Study of the Extinction Dynamics of the Mercury Beating Heart Reaction in Acid Solution and in the Presence of γ-Radiation

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The dynamics of the oscillatory mercury beating heart (MBH) reaction in acid aqueous solution with Ce^{IV} as the oxidizing agent was investigated. The reaction slowly runs down over a period of a few hours, until all oscillatory activity eventually ceases. During this period the dynamics slowly evolves, showing qualitatively different forms of oscillations. These oscillations display different modes of oscillations with geometric structures similar to heart, circle, pentagon, hexagon, and 8- and 16-pointed stars. As time proceeds, limit-cycle oscillations of period-1, period-3, and period-2 appear successively. However, these oscillations are damped and could be interpreted in terms of a subcritical Hopf bifurcation. We propose different oxidation−reduction reactions to explain the appearance of these cycles based on the formation of mercury(I) species, in the form of free Hg_2^{2+} ion or, in molecular form, as a soluble mercurous sulfate or a mercurous sulfate film. The theoretical potential values calculated for these reactions agree well with our experimental values. An experiment was performed also without adding the Ce^{IV} oxidant, generating in situ species of Hg(I) by γ-irradiating the metallic Hg in the same acid solution as before. It is shown that ^{60}Co γ-rays induce the generation of oscillations. In this way we support our claim that oscillations are due to the formation of chemical species of Hg(I) be it ionic or molecular and that extinction occurs when $[Hg(II)] \gg [Hg(I)]$.

1. Introduction

The mercury beating heart, or MBH system ,was observed by Kühne and reported by Lippmann as early as 1873.[1,2] Basically, the system consists of a given amount of liquid Hg placed in a concave or flat-bottom vessel. The top surface of the Hg is then covered with aqueous acid or base, an oxidant is added, and the circuit is closed with a metal tip (Fe or Al). The metal tip is brought near to the Hg drop periphery and the drop begins to oscillate.

Keizer et al.[3] made a detailed analysis of this reaction with the system functioning as an electrochemical cell: a tungsten electrode contacts the Hg and the potential of this tungsten electrode is set by attaching it to an Al or Fe counter electrode. The voltage between Hg and the corroding electrode undergoes periodic changes which were followed on an oscilloscope. In acidic oxidizing solutions they associated the oscillations with the formation and removal of a Hg_2SO_4 surface layer and, in the absence of strong oxidants, it was found that the presence of O_2(aq) is responsible for the modifications in surface tension of the Hg drop. Keizer et al.[3] were the first to propose a mathematical model with three variables, showing limit cycle oscillations.

Since this work the MBH system has been the object of several recent investigations[3−7] using various experimental procedures. The insertion of a variable power supply between the Al and W electrodes allows the application of a potential difference to induce oscillations. Olson et al.[5] introduced a reference electrode which allows the Hg electrode potential to be followed. The response of the Hg drop to an external oscillating field was monitored in terms of surface potential and conditions under which the MBH system can be described in terms of the electrocapillary effect were established. They showed that in neutral and basic solutions oscillations can be sustained by application of the oscillating field without formation of a surface film.

Smolin and Imbihl[7] found new modes of oscillation by confining the Hg drop to different geometries and, by varying

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the potential, they showed that transitions can be induced between them. They stated that the oscillations are generated by the coupling between electrochemical and mechanical processes. In this paper we report the dynamics seen during the entire time-course of a MBH reaction in a concave vessel and recording the electrode potential of Hg oscillating under various conditions. Because there is no refreshment of the quantity of oxidizing agent we study an "extinction" dynamics and perform a study of the different modes of motion seen in this system for high concentrations of sulfuric acid.

The second objective of the present study was to elucidate the chemistry involved in the MBH reaction when it functions as an electrochemical cell. We also aimed to investigate whether the forms of oscillation, under experimentally defined conditions, depend on the oxidizing agent, or are only a function of the concentration of the chemical species Hg(I), Hg(II), and of the concentration relation [Hg(I)]/[Hg(II)]. Finally, to show that oscillations are also triggered without the formation and removal of a surface layer an experiment was performed without adding the Ce^{IV} oxidant, but generating in situ species of Hg(I) by γ-irradiating the metallic Hg in the same acid solution as before.

2. Experimental Details

The reaction was performed in a concave vessel, a porcelain dish of 385 mL capacity. An 8 mL(106.4 g) sample of metallic Hg was placed in the dish and covered with 25 mL of 6 M sulfuric acid. In this geometry the motion of the Hg is relatively unconstrained and oscillations can occur in several modes. Analytic-grade reagents were used always. A $Ce(SO_4)_2{\cdot}4H_2O$ solution was prepared in 6 M sulfuric acid and standardized with sodium oxalate by inverse volumetric titration. At this concentration of sulfuric acid the major cerium species is [8] $[Ce^{IV}(SO_4)_3]^{2-}$ and it acts as the oxidant agent. The ceric sulfate disolves according to

$$\mathrm{Ce(SO_4)_2{\cdot}4H_2O + SO_4^{\;2-}(aq) \rightleftharpoons [Ce^{IV}(SO_4)_3]^{2-} + 4H_2O} \qquad (1)$$

A saturated calomel electrode (SCE), was used as reference electrode and a platinum wire as working electrode. This electrode was covered with Parafilm to avoid contact with the acid solution, leaving free only the tip which was within the Hg body. The voltage−time curves were measured with a TDS 520C Tektronix digital oscilloscope. The iron and platinum wires were from Aldrich with a purity of 99.9%. Hg was distilled at reduced pressure and water was triply distilled according to recommendations for radiation chemistry.[9]

The setup is depicted in Figure 1. We have verified that with this arrangement the reaction presents an oscillatory behavior with the following oxidant ions with a normal potential above 1.0 V with respect to the normal hydrogen electrode (/NHE): Ce^{IV}, MnO_4^-, $Cr_2O_7^{2-}$, BrO_3^-, IO_3^-, and VO_2^+ in H_2SO_4 solution. In this work Ce^{IV} was chosen because it has not been studied before.

