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Mercury Beating Heart: Modifications to the Classical Demonstration

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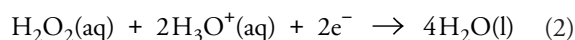
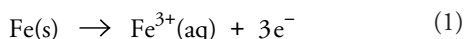
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Identifying the person who first discovered the mercury beating heart (MBH) is controversial. Berzelius, in his Spanish edition of *Chemistry*, stated that this phenomenon was observed for the first time by Ermann and further studied by Herschel's son and Pfaff (1). However, Avnir (2) stated that Carl Adolf Paalzow (1858) deserves the credit for the discovery.

The MBH is a well-known experiment that has been performed under various conditions (3–6). Generally the experiment is performed by placing a drop of mercury in a watch glass and covering it with an aqueous solution of sulfuric acid and an oxidizing agent. When the mercury drop is touched with a tip of an iron nail, oscillations start. Previous versions of this experiment are based on varying the oxidizing agent and substituting other metals for the iron. For instance, the oxidizing agent could be potassium permanganate (3), potassium chromate (3, 4, 7) or dichromate, or hydrogen peroxide.

The oscillations create different shapes of the mercury drop (oval, equilateral triangle, pentagon, etc.), depending on the experimental conditions. To understand the origin of the oscillations it is important to note the existence of an electric double layer at the interface between the mercury drop and the aqueous electrolyte. The electric double layer is formed as a consequence of the interactions between water molecules, electrolyte ions, and the mercury surface. The structure of the double layer is related to the distribution of the electric charge over the mercury surface, and it determines the surface tension of the mercury drop. When mercury is immersed in an electrolyte solution, without contact with the iron nail, a double layer with a uniform structure exists, and the surface tension is equal over all points of the mercury surface. Both the structure of the double layer and the surface tension are subject to dramatic changes when the mercury drop is touched by the tip of an iron nail. For instance, in a system consisting of an aqueous solution of sulfuric acid and hydrogen peroxide as an oxidizing agent, touching the mercury surface with the tip of the iron nail causes the following redox reactions:



Contrary to the misleading interpretations in the literature (4), it is important to stress that these two redox reactions should proceed simultaneously to maintain the charge neutrality of each phase at each instant of the experiment. By analogy to the galvanic cell (8), if a part of the mercury drop is in contact with the iron nail, oxidation of iron takes place (eq 1), whereas at the rest of the mercury surface the reduction of hydrogen peroxide occurs (eq 2). Therefore, the behavior of the mercury drop can be, to some extent, explained considering the behavior of a bipolar electrode with a nonuniform polarization over its surface. Consequently, the mercury drop is characterized by nonuniform values of the surface tension. The surface tension gradient is the driving force for oscillations of the mercury drop.

Browsing through literature we found that Berzelius described similar mercury oscillations using two electrodes connected to a battery. We propose using two electrodes as an additional version to the well-known experiment—one that can strengthen the offered explanation. Berzelius states (1) that the oscillations did not take place when alkaline solution was used. We show that this is only partly true and include a video clip of MBH in aqueous solution of potassium hydroxide.

Equipment and Chemicals

- Overhead projector
- Watch glass, 10 cm diameter
- Petri dish, 9 cm diameter
- Pencils with free graphite ends
- Electric cords with alligator clips
- Power supply with variable dc voltage 0–12 V
- “Helping hand” with alligator clips
- Paper sheet with a 9 cm hole
- Deionized or distilled water
- Aqueous solution of sulfuric acid (2 mol L⁻¹)
- Aqueous solution of potassium hydroxide (2 mol L⁻¹)
- Aqueous solution of sodium sulfate (10%)

All equipment is presented in Figure 1.

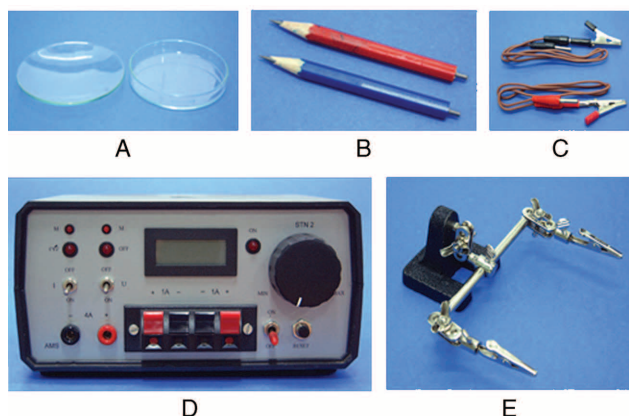


Figure 1. Equipment for the experiment: (A) watch glass and Petri dish; (B) pencils; (C) electric cords with alligator clips; (D) power supply; and (E) helping-hand stand for electrodes.

