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Mechanochemical Synthesis

Two important periods in the history of mechanochemistry

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ABSTRACT

Some form of mechanochemical experience has existed from fine grinding of materials since prehistoric times, yet the first systematic investigations on the chemical effects of mechanical action were carried out only at the end of the nineteenth century. Walthére Spring studied the consolidation and reactions of powdered materials due to high pressure at the University of Liège, in order to understand the formation of minerals in the earth's crust and M. Carey Lea carried out experiments on the decomposition of compounds by grinding in a mortar. In some of his experiments mechanical action produced distinctly different result from the effect of heat. The first part of this paper compares the circumstances and results of Spring and Lea. The other important period in the history of mechanochemistry was the 1960s, the time when the first dedicated conferences were organized and a broader community of mechanochemists formed. This happened in the Soviet Union and Eastern Europe where several groups were working on subjects related to mechanochemistry. In 1968, the first dedicated conference was organized as a special session of the yearly meeting of Soviet colloid chemists. An attempt is made to reconstruct the circumstances leading to that event and the roles played by Rebinder and Thiessen in bringing it together. The next conference on mechanochemistry was already a separate event and it started a yearly series. Extensions have led to the INCOME conferences, including this one in Košice in 2017.

Introduction

Mechanical grinding has been used to prepare food, paint, medicines, etc., since prehistoric times and given that intense grinding often induces chemical transformations, even if unintended, some experience with the chemical effects of mechanical processing has existed for a very long time [1]. Occasional remarks in the literature also confirm the early use of mechanical action to induce chemical reactions [2]. Yet, the first systematic investigations of mechanochemical transformations were only carried out at the end of the nineteenth century. Walthére Spring performed a long series of investigations on the effect of high pressure on powdered materials. His decades long effort to explain the formation of

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minerals under pressure in the earth's crust established the mechanochemistry of geology [3]. M. Carey Lea wrote only four papers on the application of mechanical action, mostly grinding in a mortar, to induce chemical reactions, but his investigations were the first to demonstrate that mechanochemical reactions are distinctly different from those caused by heat [4]. His work is still regularly cited as a clear demonstration of the uniqueness of mechanochemical reactions. The first part of this paper will compare the investigations of Spring and Lea and identify their lasting legacy.

Mechanochemistry developed slowly during the first 60 years of the twentieth century. Investigations were carried out with varied objectives in different areas of research and technology [2]. For example, Flavitsky developed an analytical kit that could be used during mineral exploration in the field, Peters explored the possibility of preparing liquid fuel from coal, and Smekal studied the increase in reactivity due to grinding. During the Second World War the sensitivity of explosives became a crucial subject. But these investigations were carried out independently with little or no connection between the different investigators [2].

It was only in the 1960s that a significant number of groups with related objectives emerged in the former Soviet Union and a few Eastern European countries. Interactions between those groups intensified and when a person with the right research interest, reputation, organizational skills and administrative power emerged, the first meeting on mechanochemistry got organized. This person was Petr A. Rebinder, a colloid chemist interested, among other subjects, in the application of chemical grinding aids to improve the efficiency of fine grinding [5]. He was a member of the Soviet Academy of Sciences and influential in determining science policy. He chaired the Organizing Committee of the 6th All-Soviet Conference on Colloid Chemistry in 1968 and added a special section on mechanochemistry [6]. This was the first opportunity for direct interaction between mechanochemists from different laboratories. Dozens of groups participated from several Soviet and a few Eastern European states. The success of this section has led to independent conferences on mechanochemistry from the following year. The 9th INCOME conference in Košice, 2017, is in part a descendent of those early All-Soviet conferences. The second part of the paper tries to reconstruct some of the related events and relationships in the 1960s.

The first systematic investigations: M. Carey Lea and Walthére Spring

The life and oeuvre of both Lea [4, 7] and Spring [8] have been described in some detail in earlier publications, thus this article concentrates only on some important parallels and differences between their education, motivation and results from the point of view of mechanochemistry.

Becoming chemists

Both M. Carey Lea and Walthére Spring came from privileged background [7, 8]. Lea was born into one of the richest families of Philadelphia in 1823. On the paternal side, his ancestors were Quaker business people, while his maternal grandfather was an Irish Catholic, who brought interest and experience in publishing to the family. Lea grew up in a highly intellectual atmosphere, where being involved in some sort of research was a family tradition. His father was a noted conchologist, his younger brother a historian of the Spanish inquisition, and his uncle an economist. It was clear that he also had to contribute to science, but the area was up to him.

