

## THE MECHANOCHEMICAL REDUCTION OF AgCl WITH METALS Revisiting an experiment of M. Faraday

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Faraday induced the mechanochemical reduction of AgCl with Zn, Sn, Fe and Cu in 1820, using trituration in a mortar. This experiment is revisited, employing a mortar-and-pestle and a ball mill as mechanochemical reactors. The reaction kinetics depends both on the thermochemical properties and the hardness of the reactants. When using Zn as the reducing agent, Faraday likely observed a mechanically induced self-sustaining process (MSR), or at least he came very close to doing so.

**Keywords:** Faraday, mechanochemistry, self-sustaining reactions

### Faraday's contribution to mechanochemistry

It is customary to associate the emergence of mechanochemistry with the papers of Carey Lea, published at the end of the 19<sup>th</sup> century. He was the first scientist to clearly point out that heat and mechanical action can induce different reactions in the same system [1]. As mentioned by Prof. Boldyrev recently [2], Michael Faraday was aware of some effects of mechanical activation much earlier. Indeed, in his book published in 1827 on 'Chemical Manipulations', a twenty-page chapter is dedicated to mortars and comminution. It begins with stating, that 'the division of matter is often highly advantageous in facilitating chemical action' [3]. Faraday's book ends with 318 practical exercises; the 58<sup>th</sup> of them reads: 'Make an intimate mixture of equal parts by mass of muriate of ammonia and quick lime; observe the ammonia evolved even at common temperatures...' [4]. He refers back to the chapter on trituration for the way to make the 'intimate mixture'. In modern terms, he asks for affecting a mechanochemical reaction between NH<sub>4</sub>Cl and CaO.

A very direct reference to a mechanochemical process appears in a paper written in 1820 on the decomposition of silver chloride [5]. He signed the paper as 'M. Faraday, Chemical Assistant'. Indeed, that was his official title at the time. He was only 29, working at the Royal Institution of London, mainly under the supervision of Sir Humphrey Davy [6]. This is not Faraday's first paper; he began publishing already in 1816 [7]. But this was the first time he was dealing with the mechanism of a reaction. He wanted to decide, whether hydrogen was capable of reducing silver chloride. He found that a stream of hydrogen gas had no such effect. Then he attempted to cause the

reduction by 'nascent' hydrogen. In order to do so, he dispersed silver chloride in dilute acids and generated hydrogen in situ by adding zinc. Hydrogen was liberated and some metallic silver was obtained, but Faraday was not convinced about the role of hydrogen. First he repeated the process using water as the dispersing medium. The reduction of silver chloride still occurred, although no obvious generation of hydrogen could be noticed. Then he directly mixed silver chloride with zinc, without any source of hydrogen. When the mixture was heated, a violently exothermic reaction took place and silver was obtained. That was a direct solid state reaction; hydrogen could not play any role. Finally, Faraday turned to mechanochemistry. As he reported:

'... if dry chloride of silver in powder be trituated in a mortar with zinc filings, the two bodies immediately act, and a heat above that of boiling water is produced.

Zinc is not the only common metal which thus rapidly decomposes chloride of silver, in the dry way. Tin acts even more powerfully when trituated with it: and copper and iron have both of them affinities for chlorine strong enough to produce the same effect.'

This passage clearly describes a mechanochemical process, dated well before the better-known papers of Carey Lea from the 1890's [8]. Moreover, Faraday mentions the 'dry way' of causing a reaction very casually, suggesting that the method was quite familiar to him. He does not emphasize it as a new discovery. Instead, he continues the paper with the interpretation of the results, stating that metals can reduce silver chloride directly, without the presence of hydrogen as an intermediary. He leaves open the question whether direct reduction by hydrogen is possible.

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It seems that this form of mechanochemistry was common knowledge to him and most likely others before him. Chemistry – and alchemy beforehand – used heat as the primary means of stimulating chemical reactions. But grinding and mixing in a mortar is often part of the preparation. It is very likely that chemical changes were also caused in the mortar, intentionally or perhaps unnoticed. The decomposition of cinnabar by rubbing was already known to the ancient Greeks [9]. Whether other written records of mechanochemical processes exist in the early literature is yet to be seen.