The study of the oscillation extinction dynamics was followed by a computerized analysis of voltage signals acquired with a National Instruments LAB-PC-1200/AI analog-to-digital converter board (data were taken every $\Delta t = 494\ \mu s$). To irradiate the $Hg/H_2SO_4(aq)$ system we used ^{60}Co γ-rays from a Gammabeam 651 PT source, with a dose rate of 1.8 kGy/h. We used UV/VIS spectrophotometry with a Series 553 Perkin-Elmer spectrophotometer for identifying the produced species. The traces were carried out with a wavelength range between 600 and 190 nm.

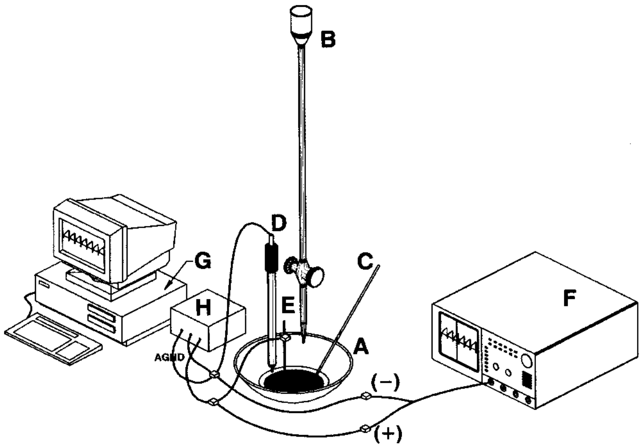

Figure 1. Experimental setup: (A) porcelain dish, (B) buret with oxidizing agent, (C) iron tip, (D) saturated calomel electrode (SCE), (E) Pt electrode, (F) oscilloscope, (G) board for data acquisition, (H) I/O connector block.

3. Results

3.1. Analysis of the Oscillations. A set of conceptual and mathematical tools of nonlinear chemical dynamics [10,11] have been developed in the past for analyzing models and experimental data of nonlinear systems as the one we study here. Specially the time series yield valuable information concerning the periodicity of the signal. In this section we analyze first the time series for the period and amplitude of oscillations and construct thereafter the corresponding phase portraits.

In the experiments a fixed volume of oxidant solution concentration was added and the solution shaken initially manually for 1 min. Then, a 2.0 mm diameter iron wire with pointed tip was inserted and placed at the Hg drop periphery. This triggers sustained oscillations of the mercury body and the evolution of the system was recorded until oscillations extinguished. Several different experiments with similar initial conditions have been carried out to ensure reproducibility of the results.

For the range of studied concentrations (roughly $(4.5-15.5) \times 10^{-3}$ mol/L) there is a lapse of time where irregular oscillations occurs (approximatively 22 min), then a period-1 orbit is developed, followed by a period-3 orbit, and finally a period-2 orbit occurs. The system spends different times in each period and that depends on the initial concentration of the oxidant.

The following figures refers to the case where a concentration of 15.5×10^{-3} mol/L of oxidant was added and will be use to exemplify the mechanism. First, in the irregular signal the potentials (the potential of mercury in contact with the acid solution with respect to the reference electrode)at the extreme of the oscillations were between 770 and 760 mV/SCE when the Hg was in contact with the Fe electrode and between 80 and 60 mV/SCE when the drop was out of contact with the counter electrode. Over an interval of approximately 22 min many different oscillating modes are observed. The geometric structures observed are that of a triangle, circle, pentagon, hexagon, and 8- and 16-pointed stars and they are shown in Figure 2 although they do not occur in the sequence shown in the picture but rather in a random sequence. This 16-pointed star could be in fact the overlapping of two 8-pointed stars. We have also observed that a film of sulfate (white color) has been created on the surface of the metallic Hg. The extreme values decrease slowly during this time interval, ranging at the