Spring was born in Liége 25 years later. His father, a native of Upper Bavaria, was appointed professor of human physiology and general anatomy at the University of Liége when he was only 25 years old. He published extensively on a variety of medical subjects. Thus, Spring grew up in an atmosphere of serious research and hard work and was expected to become a professor of medicine himself. But he preferred working with his hands in his workshop rather than studying the Greek and Latin languages and, to the dismay of his father, it became clear early that Spring would follow a different path [3].

As far as education is concerned, the backgrounds of Lea and Spring could not be any more different. Due to his weak health, Carey Lea, together with his brother, was educated at home by a private tutor, a mathematician by training, who had broad knowledge also of the arts and sciences. They learned languages from their mother. They also did a short chemistry project at prof. Booth's consulting laboratory as teenagers; the results were published as professional research papers [9, 10]. Lea returned to Booth's laboratory for some additional training later, but to a large degree he was self-taught [4, 7].

For Walthére Spring early education was a terrible experience. He attended regular school, where he had difficulties. His weak progress strained his relationship with his father who lost interest in furthering his son's education. Fortunately, Jean-Servais Stas, the prominent chemist and Spring's godfather, came to the rescue. He became Spring's mentor and helped him enter the School of Mines of Liège. From there, his career was on a straight track. He studied with interest and graduated from the School of Mines with high ranking, then continued his studies in the outstanding laboratories of the University of Bonn. There he studied chemistry under Kekulé and physics with Clausius. Spring returned to Liège in 1876, where he was appointed professor of organic and mineral chemistry. He occupied that position for the rest of his life [3, 8].

What motivated Carey Lea to choose chemistry as the subject of his investigations is more difficult to tell. His early experience with prof. Booth could play a role, although similar experience did not spark the interest of his younger brother. As a young adult, Lea was occupied with private life and only started to publish in his late 30s. He wrote a single paper on the properties of picric acid in 1858, then many more on diverse subjects beginning in 1860. He built a private laboratory in his home and worked there on his own. Lea was involved in science for the love of discovery and a desire to give back to society. He became interested in photography and in particular in the chemistry of photography and published about that subject extensively [11], even wrote a popular book in 1868 that had a second edition in 1871 [12].

Why mechanochemistry?

Spring got interested in the origin of minerals while studying at the School of Mines. Also, he was an avid hiker of the Alps, where he could experience first-hand how snow became the dense ice of glaciers under pressure from its own weight. In that case, partial melting at pressure points followed by refreezing explains the condensation [13]. But the behavior of water is unique due to the decrease in its melting point under pressure. Spring's initial question was whether other fragmented materials could be condensed by pressure into solid blocks, even without the assistance of local melting. As soon as he got his own laboratory at the University of Liège, he built a compressor, a massive device that could expose samples to about 20,000 atmospheres, mimicking geologic conditions. He published the first preliminary results in 1878 and kept using his compressor until almost the end of his life [3].

Carey Lea performed his experiments in mechanochemistry when he was already almost 70 years old. Earlier his primary field was photographic chemistry, although he always worked on several subjects simultaneously. His experiments on silver halides and their partially reduced varieties led to the discovery of a new form of silver he called "allotropic" [14], actually a silver colloid. Lea studied the properties of allotropic silver in detail and established that any form of energy—heat, light, chemical, mechanical—brings allotropic silver into a more agglomerated form, first into an intermediate state, than into the state of ordinary silver, as the length and intensity of application are increased [15]. He noticed that this behavior was similar to the transformation of silver halides, in which case the application of a small amount of energy resulted in an intermediate state that turned into silver when exposed to a mild reducing agent (a photographic developer) and a large amount of energy produced silver directly. The only exception was that attempts to obtain silver by applying mechanical energy via rubbing with the rounded end of a glass rod were unsuccessful. Lea suspected that the problem was the insufficient intensity of the mechanical action. He decided to investigate the issue in detail. The results are published in the four papers that are still cited regularly [16–19].

The results of Spring and Lea on mechanochemistry

Spring and Lea approached the problems of mechanochemistry in vastly different ways. At least initially, Spring's main objective was to prepare compacts that resembled minerals found in nature. An encouraging example was the compression of peat that resulted in a sample closely resembling brown coal. But his intention to make "artificial minerals" led him to use complicated conditions that made interpretation difficult. For example, he wetted his sodium and potassium nitrate powders to aid consolidation, assuming that any excess water will be expelled by the compression [20]. He compressed powders of several metals, metalloids, oxides, sulfides, salts and organic materials [13]. Generally softer materials could be condensed more easily, as the applied pressure created larger contact surfaces between the particles. An unfortunate flaw of his experiment was that his piston did not fit tightly into the compression cylinder, allowing some material to ooze out during compression. As a result, his loading was not uniform and it had an important shear component. He also studied the formation of metal arsenides [21] and sulfides [22] from powder mixtures of the elements. Most samples had to be compressed several times to obtain a fully reacted compact, meaning that partially reacted materials were filed into powder and compressed again. Although the final products were similar to minerals found in nature, it is difficult to tell the role of each step in such a complicated preparation process.