According to Faraday's description, the reaction between silver chloride and zinc is fast and highly exothermic, raising the possibility that he actually observed a mechanically induced self-sustaining reaction (MSR) [10]. As the mechanochemical reduction of silver halides has not been studied since, the reinvestigation of the reactions mentioned by Faraday is of interest for more than historical curiosity.

## Experimental

Nowadays the preferred equipment employed to cause mechanochemical reactions is the ball mill. A SPEX 8000 Mixer Mill with round-ended hardened steel vial and steel balls was used in these experiments. The typical charge was 6 g of AgCl-metal mixture, containing 20% more metal than required by stoichiometry, in order to compensate for partial oxidation of the metals. Two 12.7-mm and four 9.5-mm balls were used. The milling vial was filled in air, as Faraday did his experiments without the protection of an inert atmosphere as well. The temperature of the milling vial was recorded using a thermocouple, in order to see, whether a self-sustaining reaction occurred, and if it did, to determine the ignition time.

Following Faraday, the reduction of AgCl with Zn, Sn, Fe and Cu powders was investigated. Ball milling was also performed with Al and Cr for comparison. The purity of the starting materials was 98% or better.

The reactions were also induced by trituration in a small porcelain mortar. The temperature was measured with a thermocouple taped to the pestle close to its active surface. While the information obtained this way is semi-quantitative at best, it still provides useful clues about the reaction kinetics.

The phase composition of the samples was determined using an X'Pert (Philips) X-ray diffractometer equipped with a Cu tube. The fraction of Ag in the chloride and metal phases was determined by comparing the line intensities to those of a standard with known phase composition.

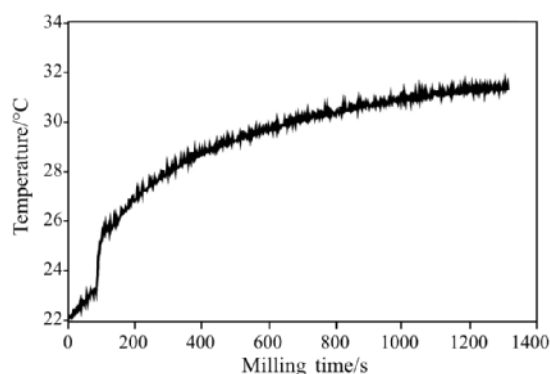
## Results and discussion

In order to determine whether the 'powerful' reactions observed by Faraday could be mechanically induced self-sustaining reactions (MSR), the thermochemical parameters have to be consulted first. Table 1 summarizes the reaction equations, the reaction heat associated with the exchange of one mole of chlorine atoms, and the simplified adiabatic temperature, i.e. the ratio of the reaction heat to the room temperature heat capacity of the products,  $\Delta H/C$ . This quantity correlates well with the true adiabatic temperature [11] and is often used to predict whether MSR is possible in a given system. A value close to or above 2000 K is needed to support MSR in oxide-metal thermite systems and simple combination reactions [10]. In order to obtain the most exothermic reactions possible, the reaction stoichiometry providing the highest value of  $\Delta H/C$  was chosen in the cases when the reducing metal has multiple oxidation numbers. Al was added to include a reaction where MSR can clearly be anticipated.

Figure 1 presents the temperature of the milling vial during the reduction of AgCl with Zn in a ball mill. The sudden temperature increase after about 90 s of milling suggests MSR, in spite of the relatively low value of  $\Delta H/C$ . This is not entirely unexpected, as MSR was observed during the reduction of Ta<sub>5</sub>Cl by Mg before, although the adiabatic temperature of that

**Table 1** The equation, reaction heat per exchanged chlorine,  $\Delta H/n$ , and simplified adiabatic temperature,  $\Delta H/C$  of the investigated reactions

Equation	$\Delta H/n/\text{kJ mol}^{-1}$	$\Delta H/C/\text{K}$
$2\text{AgCl} + \text{Zn} \rightarrow \text{ZnCl}_2 + 2\text{Ag}$	80.6	1310
$2\text{AgCl} + \text{Sn} \rightarrow \text{SnCl}_2 + 2\text{Ag}$	38.5	607
$2\text{AgCl} + \text{Fe} \rightarrow \text{FeCl}_2 + 2\text{Ag}$	43.9	688
$\text{AgCl} + \text{Cu} \rightarrow \text{CuCl} + \text{Ag}$	10.2	137
$3\text{AgCl} + \text{Al} \rightarrow \text{AlCl}_3 + 3\text{Ag}$	108.2	1933
$3\text{AgCl} + \text{Cr} \rightarrow \text{CrCl}_3 + 3\text{Ag}$	63.1	1124