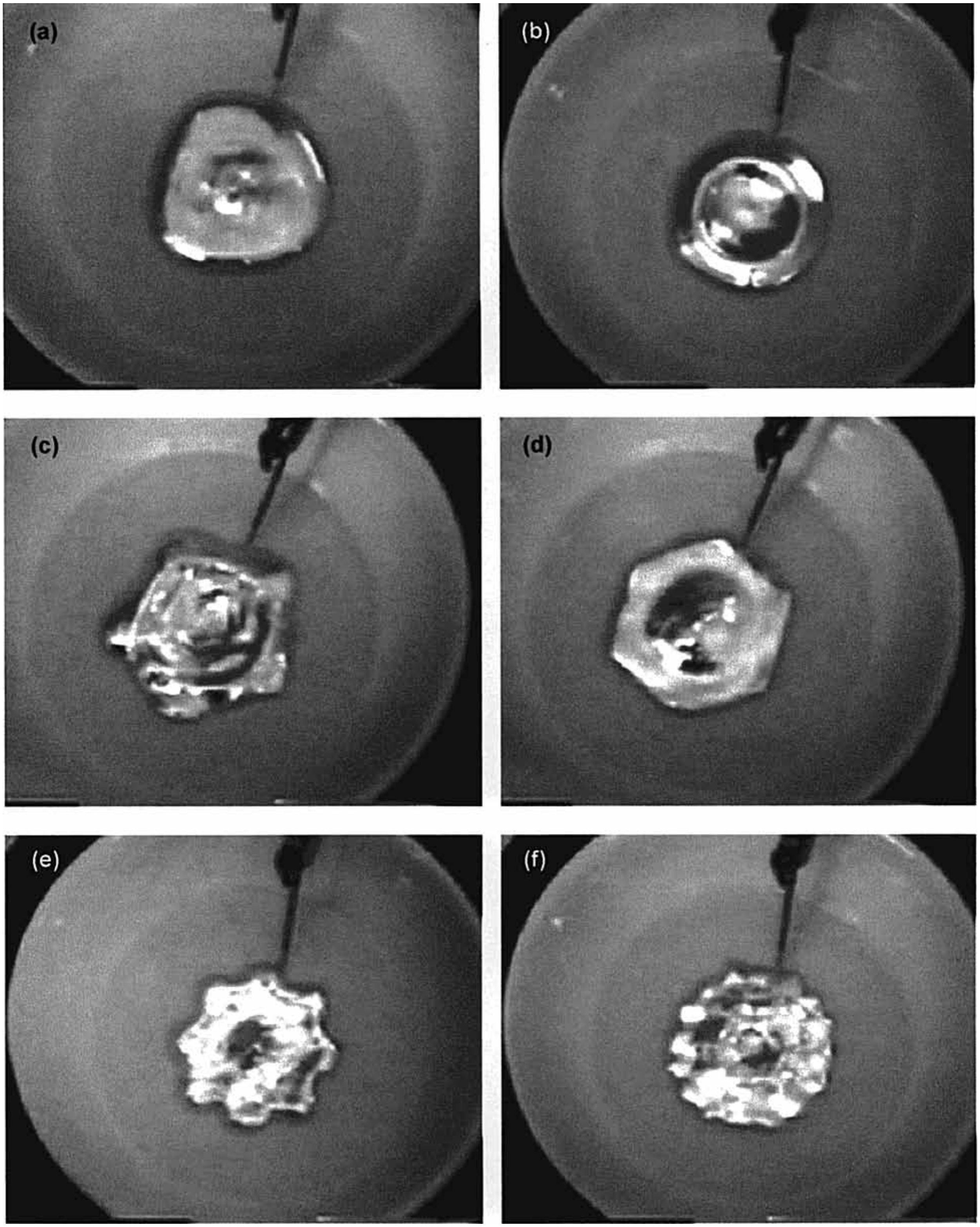

Figure 2. Different geometrical modes of oscillation (a) triangle shape or heart, (b) circle, (c) pentagon, (d) hexagon, (e) 8-pointed star, (f) 16-pointed star.

end between 740 and 720 mV/SCE for the maximun and 50−10 mV/SCE for the minimun, respectively.

Figure 3a, b, c shows the time series, the phase space representation ($\Delta V(t)$, $\Delta V(t + \tau)$, $\Delta V(t + 2\tau)$) with $\tau = 30\ \mu$s (approximately 10% of the period, about 0.03 s in this case) and the Fourier transform (FT), respectively, for the time interval 16.7−18.6 min. As can be seen from these figures, the behavior looks aperiodic in this early time of the evolution.

After the initial behavior the signal evolves and becomes periodic, showing first oscillations of period-1 for another 160 min. In this case, the extreme of the oscillations range between 660 and −0.01 mV/SCE. Figure 4a, b, c shows the time series, phase space representation, and the Fourier transform, respectively, for a selected time interval (40.5−42.2 min). There is only one frequency asociated with this mode as indicated by the FT (Figure 4c). The peaks correspond to the frequency

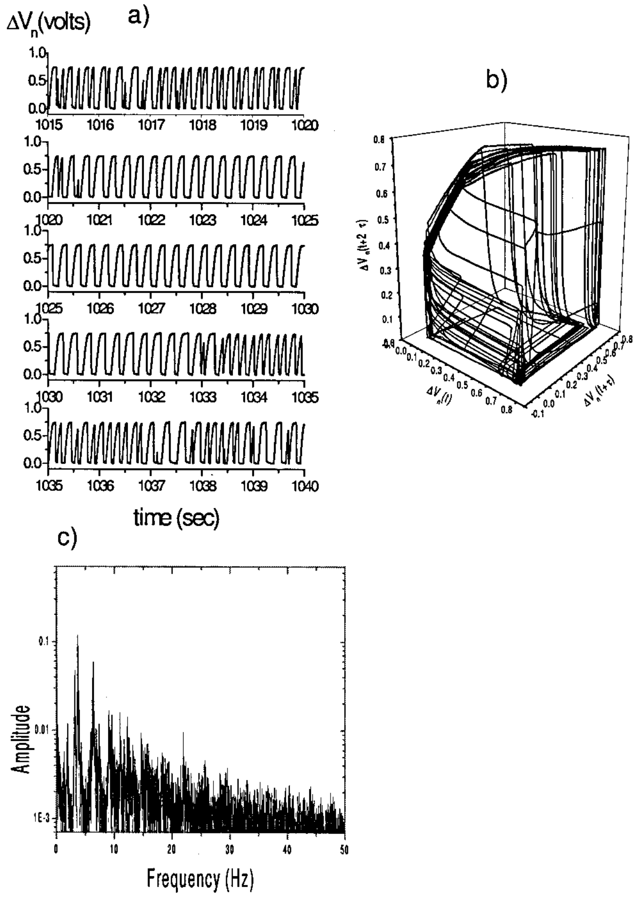

Figure 3. (a) Time series ΔV_n vs t, (b) phase portrait, and (c) Fourier transform (FT) for the time interval 16.7−18.6 min.

