

PULSATIONS ON MERCURY SURFACE CAUSED BY POLARISATION

BY K. S. GURURAJA DOSS AND BASRUR SANJIVA RAO

(*Department of Chemistry, Central College, Bangalore, University of Mysore*)

Received April 30, 1943

IF an iron wire is brought into contact with the surface of mercury, kept under a dilute solution of sulphuric acid, containing a little potassium dichromate, the mercury begins to pulsate.¹ This interesting phenomenon has been referred to as the "Mercury Heart". Its exact mechanism has been a puzzle, as can be gathered from the following observation of Thompson²: "Why iron and chromate are the only means of producing this effect, however, does not seem to have been explained."

The investigations described in this paper have elucidated the phenomenon. Mercury in contact with a solution containing acid and an oxidising agent, becomes anodically polarised. If the solution contains chloride ions, the polarisation becomes visually evident by the formation of a film of calomel. Such a surface has comparatively a low interfacial tension owing to electro-capillary effect. If an iron wire is brought into contact with the surface, a voltaic cell is formed, with iron as the anode and mercury as the cathode. The mercury now tends to get cathodically polarised and the interfacial tension rises. The mercury drop consequently contracts laterally. If the iron wire is touching at a side of the drop, the drop detaches itself from the iron wire, in the process of contraction. The mercury, now no longer in contact with iron, is once again anodically polarised and the interfacial tension, once again falls, leading to a lateral dilatation of the drop and re-establishment of the contact with the iron wire. The process gets repeated and thus leads to pulsations in the mercury.

In a study of the phenomenon, it was observed that dichromate can be replaced by other oxidising agents such as hydrogen peroxide or potassium permanganate. With hydrogen peroxide, addition of a trace of ferric chloride, greatly quickens the pulsations. It is well known that the oxidising action of hydrogen peroxide is promoted by iron salts.

That the modification of the surface by contact with the iron wire is due to cathodic polarisation has been established from the following observations: (a) The mercurous chloride film, which as already stated, is formed

on the surface of mercury in presence of hydrochloric acid and an oxidising agent, disappears when the iron wire is placed at the interface between mercury and solution. The disappearance of the film can be observed visually. It takes place very quickly over the entire surface and can only be due to cathodic reduction. (b) The pulsations can also be obtained in the following way:—An iron wire is dipped into the solution and connected externally to a graphite rod (the “lead” of a pencil) and the latter is brought into contact with the mercury/solution interface. (c) It is possible to obtain pulsations, without the use of iron or other base metal, by employing two graphite rods, dipping in the solution and connected to a potentiometric arrangement, the cathodic rod being in contact with the mercury.

These results indicate that a similar phenomenon should be observed with a reducing agent in place of the oxidising agent, the graphite rod touching the interface however, being *anodically* polarised. We have been able to produce the expected effect, using a reducing agent such as stannous chloride or titanous chloride. It is of interest to note that if an “arc carbon” is used instead of graphite, in this experiment, the pulsations persist for some time, even after the polarising E.M.F. has been cut off. This is probably due to chlorine occluded by the carbon rod, which makes it function as a chlorine electrode for a time, after the E.M.F. is removed. Another interesting observation was made. Carbon rods, on being worked in the arc for some time, were found to create pulsations in mercury (under reducing solutions) even without any anodic polarisation. The effect, though rather feeble, persisted for considerable time. It is probable that at the temperature of the arc, an oxidising agent is produced in the rod. We noticed that a carbon rod, after working in an arc lamp, produces a thick film of calomel, when brought at the interface: mercury/dilute hydrochloric acid.

It is of importance to note that to secure pulsations in mercury under an oxidising agent, the iron wire (or the cathodically polarised electrode) must contact the mercury at the *side* of the drop. Under reducing agents however, the mercury has to be touched at the *apex* of the drop, by the anodically polarised electrode. This difference in procedure is rendered necessary by the fact that in our experiments, when cathodically polarised electrodes contact mercury kept under an oxidising medium, the interfacial tension *increases* bringing about an immediate lateral *contraction*. On the other hand, the interfacial tension *decreases* and a lateral *expansion* is produced, when an anodically polarised electrode touches mercury kept under the reducing solution.

Finally it may be noted that pulsations in mercury can be brought about even without the use of any oxidising or reducing solution. The following procedure

is adopted. The mercury is kept under an aqueous solution of an electrolyte (e.g. dilute sulphuric acid). Two graphite electrodes ("Lead" pencils) connected to a source of E.M.F. are used. The anode is kept vertically above the drop and the cathode kept at the side. The distances are so arranged that both the electrodes do not come into contact with the mercury drop *at the same time*. A resistance is used in series with the electrodes so as to avoid any accidental short-circuiting. The pulsations are effectively produced by employing about one c.c. of mercury in a shallow basin with a slight curvature at the bottom, and covering it with 0.2 N sulphuric acid. A potential of one to two volts is applied. It is found that the pulsations persist even when a resistance of over 10,000 ohms is included in the circuit.

REFERENCES

1. Walden and Drucker .. *Handb. allgem. Chem.*, 1930, 8, pt. 1, 230.
2. Thompson .. *Theoretical and Applied Chemistry*, 1939, 107.