The Demonstration

The paper is placed on the overhead projector and the apparatus is assembled as shown in Figure 2. Alternatively, a camera connected to a video projector might be used. A watch glass is placed on a Petri dish for support and mercury is added to form a drop about 1.5 cm in diameter. The Petri dish may be placed in a flat-bottomed glass dish for mercury control. The Petri dish is carefully placed on the overhead projector exactly over the hole in the paper. Graphite electrodes are inserted into the alligator clips of the helping hand and are connected to the dc power supply. The mercury is covered with an electrolyte (originally, an aqueous solution of sulfuric acid). When the power is on, increasing the voltage first distorts (stretches) the mercury, and eventually oscillations start (the actual voltage where these changes occur depends on the type of electrolyte, the concentration, the distance between the electrodes, etc.). Instead of sulfuric acid, a solution of sodium sulfate or potassium hydroxide can be used and differences in the behavior can be demonstrated.

In another type of demonstration, the mercury was only partly covered with water and oscillations were initiated by touching the underwater surface of the mercury drop with a graphite electrode.

MBH in Water

When the mercury drop is only partly covered with water (the top is not covered, thus providing dry circular surface), a touch of the wet surface with the point of graphite cathode induces an increase of the dry surface area (Figure 3A). In this arrangement, the mercury is externally polarized by an electric power supply. It is expected that the mercury surface will be uniformly polarized with an excess of either positive or negative charge, depending on whether it is touched by the anode or cathode, respectively. However, since part of the mercury is in contact with air and the rest with the aqueous solution, the structure of the double layer is non-

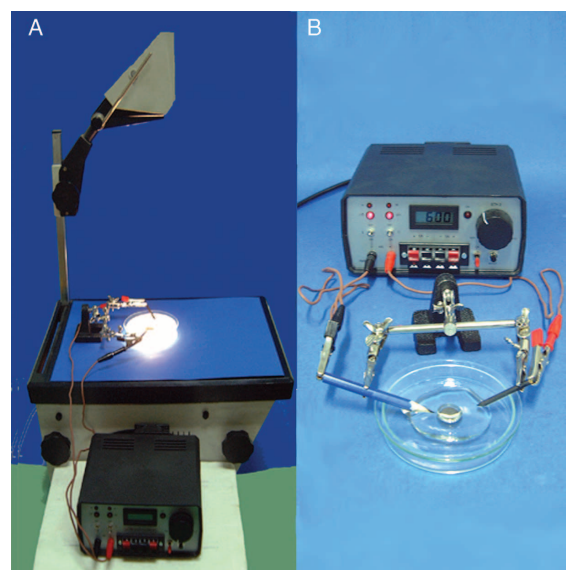


Figure 2. (A) Apparatus with overhead projector. (B) Closeup of the apparatus without the overhead projector.

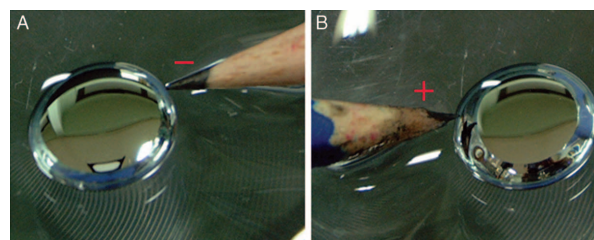


Figure 3. Surface changes of mercury with the touch of (A) cathode or (B) anode.

uniform over the entire surface. This causes a gradient of the surface tension values and initiates mercury surface oscillations. When touched by the cathode, the mercury surface experiences an excess of a negative charge. The part of the drop in a contact with aqueous electrolyte resembles the behavior of the part of the mercury near the iron nail in the classical version of the experiment.

If the mercury drop is touched with the anode, the opposite process occurs (i.e., the dry surface decreases owing to decrease in the surface tension) and the mercury drop flattens (Figure 3B). If the electrodes are placed close to the mercury drop at a fixed position, certain voltages can produce oscillations.