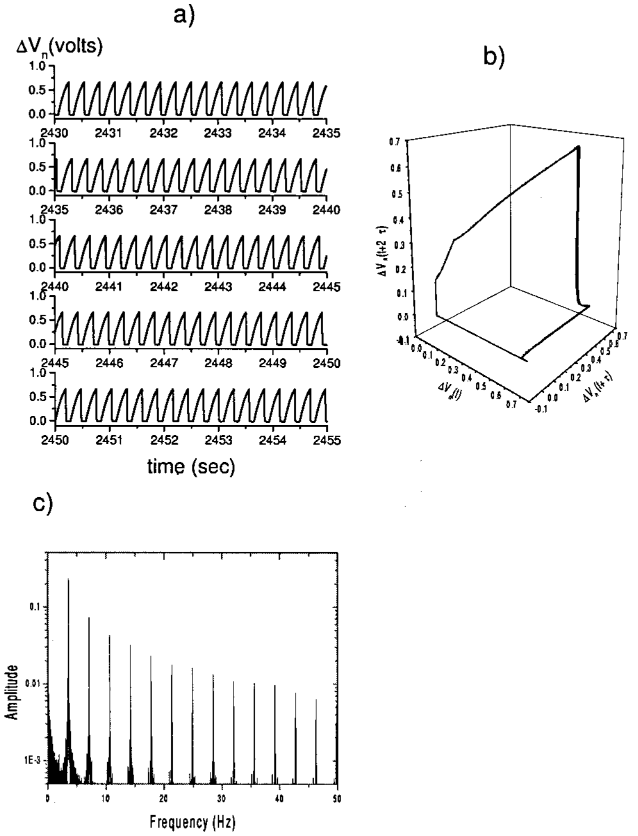

Figure 4. (a) Time series ΔV_n vs t, (b) phase portrait, and (c) Fourier transform for the selected time interval (40.5−42.2 min). There is a period-1 limit cycle asociated with this oscillatory mode.

$\omega_1 = 3.5598$ Hz and harmonics $2\omega_0$, $3\omega_0$,.... We have observed from the time series that during the time for which the period-1 signal persists the frequency decreases to $\omega_1 = 3.07$ Hz, that is, the mode slows down. The maximun in amplitude also decreases slowly to 560 and the minimun to −0.003 mV/SCE (Figure 4a). At the end of this interval the flat portion of the signal (associated with the quantity of Hg to be reduced) also shortens and the rise of the signal (related with the oxidation) is slower. During this period the kinetics of oxidation reactions are slower than the kinetics of the reduction reactions (as seen from the abrupt fall in the signal).

The system then turns for another 45 min into a period-3 attractor. In this case the FT shows peaks corresponding to three independent frequencies ($\omega_1 = 0.4942$ Hz, $\omega_2 = 0.5019$ Hz, $\omega_3 = 3.0270$ Hz) and linear combinations of them (not shown). Finally, the system spends the next 33 min in a period-2 attractor (Figure 5a, b, c). Again the FT analysis shows peaks corresponding to two independent frequencies ($\omega_1 = 0.5946$ Hz, $\omega_2 = 2.3938$ Hz) and linear combinations of them. The maxima and minima for the two peaks showed in Figure 5a are 650, 490 mV/SCE and 45, −10 mV/SCE, respectively.

Figure 6 shows the change from aperiodic to period-1 (Figure 6a), from period-1 to period-3 (Figure 6b), and from period-3 to period-2 (Figure 6c). As can be seen in the two first cases the passage from one periodic attractor to another is abrupt but in the transition period-3 → period-2 there are mixed signals of differents periods for some minutes before the period-2 is finally stabilized. This figure also shows that the oscillations are very regular and are not interrupted by phases of disorder as in an intermittency transition.

After 265 min the reaction stops, the oscillating potential signal disappears and a constant potential of 700 mV is established, corresponding to the initial potential value of the system constituted by Hg/H_2SO_4 6 M/electrodes, that is, the system before adding the oxidant and performing the reaction with metallic iron.

In conclusion, the system undergoes initially aperiodic oscillations, and as the reaction runs down the system becomes periodic showing period-1, period-3, and period-2 oscillations. The oscillatory behavior in each time interval is damped. We must remark, however, that the current notation for period-2, period-3, etc., oscillations in non linear systems refers to oscillations with fixed frequency and these terms are commonly associated with the Universal Sequence, which it is not the case of the present experiment. Damped oscillations separated by intermittent quiescent periods is what is called bursting and the above transitions could be connected with a subcritical Hopf bifurcation. With this interpretation the transition from period-1 to a periodic bursting with three peaks, to a periodic bursting with two peaks would reflect a Hopf bifurcation. This has great similarity with the bursting behavior observed with two coupled CSTRs.[12]

3.2. Mechanism of the Oscillations. Since the work of Keizer et al.[3] it is known that when the system is in an acidic, oxidizing solution, the formation and removal of a surface film is the main element in the mechanism for the oscillations. According to Keizer,[3] the mercury surface changes through the Hg−Fe voltage difference and surface-tension changes due to film formation. When the Hg surface flattens, electrical contact is made with the Fe-tip and the sulfate film is reduced. Here we propose the formation of different chemical species in the