According to Spring's opinion, consolidation and reactions under pressure took place according to the laws of thermodynamics. He did not think that mechanical action like pressure or kneading would cause transformations directly, like heat and electricity do. They only increase the area of the interface between powder particles, but the transformations themselves occur by ordinary diffusion [23]. He assumed flow under pressure, but whether he meant liquid-like flow in the solid state or true melting was not always clear [8].

The uncertain experimental conditions and unclear interpretation have led to several disputes as discussed separately [8]. In a detailed and careful review published 2 years after Spring's death, Johnston and Adams refuted all the main results of Spring [24]. As a result, Spring's results in the area of mechanochemistry are not considered valid and they are largely forgotten. Nevertheless, he asked important questions and initiated investigations in important areas. His role in bolstering mechanochemistry is undeniable.

Lea began his mechanochemical investigations with a very specific question: Can strong enough mechanical action decompose silver halides? He applied both static pressure to 6,900 atm and hand trituration in a porcelain mortar and tried to decompose the chloride, bromide and iodide of silver [16]. Some decomposition was observed in each case, even for the iodide that does not decompose under light. To Lea's surprise, the relatively weak shearing force affected with the pestle was more efficient in causing decomposition than the much larger static forces due to pressing.

Encouraged by the initial success, Lea carried out systematic investigations on the decomposition of a variety of materials due to grinding in a mortar and wrote three more papers about the subject [17–19]. He made the statement, that the action of mechanical energy is distinctly different from the action of heat, the most squarely in the last paper [19]. He contrasted two examples to make his point: "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 sulfate which heat does not." His other frequently cited examples are silver and mercury chlorides that decompose under trituration but melt or sublime without decomposition when heated. This clear distinction between behaviors establishes mechanochemistry as a separate branch of chemistry [4, 7].

Not everything is perfect about Lea's interpretation either. He emphasized that the decomposition of stable compounds is an endothermic process and therefore the continuous delivery of energy was necessary to keep the reaction going. But he assumed that this energy had to be provided entirely by the mechanical action and ignored the possible contribution of heat. Lea was a very skilled experimenter and followed very strict logic, but his theoretical background was less solid. Nevertheless, his experiments and clearly stated conclusions rightfully identify him as the person who established mechanochemistry as a separate discipline.

Forming the first community of mechanochemists

The healthy development of a research area requires more than productive work by several investigators and publications in well-circulated periodicals. It also needs a broader community that provides opportunities for the direct exchange of ideas, coordination of research efforts and cooperation. The best forums for such interaction are research conferences. After many years of fragmented research, the conditions to organize the first conferences on mechanochemistry came together in the Soviet Union in the late 1960s and the first meeting was organized in 1968. The following is an attempt to reconstruct the events that contributed to this development and to identify some key players.

By the 1950s, several groups in the Soviet Union were involved in research related to mechanochemistry, including the ones in Moscow (P. Yu. Butyagin), Leningrad (S. N. Zhurkov) and Tomsk (V. V. Boldyrev) [1]. Yet, the spark that resulted in increased activity was probably a chance encounter between two colloid chemists with initially only secondary interest in mechanochemistry: P. A. Rebinder and P. A. Thiessen.

Rebinder, Thiessen and their relationship

Petr Aleksandrovich Rebinder (1898–1972) was born in St. Petersburg [6]. He studied at the University of Rostov on Don and at the State University of Moscow during tumultuous times and graduated in 1924. He was appointed professor at the Karl Liebknecht Pedagogical Institute, Moscow, in 1929. He led the Department of Dispersed Systems at the Institute of Physical Chemistry from 1934 and from 1942 also chaired the Department of Colloid Chemistry at Moscow State University [5, 25]. Rebinder studied how surface-active agents improved the efficiency of fine grinding and in 1928 discovered the effect named after him. His work has practical significance also in boring solid rocks and cutting metals. He also contributed to the theory of flotation, a process essential in mineral processing. He was involved in developing science policy for both basic and applied chemistry from the 1930s and participated in several academic committees. He chaired the committee on fine grinding [5, 25]. Rebinder was elected corresponding member of the Soviet Academy of Sciences in 1933 and became full member in 1946. He was awarded a Stalin Prize in 1942. He was editor and from 1968 editor-in-chief of the Colloid Journal [6].

