A Study of Some Electrochemical Effects in a Field of Stationary Ultrasonic Waves

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An interesting electrochemical experiment with ultrasonic waves has been reported by Young and Kersten. Electrolysis in a field of stationary ultrasonic waves was found to produce ripples on the cathode (which was arranged parallel with the direction of sound propagation). The distances between these ripples corresponded to half sound wave lengths. As an explanation of the phenomenon it was suggested that concentration differences are set up in the acoustic field. In connection with work on the possibility of a permanent separation in a field of stationary ultrasonic waves a study was therefore undertaken of this and adjacent phenomena.

EXPERIMENTAL DETAILS

Apparatus

The ultrasonic apparatus was a commercial unit, Crystalab Ultrasonicator Model SL 520, giving the frequencies 400, 700, 1 000 and 1 500 kc/s. In the experiments reported here only the frequencies 400 and 700 kc/s were used because of the need for rather long wavelengths.

In order to fit our purpose it was necessary to make a modification of the sound emitter unit. The crystal is here mounted in a comparatively small vessel which is placed above the frame of the Tesla transformer in its oil bath. The oil in the crystal vessel is thermostated by circulation through a cooling bath and a heater coil (max. pump velocity 7 liters/min). The fast rate of circulation permits a rapid temperature control quick in response.

The necessity of arranging the reaction vessel in a fixed and defined position has been pointed out in the literature. In Fig. 1 is shown how this was attained in these experiments. By means of the three screws the ring was adjusted parallel with and at the desired distance from the quartz plate. The accuracy in the position and parallelism was not very high and amounted to some 0.01 mm. In the ring there are turned notches which fit with the separation cell and keep it in position. Since the separation cells were all of the same size this ring and frame could be used throughout in the experiments.
In order to obtain a good stationary wave system it was necessary to know the sound velocity in the actual transformer oil so as to be able to compute an appropriate value for the position of the ring. The sound velocity in question was therefore determined, \( v_{25^\circ C} = 1416 \text{ m/s}, \frac{dv}{dt} = -3.7 \text{ m/s} \cdot ^\circ \text{C}, \) by means of a simple and reliable method utilizing thermistors, as has been described elsewhere. Now it has to be pointed out that the adjustment of the stationary wave system is not critical. Instead it is found that the states of non-resonance are very distinct and sensitive.

**Acoustic Window**

The cells in which the separation were to take place will be described in a following section. However, concerning the two fundamental parts, the acoustic window and the reflector, some general remarks will be given here.

The reflectors were made with the non-resonant thickness of 1/4 \( \lambda \), and furthermore the upper surface was in contact with air. The reflection is for this arrangement very near 100 %.

An acoustic window is made either as thin as possible or with the resonant thickness of 1/2 \( \lambda \). The two alternatives show some differences in their properties.

A "thick acoustic window" permits a defined and stable design and under suitable conditions the sound transmission may be very high. Especially suited materials for the thick windows are polystyrene or plexiglass, which have rather low values for the acoustic resistance. At higher acoustic intensities, however, there are some complicating factors. The production of heat in the window will increase its temperature and thereby change the sound velocity in it. In this way the window more or less will come out of resonance with an accompanying lower transmittance. Furthermore the thickness of the window is a cause of poor heat transference from the reaction vessel and thus makes the temperature control more difficult.

Of these reasons the author has preferred to use thin metal windows in these experiments except for one special case.

**DECREASE OF SOUND INTENSITY BY LIQUID STREAMING**

Another very important problem in connection with these general experimental considerations deserves mention, especially as the phenomenon in question does not seem to have been observed before.
Fig. 2. Decrease of sound by liquid streaming. The points refer to the relative acoustic intensity; the circles to the factor

\[ f = \frac{(E_b)_{w=0}}{(E_b)_{w}}. \]

In order to secure good thermostating and to carry away gas bubbles formed by cavitation the experimental setup was usually so arranged that part of the circulating oil was sweeping through the interspace between the quartz and the window of the separation cell. It was not at first thought that this could disturb the sound transmission. However, during the course of the investigation it was realized that the liquid streaming had a very marked influence on the acoustic intensity as measured within the cell. The very interesting thing revealed by the diagram in Fig. 2 is that at high rates of oil circulation the sound in the cell is reduced to less than one quarter of the value for a stationary liquid. (The relative acoustic intensities have been determined by measurements of the sound pressure with the aid of a conical reflector suspended from a weighing balance.) This effect is somewhat surprising as there are very great differences between the sound velocity in the oil and the streaming velocities in question.