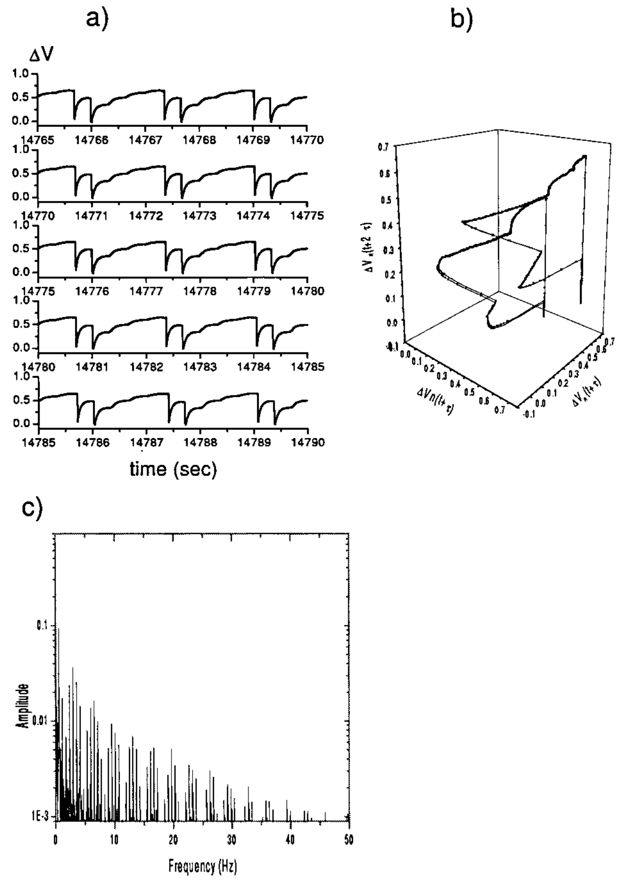

Figure 5. (a) Time series ΔV_n vs t, (b) phase portraits, and (c) Fourier transform for the selected time interval (246.1−247.7 min). There is a period-2 limit cycle asociated with this mode.

oxidation−reduction cycles which are responsible for the oscillations of the different periods. We construct the mechanism based on the formal reduction electrode potentials in acid solution.

(i) Start and Period-1 Oscillations. The oxidant Ce^{IV} reacts with the metallic Hg (referred hereafter as Hg^0) according to the following reactions:

$$2[Ce^{IV}(SO_4)_3]^{2-} + 2Hg^0 \rightleftharpoons Hg_2^{2+} + 2[Ce^{III}(SO_4)]^+ + 4SO_4^{2-}(aq) \quad \Delta V_n = 0.876\ \mathrm{V/SCE} \quad (2a)$$

$$2[Ce^{IV}(SO_4)_3]^{2-} + 2Hg^0 \rightleftharpoons Hg_2SO_4(sol\ ) + 2[Ce^{III}SO_4]^+ + 3SO_4^{2-}(aq) \quad \Delta V_n = 0.785\ \mathrm{V/SCE} \quad (2b)$$

$$2[Ce^{IV}(SO_4)_3]^{2-} + 2Hg^0 \rightleftharpoons Hg_2SO_4(ins) + 2[Ce^{III}SO_4]^+ + 3SO_4^{2-}(aq) \quad \Delta V_n = 0.785\ \mathrm{V/SCE} \quad (2c)$$

Here Hg_2^{2+} is the free ion in dissolution, Hg_2SO_4(sol) is the soluble molecular mercury sulfate, and Hg_2SO_4(ins) is the precipitated or insoluble mercury sulfate (film). We will denote here as Hg(I) any of these species. This three reactions occur in parallel with different kinetics given as a result an equilibrium potential of the system in agreement with the experimental values.

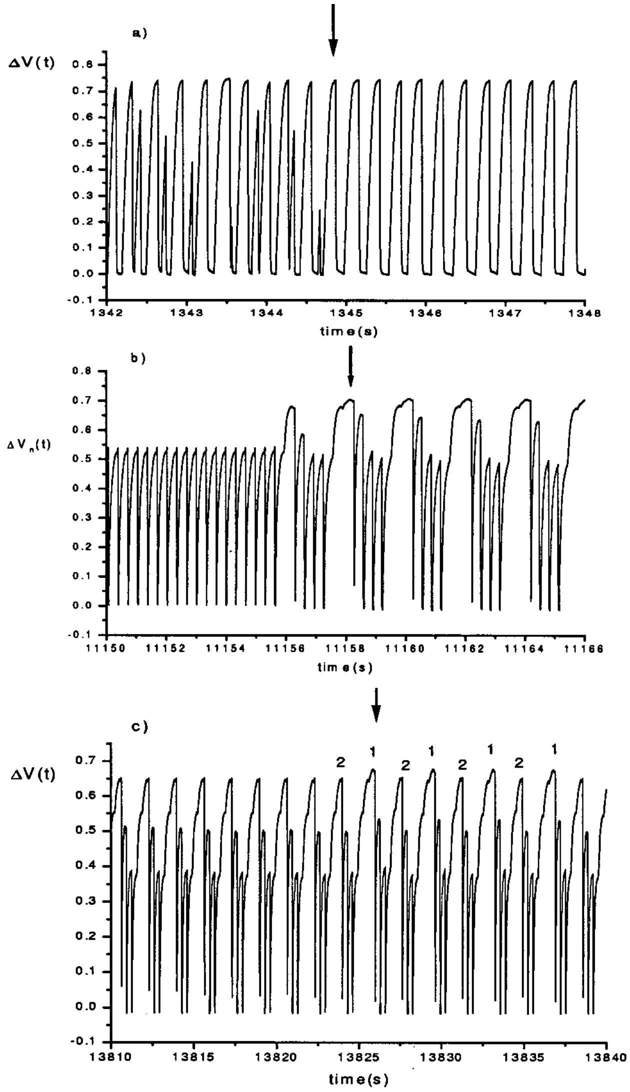

Figure 6. (a) Transition from aperiodic to period-1, (b) transition from period-1 to period-3, (c) transition from period-3 to period-2, the numbers are put only to distinguish between the two mixed periods. In all cases the arrows indicate the beginning of the transition.

