic study.

Lea himself made reference to two earlier investigations, those of Spring in Ref. 15 and 10 and of Hallock in Ref. 10. He wrote (10):

> 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.

Therefore, Lea not only knew about earlier investigations but acknowledged them in his own papers.

In spite of these references, Professor Walter Spring at the University of Liége made a strongly worded claim of priority. This, together with the response from Carey Lea, can be found in *Zeitschrift für Anorganische Chemie* (29-31). Whether the claim of Spring is well founded or not is open to question. It is certainly true that his investigations were published about 10 years before Lea's interest turned to mechanochemistry (32, 33). It is also true that Spring's experiments covered several reactions and involved both pressure and shearing stress, but he studied only exothermic reactions. Lea never claimed that his had been the first observation of a chemical effect by mechanical action, only that he was the first to induce endothermic reactions by mechanical energy. Also, the early studies of Lea on the effect of pressure on sensitized photographic plates were performed in 1866, pre-dating Spring's investigations by another 15 years. In any case, it is worth taking a careful look at Spring's papers and giving them proper credit in the history of mechanochemistry.

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 (34, 35). This question is of utmost importance for the geologist, but it is somewhat farther from the main issues of mechanochemistry.

Epilogue

In this study the scientific achievements of Carey Lea have been analyzed from the point of view of mechanochemistry. His well-known experiments were performed when he was already seventy years of age, but they followed logically from his earlier investigations. Hints on the chemical effects of mechanical stress were already observed during his work in photochemistry, and the methods and materials of the later studies reflect that experience. His desire to develop a consistent theoretical framework for the action of different forms of energy gave him the direct motivation to study mechanochemical reactions.

While Lea investigated the effect of pressure and shearing stress on dozens of materials, some of his results stand out as the clearest demonstrations of the difference between the action of heat and mechanical energy. These most important findings are:

- Silver halides decompose by trituration, but melt when heated.
- Mercuric chloride decomposes with trituration but not with pressure or heat.
- Cupric chloride is reduced to cuprous when heated, but does not respond to trituration.
- Ferric ammonia alum is reduced to ferrous by trituration but not by heat.

During his life, Carey Lea was known as a pioneer in photographic chemistry, and later his discoveries on allotropic silver were praised widely. These are the two achievements mentioned in the obituary published in the *American Journal of Science* (36). New instrumental methods and intense development brought tremendous advances in photographic chemistry, few statements of Lea are considered strictly valid today. The allotropic forms of silver were shown to be silver colloids instead. These results were important steps in the development of chemistry, but they were superseded by new ideas. However, Lea's results on the decomposition of some compounds by mechanical action are still the clearest demonstrations of the fact that the chemical changes produced by mechanical action are distinctly different from those effected by heat. These results secure for Matthew Carey Lea a place among the great chemists whose contributions are valid and important more than one hundred years after their publication.

ACKNOWLEDGMENTS

The author is indebted to Prof. P. Balá? whose article on the past of mechanochemistry (37) and copies of several original publications from his collection provided the impetus and seed material for this paper. Acknowledgement is due to Virginia Ward of the Franklin Institute Library for locating some unique items concerning Carey Lea.

REFERENCES AND NOTES

1. G. F. Barker, "Biographical Memoir of Matthew Carey Lea," in *Biogr. Mem. Natl. Acad. Sci. USA*, **1905,** *5*, 155-208.
2. E. F. Smith, *M. Carey Lea, Chemist*, University of Pennsylvania Press, Philadelphia, PA, 1923.
3. V. V. Boldyrev and K. Tká?ová, "Mechanochemistry of Solids: Past, Present, and Prospects," *J. Mater. Synth. Process.* **2000,** *8*, 121-132.
4. von P. A. Thiessen, G. Heinicke, and E. Schober, "Zur Tribochemischen Umsetzung von Gold und CO$_2$ mit Hilfe Radioaktiver Markierung," *Z. Anorg. Allg. Chem.* **1970,** *377*, 20-28.
5. E. G. Avvakumov, *Mechanical Methods of the Activation of Chemical Processes*, Nauka, Novosibirsk, 1986 (in Russian.)
6. A. Z. Juhász and L. Opoczky, *Mechanical Activation of Minerals by Grinding, Pulverizing and Morphology of Particles*, Ellis Horwood, London, 1990.
7. P. Balá?, *Extractive Metallurgy of Activated Minerals*, Elsevier, Amsterdam, 2000.
8. C. Suryanarayana, "Mechanical Alloying and Milling," *Prog. Mater. Sci.* **2001**, *46*, 1-184.
9. M. Carey Lea, "Disruption of the Silver Haloid Molecule by Mechanical Force," *Am. J. Sci.* **1892**, 3rd Series, *43*, 527-531 and *Philos. Mag.* **1892**, *34*, 46-50.
10. M. C. Lea, "On Endothermic Reactions Effected by Mechanical Force," *Am. J. Sci.* **1893,** 3rd Series, *46*, 241-244 and *Philos. Mag.* **1893,** *36*, 351-354. In German: *Z. Anorg. Chem.* **1893,** *5*, 330-333.
11. M. C. Lea, "On Endothermic Decompositions Obtained by Pressure. Second Part. Transformations of Energy by Shearing Stress," *Am. J. Sci.* **1893**, 3rd Series, *46*, 413-420 and *Philos. Mag.* **1894**, *37*, 31-38. In German: *Z. Anorg. Chem.* **1894**, *6*, 2-10.
12. M. C. Lea, "Transformations of Mechanical into Chemical Energy. (Third Paper.) Action of Shearing-Stress (Continued)," *Am. J. Sci.* **1894**, 3rd Series, *47*, 377-382 and *Philos. Mag.* **1894**, *37*, 470-475. In German: *Z. Anorg. Chem.* **1894**, *6*, 349-354.
13. M. C. Lea, "Researches on the Latent Image," *The Philadelphia Photographer*, **1866**, *3*, 74 and *The British Journal of Photography*, **1866**, *13*, 84.