The phenomenon, however, probably depends on the fact that the circulating oil will carry with it part of the energy accumulated in the acoustic field. Preliminary considerations on this lead to the formula

\[ f = 1 + \frac{w}{c} \cdot V \]  

(1)

where \( f \) is the ratio between the maximum value for the integrated acoustic energy density at the streaming velocity \( w = 0 \) and the value at the actual velocity; \( V \) is the considered volume of the interspace between the quartz and the cell; and \( c \) is a constant which is closely connected with the coefficient of sound absorption.

This function is demonstrated in Fig. 2 where, as an alternative ordinate, \( f \) is given as a function of \( w \). It is seen that above a certain value for the oil velocity the factor \( f \) is a linear function of \( w \). The reason for the "induction period" which does not come out in the given theoretical relation, is to be found in the actual experimental conditions. The reflector by means of which the acoustic intensity was determined was of a less diameter, \( = 2.1 \text{ cm} \), than the acoustic field, the diameter of which was about \( 3.0 \text{ cm} \). The decrease in the energy density will set in at the side where the fresh liquid is coming. Under the actual experimental conditions therefore a certain threshold value for the oil velocity is necessary in order that the zone with a less energy density will come within the range of the reflector.

To avoid the influence of the phenomenon which has been described here a compromise solution had to be applied. The diameter of the separation cell was made a little less than
the acoustic field and the oil velocity was moderated as to give sufficient chilling and to carry away gas bubbles, however, without affecting the acoustic energy transmitted to the cell.

ELECTROCHEMICAL EXPERIMENTS

Ripples on electrolysis

Young and Kersten’s experiments ¹, in which ripples were obtained on electrolysis in an ultrasonic field, seemed worth further study in order to find out whether the ripples were caused by real concentration changes or could be explained as a pure electrochemical phenomenon.

It is of interest to know whether the preferred metal ion discharge does take place in the nodes or in the antinodes. For this purpose the arrangement described in Fig. 3 was utilized. Here the cathode is applied on the reflector in a fixed position. In a) there will be a node in the reflector plane and in b) an antinode. By measurements of the distances between the ripples and the reflector it was found that the preferred metal ion discharge took place in the antinodal planes which so far was in harmony with the separation observed in suspensions.

The first experiments on this were made with iron much in the same way as described by Young and Kersten. However, in this case the conditions did not seem quite defined depending on simultaneous hydrogen evolution. Such complications may come out also in the other formerly reported cases, so it was decided to perform some experiments under coulometer conditions. A copper coulometer electrolyte was chosen for this purpose (CuSO₄ · 5 aq, 125 g/l; H₂SO₄ conc., 50 g/l; C₂H₅OH, 50 g/l; current density 0.02 A/cm²; temperature ~ 50° C). The cathodes were of polished steel or of copper. In these experiments there was no detectable gas evolution and distinct ripples were formed even at such low ultrasonic intensities as 0.1—0.2 W/cm². Furthermore it was observed that the ripples became visible simultaneously with the first appearance of the electrolytic discharge. (The sound and the electrolysis were started on the same time.) The relaxation time for the process leading to ripples thus seemed to be less than thirty seconds. — A separation, however, should occur by diffusion and convection and presumably
take a longer time. — When electrolyzing small quantities of copper on the stainless steel cathode it was also convincingly demonstrated that the ripples really corresponded to differing quantities of discharged material and not to variations in structure and appearance.

**Emf measurements**

It seemed reasonable that some study of electrode potentials in the ultrasonic field might give further information concerning the origin of the ripple formation.

*Temporary* changes in the electrode potentials with the same frequency as the applied sound have been studied by Nikitin\(^6\). Such variations have also been shown to occur at a hydrogen electrode, the cause, however, here being the rapid changes of state in the hydrogen gas\(^7\).