The corresponding reduction reactions are (the metallic Fe is denoted as Fe^0)

$$Fe^0 + Hg_2^{2+} \rightleftharpoons Fe^{2+}(aq) + 2Hg^0 \quad \Delta V_n = -0.064\ \mathrm{V/SCE} \quad (3a)$$

$$Fe^0 + Hg_2SO_4(sol\ ) \rightleftharpoons Fe^{2+}(aq) + 2Hg^0 + SO_4^{2-}(aq) \quad \Delta V_n = -0.155\ \mathrm{V/SCE} \quad (3b)$$

$$Fe^0 + Hg_2SO_4(ins) \rightleftharpoons Fe^{2+}(aq) + 2Hg^0 + SO_4^{2-}(aq) \quad \Delta V_n = -0.155\ \mathrm{V/SCE} \quad (3c)$$

It has to be pointed out that the theoretical values calculated for eqs 2 and 3 have been done with the Nernst equation from standard normal potentials for each system, as reported in the literature corresponding to aqueous solutions. Strictly, a correction corresponding to the true 6 M sulfuric acid solution should be made. The potentials in sulfuric 6 M are not available in the literature and their determination is beyond the scope of this work. The theoretical potential values in the above and next equations can thus be compared only qualitatively with our experimental values.

We have observed the film presence during all the initial time interval, but at the end of that interval the film is not observable. The formation of the species Hg_2SO_4(sol) allows the establishment of an equilibrium between the free ionic mercury species in solution and the insoluble mercurous sulfate:

$$Hg_2^{2+} + SO_4^{2-} \rightleftharpoons Hg_2SO_4(\mathrm{sol}) \rightleftharpoons Hg_2SO_4(\mathrm{ins}) \quad (4)$$

As time goes on, the equilibrium is displaced toward the left part of reaction 4 in such a way that soluble and insoluble sulfate are consumed, only eqs 2a, 3a occur, and the period-1 is stabilized. This agrees well with the experimental values of $V \approx 770$ mV/SCE.

(ii) Period-3 Oscillations. When Ce^{IV} has been depleted, a second oxidant, the dissolved O_2, reacts with Hg^0 and the three oxidation reactions for this period-3 signal are

$$O_2 + 2Hg^0 + 4H^+ \rightleftharpoons 2Hg^{2+} + 2H_2O \qquad \Delta V_n = 0.796 \text{ V/SCE} \quad (5a)$$

$$Hg^{2+} + Hg^0 \rightleftharpoons Hg_2^{2+} \qquad \Delta V_n = 0.611 \text{ V/SCE} \quad (5b)$$

$$2[Fe^{III}(SO_4)_2]^- + 2Hg^0 \rightleftharpoons 2Fe^{2+} + Hg_2SO_4(\mathrm{sol}) + 3SO_4^{2-}(\mathrm{aq}) \qquad \Delta V_n = 0.450 \text{ V/SCE} \quad (5c)$$

(Hg^{2+} is also denoted as mercury(II)) and the corresponding reduction reactions are

$$Fe^0 + Hg^{2+} \rightleftharpoons Fe^{2+} + Hg^0 \qquad \Delta V_n = -0.035 \text{ V/SCE} \quad (6a)$$

$$Fe^0 + Hg_2^{2+} \rightleftharpoons Fe^{2+} + 2Hg^0 \qquad \Delta V_n = -0.064 \text{ V/SCE} \quad (6b)$$

$$Fe^0 + Hg_2SO_4(\mathrm{sol}) \rightleftharpoons Fe^{2+} + 2Hg^0 + SO_4^{2-} \qquad \Delta V_n = -0.155 \text{ V/SCE} \quad (6c)$$

The Fe^{III} is produced in the reactions

$$Fe^0 + 2H^+ \rightleftharpoons Fe^{2+} + H_2$$

$$2Fe^{2+} + Hg_2^{2+} + 4SO_4^{2-}(\mathrm{aq}) \rightleftharpoons 2[Fe^{III}(SO_4)_2]^- + 2Hg^0$$

The above potentials are also in agreement with the experimental values.

(iii) Period-2 Oscillations. The production of Hg_2^{2+} is very low now because Fe^{III} remains constant because the reaction

$$2Fe^{2+} + Hg_2^{2+} + 4SO_4^{2-}(\mathrm{aq}) \rightleftharpoons 2[Fe^{III}(SO_4)_2]^- + 2Hg^0 \qquad \Delta V_n = 0.541 \text{ V/SCE}$$

does not occur anymore. The concentration of Hg^{2+} grows such that $[Hg^{2+}] \gg [Hg_2^{2+}]$ and only reactions eqs 5a and b and 6a and b are produced.

In conclusion, Hg^0 reacts with oxidizing agents according to their oxidizing strength. During the initial step the reaction with Ce^{IV} can produce the species Hg(I) and Hg(II) due to its oxidizing strength. In the first lapse, the only species formed is Hg(I) since there is competition between the formation of Hg(I) with slow kinetics and Hg(II) with fast kinetics; only the slow kinetics mechanism can be observed. When the Ce^{IV} is entirely depleted, Hg^0 reacts with the oxygen dissolved in the aqueous solution; then with Hg^{2+} as the concentration of this species increases, and finally with the formed Fe^{III}. The proposed reactions to regenerate Hg^0 are the reductions of Hg(I) by the reducers Fe^0, Fe^{2+}, and H_2. When Hg(II) ≫ Hg(I) the reaction stops oscillating. This is supported by a γ-irradiation study in the next section.