MBH in an Aqueous Solution of Sulfuric Acid

When mercury is covered with aqueous solution of sulfuric acid, a touch with a graphite cathode produces rapid pulsations of the mercury at ≈ 4 V. Further increase of the voltage noticeably increases the beating frequency. In this case, the entire mercury surface is uniformly polarized with an ex-

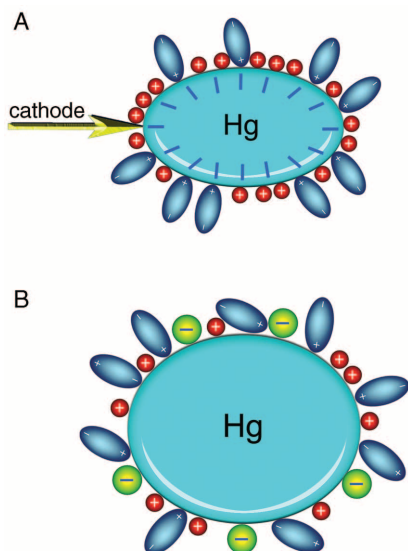


Figure 4. A simplified scheme of the structure of the double layer: (A) upon touch of cathode and (B) in the detached state. (Note that the lines in A represent the negative charges inside the mercury drop.)



Figure 5. Sodium amalgam: product formed during performing the experiment in aqueous solution of sodium sulfate.

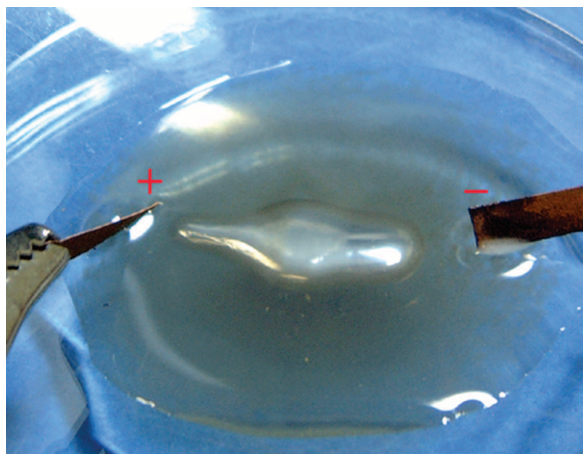
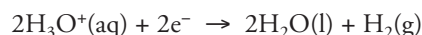


Figure 6. Stretching of mercury drop to both cathode and anode in solution of sodium sulfate.

cess of a negative charge (Figure 4A), which causes uniform changes of the surface tension over the entire mercury surface. The variation of the surface tension is equivalent to the variation occurring at the part of the mercury drop in a contact with the iron nail in the classical version of the experiment.

When the drop is negatively polarized, the surface tension increases causing a decrease of the mercury drop surface. This is an example of the electrocapillary effect (4). As a consequence, the mercury drop is detached from the electrode, and the drop relaxes back to the initial position (Figure 4B). Things might be a bit more complicated. We found that if the mercury is first treated with H_2O_2 , and then thoroughly washed with water and put in an aqueous solution of H_2SO_4 , in a contact with the iron nail strong oscillations also occur, which suggests that earlier explanations should be made more general or even modified.

The electrode reaction occurring at the mercury drop in contact with the cathode is



The overall electrochemical process is electrolysis of water. At a relatively high voltage (≈ 12 V), the rate of the electrode reaction is markedly increased resulting in a vigorous gas evolution. If working close to the apparatus, one can even experience a problem (irritation of the breathing system) that is due to the formation of aerosol containing sulfuric acid.

Interestingly, under sufficiently high voltage, the oscillation can even be observed without direct contact between the cathode and the mercury surface, if the distance between the mercury drop and the cathode is gradually decreased. In this case pulsations occur mostly in the part of the mercury drop adjacent to the cathode. Being under the influence of the electric field imposed between the electrodes, the mercury drop is nonuniformly polarized, which causes a gradient of the surface tension values and initiates oscillations.

The part of the mercury that is near the cathode has partly positive charge (that is why it stretches). After being neutralized by the negative ions, it springs back (close to oval shape).

MBH in an Aqueous Solution of Sodium Sulfate

The behavior of the MBH varies depending on the nature of the aqueous solutions since the electrolyte composition affects the structure of the electric double layer. In this case, when the cathode touches the mercury it induces pulsations, but sodium amalgam also forms (Figure 5), accompanied with a change in the pH value in that part of the solution.