**Fig. 1** Temperature of the milling vial during the reaction of AgCl with Zn in a ball mill

reaction is also quite low [12]. Closer inspection shows that although the reaction starts very early, it is more sluggish than a typical MSR; the temperature ‘jump’ takes 15–20 s, while it happens within 2 s in oxide-metal and many other MSR systems [10]. Although the reaction clearly accelerates due to self-heating, it does not propagate across the entire charge easily. Stopping the mill at the beginning of the process would probably arrest the reaction. This behavior may relate to the softness of AgCl, that makes it easy to achieve close contact between the reactants. As a result, local reactions take place due to shearing early, before sufficient mixing could take place to propagate the reaction through the charge. According to X-ray diffraction (XRD), the reduction of AgCl is practically complete after 20 min of milling (Fig. 2); about 3% of the Ag remains in the chloride phase, probably due to partial oxidation of the Zn powder. As anticipated, the reduction of AgCl with Al also takes place in the self-sustaining way and it results in practically full transformation in a short time.

No temperature jump is observed when Sn is used as the reducing metal, but the reaction is practically complete after 20 min of milling as shown by the XRD pattern (Fig. 2). If the reaction of AgCl appeared more ‘powerful’ with Sn than with Zn to Faraday, it was not because of the total amount of evolved heat. What distinguishes Sn is its softness that increases the efficiency of trituration.

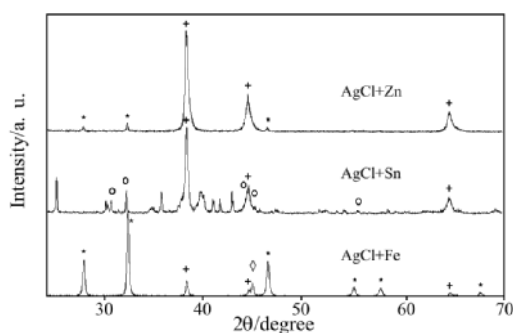
The importance of hardness is clearly brought out by an attempt to reduce AgCl with Fe. Even after 60 min of ball milling, only about 12% of the silver was in the metallic state (Fig. 2), although the reaction is about as exothermic as the reaction with Sn. Although Cr is much more reactive than Fe, it is also harder. Consequently, 60 min of milling with Cr reduced only 13% of silver in AgCl, essentially the same as Fe. Copper is less reactive but softer; as a result, ball milling with copper reduced 88% of the silver in 60 min and already 28% in 20 min. In any case, the reaction of AgCl with Fe or Cu is far from being as intense as the reaction

with Zn or Sn, in spite of Faraday’s claim to the contrary.

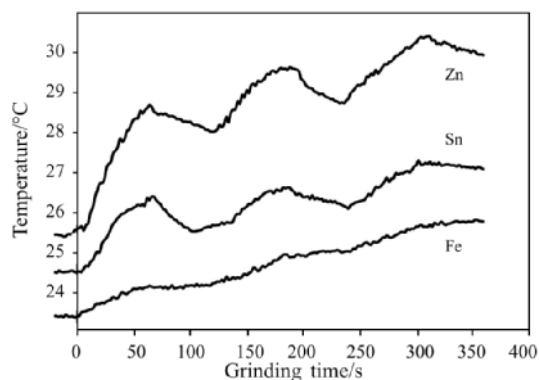
Local melting may also contribute to the high reactivity between AgCl and Zn. The  $\Delta H/C$  value for their reaction is 1310 K, much higher than the melting points of AgCl (728 K) and Zn (693 K) and the product, ZnCl<sub>2</sub> (591 K). The reaction between AgCl and Al is also exothermic enough to melt the reactants. The other investigated reactions are less exothermic or, in the case of Cr, the melting temperature is very high, thus melting is not possible. The fast rate of the reaction between Ta<sub>5</sub>Cl and Mg was also explained by local melting [12].