Peter Adolf Thiessen (1899–1990) was born in Schweidnitz, today in Poland. He studied colloid chemistry in Göttingen under the direction of Richard Zsigmondy [26, 27], the Nobel Laureate who showed that Carey Lea's allotropic silver was in fact a colloid [2]. Thiessen himself worked on gold colloids for his doctorate. When Zsigmondy became ill, Thiessen took over the management of his institute, first unofficially and from 1928 as appointed director. Thus, he was in a leadership position from a rather young age. In 1933 he moved to Berlin to work at the Institute for Physical Chemistry and Electrochemistry of the Kaiser Wilhelm Institute (the former institute of Fritz Haber). The institute was an important component of the German war effort. He was appointed director in 1935 and occupied that position until the end of the war. He was elected member of the Academy of Sciences in 1939. After the war, Thiessen worked for the Soviet nuclear bomb project for 10 years as part of the war reparation. He enjoyed relative freedom and carried out his research alongside his Russian colleagues. He was awarded the Stalin Prize, first class in 1951 for his work on diffusion membranes for uranium enrichment. He was awarded another Stalin prize (second class) in 1956 before returning to Berlin. He also received the Lenin order [26].

Thiessen met Rebinder during his time in the Soviet Union [27]. How close their relationship was is difficult to tell. But they were the same age; they were both involved in colloid chemistry and physical chemistry; they were interested in both fundamental research and applications; they were both involved in science organization and policymaking. They stayed in contact and years later Rebinder led delegations to Berlin to the colloquia honoring Thiessen on his 65th and 70th birthdays and he gave a lecture at both events [6]. Thus, their relationship was certainly far from superficial. Most probably it was Rebinder who advised Thiessen to initiate research in mechanochemistry or—as it was termed at the time—tribochemistry, before he returned to East Germany. Thiessen also met Walther Ulbricht, the later head of state of the GDR, during his stay in the Soviet Union [27]. That connection was helpful upon returning to East Germany in 1956. He was appointed director of the new Institute for Physical Chemistry in Berlin-Adelsdorf in 1957. The GDR intended to develop its chemical industry and Thiessen's institute provided the research background for that effort. Consequently, he became an important figure in determining science and industrial policy. He established a tribochemistry group in his institute, led by Gerhard Heinicke. Thiessen had to spend much of his time on administrative duties, but the little time he could save for research was spent in the tribochemistry laboratory [26, 27]. In the early 1960s, his was the strongest group in tribochemistry, as demonstrated by publishing the first comprehensive book on the subject [28].

The first conferences

The first meeting of researchers working in mechanochemistry was organized as a special session of the 6th All-Soviet Conf. on Colloid Chemistry, Voronezh, 1968. The Chair of the Organizing Committee was Rebinder [6]. Whether adding the mechanochemistry session was his own initiative, the result of discussions with Thiessen, or it was also discussed with Soviet scientists, is difficult to reconstruct. But it is certain that the session was very successful, as a separate conference, officially the 2nd All-Soviet Symposium on the Mechanoemission and Mechanochemistry of Solids, was organized in Frunze, Kyrgyzstan, the following year [29].

About 150 researchers were present at the meeting in Frunze, representing more than 20 groups from the Soviet Union and a few more from East Germany, Poland and Czechoslovakia. The Preface of the abstract booklet was signed by Academician Rebinder and N. A. Krotova. Many authors at the conference played lasting role in the development of mechanochemistry, including E.G. Avvakumov, N. K. Baramboin, V. V. Boldyrev, P. Yu. Butyagin, E. M. Gutman, G. Heinicke and A. N. Streleckij.

The conferences increased the activity in mechanochemistry research and also gave it more visibility. Rebinder's continued support was also very helpful. A group dedicated to mechanochemistry was established in 1968 under the leadership of E.G. Avvakumov within the institute led by V. V. Boldyrev in Akademgorodok, Novosibirsk. Later the name of the institute was changed to Institute of Solid State Chemistry and Mechanochemistry. It is still the only institute that has the term "mechanochemistry" in its name. A visit to Thiessen's laboratory accelerated progress in the new group and established cooperation between the teams in Novosibirsk and Berlin [30].

Later developments

The Soviet conferences on mechanochemistry continued as a yearly event with increasingly broad participation, both from the Soviet Union and Eastern Europe. An important addition was the group from the Institute of Geotechnics, Košice, Slovakia, led by K. Tkáčová. They organized their own conferences called "Theoretical and Technological Aspects of Disintegration and Mechanical Activation of Minerals" beginning in 1970. Connecting the two communities and later adding cooperation with the group of M. Senna from Keio University, Japan led to the formation of the International Mechanochemical Association in 1984 and eventually to the organization of INCOME (International Conference on Mechanochemistry and Mechanical Alloying), the first fully international conference series [2]. The first INCOME was held in Košice in 1993 and it returned to the same city in 2017.

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Compliance with ethical standards

Conflict of interest The author has no conflict of interest related to this paper.

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