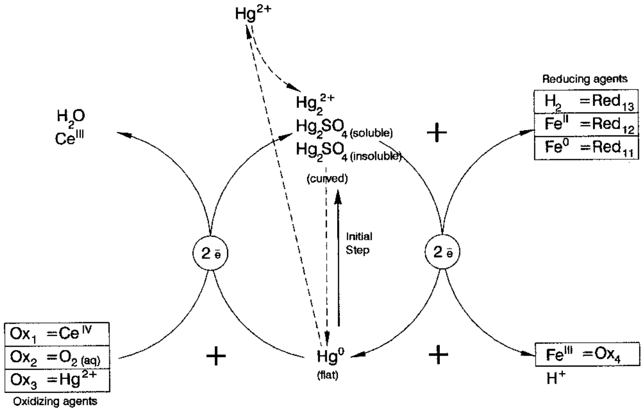

Figure 7. Probable mechanism of reaction for the mercury beating heart system. The oxidant Ce^{IV} is added at the beginning of the reaction, O_2(aq) exists from the atmosphere, and Hg^{2+} and Fe^{III} are generated in the course of the reaction. Fe^0, Fe^{II}, and H_2 are the reducing agents.

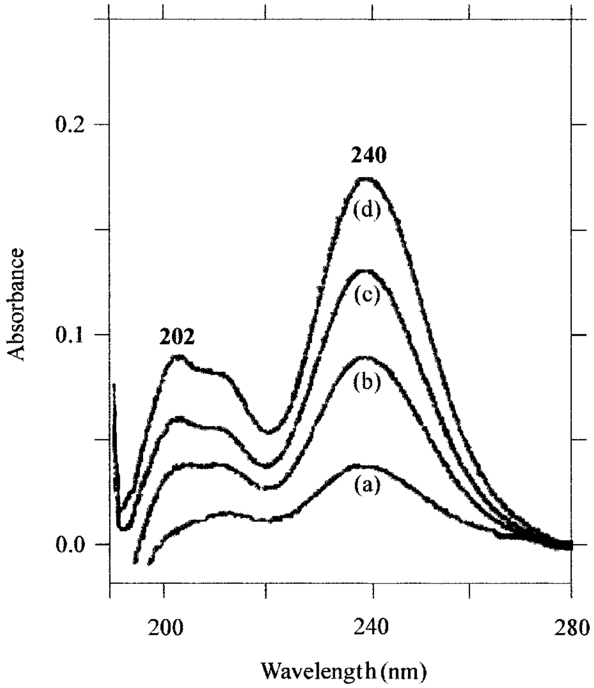

Figure 8. Absorbance spectrum of the Hg^0/H_2SO_4(aq) system. (a) Spectrum for the initial system after 15 min, (b) 1 h later, (c) 2 h later, (d) 3 h later.

We can summarize the mechanism of reaction through Figure 7 which shows the dynamics in terms of the chemical species.

3.3. γ-Irradiation. To demonstrate that chemical oscillations are possible even in the absence of Ce^{IV} oxidant we have performed experiments where mercury in 6 M aqueous solution of sulfuric acid was subjected to γ-irradiation. We show next that γ-irradiation generates in situ mercury Hg_2^{2+} which participates in the oxidation-reaction cycle described above.[13,14]

First, calibration curves for Hg_2^{2+}, Hg^{2+}, and Fe^{III} in 6 M sulfuric acid solution were prepared using standard salts: Hg_2SO_4, $Hg(NO_3)_2 \cdot H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, all from Merck

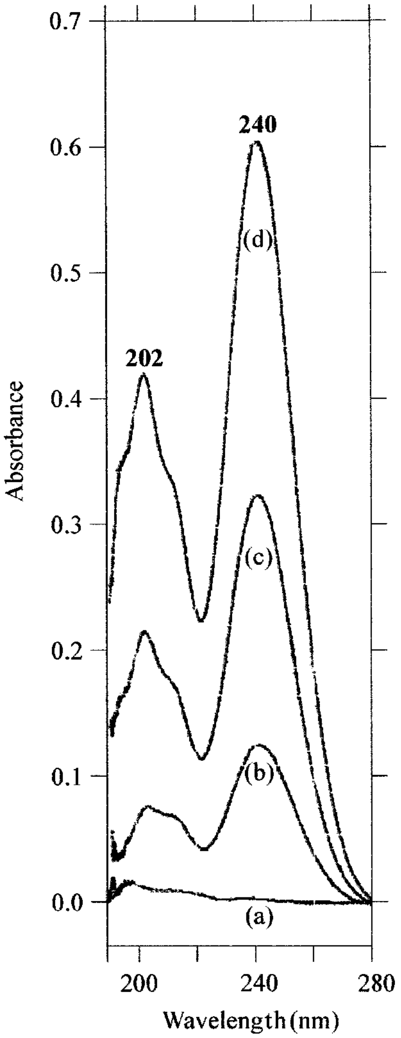

Figure 9. (a) Absorbance spectrum of the sample with no radiation of a system constituted by 8 mL of metallic Hg covered with 25 mL of 6 M H_2SO_4; (b) spectra of the system irradiated with doses of 150 Gy, (c) irradiated with 300 Gy, and (d) irradiated with 450 Gy.

(Fe^{2+}, which is the other species participating in eqs 3, 5, 6, does not absorb in the UV/VIS region). In this way the spectra show two absorption peaks at 240 and 202 nm which characterize Hg_2^{2+} and an unique absorption peak at 199 nm characterizes Hg^{2+}. The absorption spectrum of Fe^{III} shows two peaks at 221 and 300 nm.

Second, the stability of the Hg^0/H_2SO_4(aq) under the presence of atmospheric oxygen was studied. The curves in Figure 8 show the corresponding spectra for samples taken every hour (b,c,d) as compared with the initial spectrum (a). We found that atmospheric oxygen oxidizes Hg^0 producing small amounts of Hg_2^{2+} of the order of $(1.0-1.3) \times 10^{-4}$ M as calculated from curves b−d.