It would be interesting to compare the above results with data from the literature. However, the only long-term program on MSR and related reactions of halides is that of the group of McCormick [12–14]. The author of this paper is not aware of any recent study on the mechanochemical reactions of Ag halides. In general, halides are not convenient model systems, as they are often hygroscopic and consequently difficult to work with. On the other hand, the fact that many halides dissolve in water or alcohol easily provides an opportunity to prepare metal [13, 15] or oxide [14] nanopowders using halide precursors.

Ball milling is more suitable for obtaining reproducible results than manual trituration in a mortar, but the mechanical actions are different. Therefore, it has to be verified whether conclusions drawn from ball milling experiments are also applicable to experiments employing hand trituration. Figure 3 shows the temperature measured close to the active surface of the pestle during the processing of 3-g batches of powder mixture. The powder was rubbed vigorously for 60 s, followed by 60 s rest, repeated three times. When AgCl was rubbed with Fe, the temperature increased only slightly and quite smoothly. Much of the increase came from the warmth of the hand; the little undulation is probably due to the heat evolved by friction. According to XRD, only about 2% of the silver could be reduced even when the trituration was continued for 15 min. Cu gave somewhat better results, about 7% transformation in 15 min, consistent with the ball milling experiments. Clear heating and cooling periods could be observed when Sn was used, showing the effect of the heat generated by the reaction. 40% transformation was achieved by 3 min of trituration. The temperature change is larger with Zn due to the larger reaction heat. The transformation rate is much higher as well, more than 90% of the reaction is complete after 3 min of working. Yet, the fast temperature increase stops as soon as the trituration is paused and re-starts only when the rubbing starts again. Under our conditions, the reaction is fast, but requires constant mechanical agitation; it does not become self-propagating.



**Fig. 2** X-ray diffraction patterns of ball-milled AgCl – metal mixtures. The symbols indicate the lines of \* – AgCl, + – Ag, o – Sn and ◇ – Fe. The unmarked lines of the middle pattern correspond to SnCl<sub>2</sub>



**Fig. 3** Temperature close to the end of the pestle during trituration of AgCl with Fe, Sn and Zn powders in a mortar. (The Sn and Zn curves are shifted up by a degree for clarity.)

The question remains whether Faraday induced a true MSR, or only a fast, highly exothermic reaction. He claimed to produce temperatures above 100°C, our temperature never got even close to that level. Higher temperature requires less significant heat loss to the mortar and the air, suggesting that Faraday was using larger quantities of the materials. In order to deliver sufficiently intense mechanical action, he had to labor with the pestle very hard. Faraday was a strong young man. During his bookbinding apprentice years, he ‘could strike 1000 blows with the mallet in succession without resting’ [16]. He was also skilled in chemical preparation and knew how to use the mortar and pestle efficiently. Maybe he did see a real MSR after all. The true test would have been to interrupt the rubbing and see whether the reaction continued thermally by its own heat. Faraday did not report such an experiment.

## Conclusions

Michael Faraday used trituration in a mortar as a natural tool to induce reactions the ‘dry way’, showing that mechanochemistry was probably used earlier and more widely than usually believed. It is possible that while the written record of early chemistry emphasizes the magic of changing materials by fire, distillation, or by mixing solutions, a lot of practical knowledge accumulated on the use of the mortar as well. It is possible that more signs of this early knowledge will be discovered in the future. Although Faraday’s paper from 1820 is an interesting early result, it probably does not mark the beginning of mechanochemistry.

One can claim that Faraday was mistaken about many details: the effect of Sn is certainly weaker than the effect of Zn and the reducing ability of Fe and Cu is almost negligible in comparison. Yet, it would be unfair to overemphasize this fact. Faraday did not know the thermochemical properties of the materials

and could not perform phase analysis using XRD. Given the chemical knowledge of his time and the techniques available to him, his assessment of the observed phenomena is quite remarkable. Nevertheless, the inaccuracies of his paper show that results from the early literature have to be considered with caution and reproduced if possible..

When reducing silver chloride with zinc via trituration in a mortar, Faraday induced a self-sustaining reaction, or at least he came very close to doing so. The systematic investigation of mechanically induced self-sustaining reactions did not begin until the works of Tschakarov 160 years later [17].

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