14. M. C. Lea, "On Gold-Colored Allotropic Silver, Part I," *Am. J. Sci*. **1891**, 3rd Series, *41*, 179-190 and *Philos. Mag*. **1891**, *31*, 238-250.
15. M. C. Lea, "On Allotropic Silver, Part II, Relations of Allotropic Silver with Silver as it Exists in Silver Compounds," *Am. J. Sci*. **1891**, 3rd Series, *41*, 259-267 and *Philos. Mag*. **1891**, *31*, 320-329.
16. M. C. Lea, "Allotropic Silver, Part III, Blue Silver, Soluble and Insoluble Forms," *Am. J. Sci*. **1891**, 3rd Series, *41*, 482-489 and *Philos. Mag*. **1891**, *31*, 497-504.
17. E. S. Bradley, Henry Charles Lea, a Biography, University of Pennsylvania Press, Philadelphia, PA, 1931.
18. M. C. Lea, A Manual of Photography: Intended as a Text Book for Beginners and a Book of Reference for Advanced Photographers, Benerman and Wilson, Philadelphia, PA, 1868 and 1871.
19. T. Tani, *Photographic Sensitivity, Theory and Mechanisms*, Oxford University Press, New York, 1995.
20. M. C. Lea, "On the Nature of the Action of Light upon Iodid of Silver," *Am. J. Sci*. **1866**, 2nd Series, *42*, 198-205.
21. M. C. Lea, "On Allotropic Forms of Silver," *Am. J. Sci*. **1889**, 3rd Series, *37*, 476-491.
22. M. C. Lea, "On Allotropic Forms of Silver," *Am. J. Sci*. **1889**, 3rd Series, *38*, 47-50.
23. M. C. Lea, *Photogenic Collection on the Properties of Allotropic Silver*, Library of the Franklin Institute, Philadelphia, PA, 1891.
24. R. P. Devaty and A. J. Sievers,, "Far-Infrared Absorption by Small Silver Particles in Gelatin," *Phys. Rev. B*, **1990**, *41*, 7421-7439.
25. M. C. Lea, "The Properties of Allotropic Silver," *Am. J. Sci*. **1889**, 3rd Series, *38*, 237 240.
26. M. C. Lea, "Notes on Allotropic Silver," *Am. J. Sci*. **1891**, 3rd Series, *42*, 312-317.
27. W. Ostwald, *Lehrbuch der Allgemeinen Chemie*, W. Engelmann, Leipzig, 1885-87.
28. L. Takacs, "Quicksilver from Cinnabar: The First Documented Mechanochemical Reaction?" *J. Metals*, **2000**, *52*, 12-13.
29. W. Spring, "Eine Prioritätseinwendung gegen M. Carey Lea," *Z. Anorg. Chem*. **1894**, *6*, 176.
30. M. C. Lea, "Über den Prioritätsanspruch von Prof. Spring," *Z. Anorg. Chem*. **1894**, *7*, 50-51.
31. W. Spring, "Erwiederung auf Vorhergehende Zeilen von M. Carey Lea," *Z. Anorg. Chem*. **1894**, *7*, 51.
32. W. Spring, "Formation d'Arséniures par la Pression," *Bull. Soc. Chim. Fr.*, **1883**, *40*, 195-196.
33. W. Spring, "Formation de Quelques Sulfures par l'Action de la Pression. Considérations qui en Découlent Touchant les Propriétés des États Allotropiques du Phosphore et du Carbone," *Bull. Soc. Chim. Fr.*, **1883,** *40*, 641-647.
34. W. Hallock, "The Flow of Solids: or Liquefaction by Pressure," *Am. J. Sci*. **1887,** 3rd Series, *34*, 277-281.
35. W. Hallock, "Chemical Action between Solids," *Am. J. Sci*. **1889,** 3rd Series, *37*, 402 406.
36. G. F. B. "Scientific Intelligence," *Am. J. Sci*. **1897**, 4th Series, *3*, 428.
37. P. Balá?, "Mechanochemistry in Extractive Metallurgy: The Modern Science with an Old Routes," Acta Met. Slovaca, **2001**, *4*, 23-28

ABOUT THE AUTHOR

Laszlo Takacs is associate professor of physics at the University of Maryland, Baltimore County, Baltimore, MD 21250. His primary research interests are mechanochemistry and its application to the preparation of magnetic materials. He can be reached by e-mail: takacs@umbc.edu.