Note that although the reduction of H^+ ions is thermodynamically favored compared to the reduction of Na^+ , it is well-known that the reduction of the former involves a high overvoltage at the mercury surface. Further differences arise now. In an acidic medium (as demonstrated above) the cathode attracts the mercury drop.

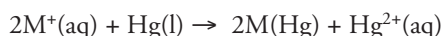
However, in aqueous solution of sodium sulfate the mercury is attracted to both cathode and anode (Figure 6), the latter being more pronounced. At this point it is important to stress that the oscillations of the mercury surface have to

be accompanied by a streaming of the mercury inside the drop. This process affects the overall type of the oscillations. Consequently, it is expected that the amalgam forming metals will influence the type of oscillations.

MBH in an Aqueous Solution of Potassium Hydroxide

The mechanism for these oscillations is similar to the one above, and the mercury drop is attracted to both electrodes. It is interesting to note that formation of an amalgam was observed when the cathode was close enough to the mercury drop in both the aqueous sodium hydroxide and potassium hydroxide solutions. In the latter electrolyte the amalgam formation was even more pronounced. The amalgam was formed at the side of the mercury drop close to the cathode (Figure 7). As previously mentioned, under the influence of the strong electric field imposed between the graphite electrodes, the mercury drop is polarized even without being in a direct contact with the electrodes. The side of the mercury drop close to the cathode has to be positively polarized. The formation of an amalgam into the mercury drop is a clear evidence for reduction of the alkali metal cations present in the aqueous solution. Besides the reduction process, a simultaneous oxidation process must proceed, serving as a source of electrons consumed by reduction of alkali metal ions. On the other hand, the oxidation of any species present in the aqueous solution, for example, OH^- and H_2O , is excluded since this process requires higher overpotential than the oxidation of mercury itself.

The strong positive polarization of the mercury drop close to the cathode causes simultaneous oxidation of mercury and reduction of alkali metal ions. The overall process can be described by the following redox reaction:



The proposed mechanism was supported by identification of mercury ions in the electrolyte solution. For example, the mercury beating heart experiment was performed with aqueous sodium sulfate solution as the electrolyte, without physical contact of the mercury drop with electrodes. After some time a portion of the electrolyte was subjected to analysis. Reaction with hydrogen sulfide was performed and black precipitate was formed due to the presence of mercury ions in the solution as a consequence of mercury oxidation.

When copper electrodes are used, owing to the higher strength of the electric field the amplitudes of the oscillations are larger, but due to a precipitate formation the whole picture is aesthetically less appealing.

Hazards

Mercury and its compounds are highly poisonous. Spilled mercury should be collected and saved in a closed labeled container. In some countries mercury spill kits are available in science supply houses. Sulfur powder may also be used onto the spilled droplets of mercury. To prevent mercury spills one may want to work in a glass tray. Mercury vapor is especially dangerous, thus in badly ventilated laboratories the spilled

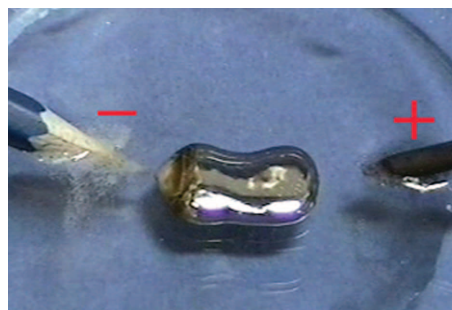


Figure 7. Formation of coating on the mercury surface at the side near cathode.

mercury may induce chronic mercury poisoning. The aqueous solutions of sulfuric acid and potassium hydroxide are corrosive but in a diluted state they are not dangerous.

In some countries mercury comes with its own set of cautions and disposal requirements (United States). In other countries (European Union) you may have product known as Chemizorb (Merck). Mercury can be resorbed with it, placed into a plastic container and labeled "poison". The aqueous solutions after the demonstration have to be disposed of as mercury.

Summary

Several new demonstrations of the MBH on overhead projector have been presented. One is similar to the original version of Berzelius's experiment, another is a MBH in solution of sodium sulfate and the third is the MBH in basic media. The choice of the voltage used allows a variety of related demonstrations of this phenomenon.

Supplemental Material

Videos of these experiments are available in this issue of *JCE Online*.

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