Third, the Hg^0/H_2SO_4(aq) system was irradiated with γ-rays at various doses to determine the kind of Hg species which are produced. Figure 9 (a) shows the spectra of absorption of the sample without irradiation and with different doses of irradiation, (b) = 150 Gy, (c) = 300 Gy, (d) = 450 Gy. It can be seen that Hg_2^{2+} is the only species produced.

When the metallic iron-tip was included in the system the reaction displayed periodic oscillations with a total lifetime of reaction of 2 min for the dose of 150 Gy. In this case there is no film formation. The in situ increment of Hg_2^{2+} also increased the lifetime of reaction. So oscillations were obtained for almost 7 h with a dose of 900 Gy. In general terms the oscillations showed the same pattern of behavior as that obtained in Section 3.1 when oxidant was added, showing period-1 orbits, mixed period-4 or -3 orbits, and period-2 orbits in the final phase of the reaction.

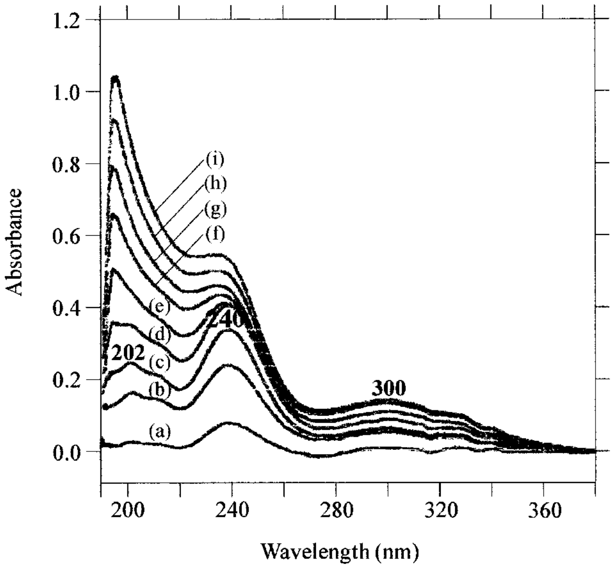

Figure 10. (a) Absorbance spectrum of the system Hg^0 in sulfuric acid + standard mercurous sulfate salt. The plots refer after the metallic iron was put into contact and the oscillatory reaction begun: (b) at 15 min, (c) at 30 min, (d) 45 min, (e) 60 min, (f) 75 min, (g) 90 min, (h) 105 min, and (i) 120 min.

Besides, we have verified that when extra Hg_2^{2+} was added to the system $Hg^0/H_2SO_4(aq)/Fe^0$ (this is done by adding a very small amount of the standard mercurous salt) the production of Hg^{2+} was detected. Figure 10 shows the spectra where the reaction was monitored every 15 min. The spectra (a), (b), (c), and (d) show the absorption peaks corresponding to Hg_2^{2+} and the production of Hg^{2+} can be observed from (e) on. We observed that the oscillations became extinguished when $[Hg^{2+}] \geq 6[Hg_2^{2+}]$.

The fact that the Hg^{2+} concentration limits the oscillations can be tested again by repeating the reaction, left to oscillate for a certain time lapse, and then adding by hand the necessary amount of standard mercuric salt which produces Hg^{2+}. In fact, this stops the reaction.

4. Conclusion

We have studied experimentally that in the "mercury beating heart" system oscillations are induced by chemical reactions which occur in the Hg/solution interface generating mercury(I) in the form of free Hg_2^{2+} ion or, in molecular form, as a soluble mercurous sulfate or a mercurous sulfate film. We have proposed the presence of the species Hg_2SO_4(sol) which allows the establishment of an equilibrium between the free ionic species in solution and the insoluble mercurous sulfate through eq 4.

From the electrochemical point of view, the pairs Hg^0/Hg(I), Fe^0/Fe^{2+} generate an electrical field which affects the surface tension and generates modes of oscillations. The modes of oscillation are a function of the value of the global potential difference between the chemical reactions. When the chemical species involved produce a potential difference between 770 and 760 mV/SCE, the produced voltage signal is irregular, and apparently all the intrinsic modes of oscillation of the MBH reaction appear. In this case the modes of oscillation are heart, circle, pentagon, hexagon, 8- and 16-pointed stars, as shown in

Figure 2. To our knowledge all these different modes of oscillations have not been published before.

For the high concentrations of the acid we have studied, we have shown that there exists a transition between three regimes which correspond to limit cycles of period-1, -2, and -3 (damped oscillations). For these regimes we propose oxidation−reduction reactions, eqs 2−6, where the calculated potential for each maxima agree well with the experimental values. The oscillatory dynamics of the MBH extincts, that is, stops oscillating when [Hg(II)] $\gg$ [Hg(I)]. We do not think that the sequence of these transitions is universal but instead it depends on the specific concentrations of the reactants and as it was noted before, could be interpreted in terms of a subcritical Hopf bifurcation. The study of the nature of these transitions deserves more studies.

Finally, we have demonstrated that γ-radiolysis of Hg^0 in 6 M sulfuric acid solution, in air, generates primary oxidizing species which cause the oxidation of Hg^0 to Hg_2^{2+}, in such a way, that it may be said that ^{60}Co γ-rays induce the generation of oscillations. This investigation opens a perspective to radiation chemistry for the study of oscillatory reactions, favoring an increase in reaction time by the in situ generation of the species which drives the oscillations.

There are still many open questions in the MBH reaction, for example the nature of the transitions between the different regimes, their sequence, and the exact role of the concentrations, just to mention a few of them.

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