Marinesco has observed a more *permanent* change of the electrode potential. He noticed that the emf of an element with one electrode subjected to ultrasonic waves changed so as to correspond to an increased ionization tendency of the ultrasonorated electrode\(^8\). On the other hand Schmid and Ehret reported that no change could be observed on the equilibrium potential of a copper electrode in 0.1 \(M\) \(\text{CuSO}_4\) solution\(^9\). Their negative result may be due to that the conditions for forming stationary waves were not good in the utilized experimental arrangements; the sound was focussed by means of a kind of funnel on to the electrode.

The present investigation was chosen to study the influence on silver electrodes in silver nitrate solutions.
For most of these experiments a cell was used, the principles of which appear in Fig. 4. The upper electrode is here attached to the reflector and is therefore situated in a node; the other electrode, which simultaneously functions as a thin acoustic window, is arranged 1/4 λ from there, viz. in the nearest antinode. Smaller adjustments in the acoustic distance between the quartz and the cell are obtained by varying the oil temperature and within the cell by altering the reflector position with the micrometer screw. It was hoped to match the acoustic properties of the system in this way in order to obtain as good stationary waves as possible and a maximum in the observed potential difference between the nodal and the antinodal electrode. However, this approach was not very successful. Among the many factors, which make it difficult to obtain reproducible results, is to mention the heterogeneity in the acoustic field itself as emitted from the quartz and the fact that the geometry in the experimental apparatus was not ideal; optical parallelism was probably necessary. Difficulties of this kind are not easy to overcome even by a most careful design of the experiments as can be inferred from other partly analogous work on ultrasonic stationary waves where furthermore the need for quantitative results has been of first class importance.\textsuperscript{9,10}

The silver electrodes were cleaned with diluted nitric acid and rinsed in distilled water before use. The solutions were degassed in vacuum; the cell was also put under the vacuum after the filling in order to remove any air bubbles which might adhere to the electrodes. The emf was registered by means of a 10 mV printing potentiometer (depending on the instability of the emf it was necessary to couple all the six measuring circuits of the used potentiometer in parallel, thus the instrument worked as a single function writer).

The results for some runs at 400 kc/s, 25° C and 0.1 M AgNO\textsubscript{3} are given in Fig. 5. Accurate values for the actual acoustic intensity within the cell are very difficult to obtain. Therefore in the diagram the electric input fed to the h.f. generator is given. However, from some single experiments in which the sound pressure within the cell was measured a conversion factor was computed; by multiplication with 0.03 the electric input is converted to give an approximate value for the acoustic efficiency in W/cm\textsuperscript{2} within the cell. Some probable reasons for the bad reproducibility which appears in the diagram have been mentioned above. From the diagram, however, it is
clearly seen that potential differences are set up, the value of which increase with increasing sound intensity. The electrode in the antinodal position is more positive which is in harmony with the results of the ripple experiments. The magnitude of the effect in these experiments is seen to be of the order of $3 \pm 2$ mV per 1 W/cm$^2$.

Ultrasonic experiments are always complicated by the production of heat which accompanies sound absorption. Therefore it was necessary to learn if the resulting emfs could be caused by thermal effects, depending on the temperature inequalities in the cell.

In separate experiments the temperature coefficient of the element in question was determined to be $\sim -0.15$ mV/°C (the warmer electrode is more negative). In order to obtain a value for the actual temperature differences that might occur, some experiments were performed with a special cell, provided with thermocouples, one in the $1/3\lambda$ window of polystyrene and the other in the reflector. This cell was placed on a warm plate and the temperature difference and the emf of the cell were observed. The "apparent temperature coefficient" was in this way found to be $\sim -0.03$ mV/°C; thus $0.03/0.15 = 20\%$ of the temperature difference between the thermocouples appeared between the electrodes and was measured as a "thermal emf". On the other hand the temperature differences which were observed on ultrasonic treatment at 20 W electrical input were of the order of some 0.1 °C, whereas the emf-values amounted to some mV. The "thermal emf" in this case may thus be ascertained to be less than 1% of the actual value.

**Kinetic study**

As a possible way to find the cause of the ultrasonic emfs a study of the kinetics of the electrode processes in question was undertaken.

In Fig. 6 a typical run is reproduced as it comes out on the recorder's strip chart. It is recognized that a suitable part for a kinetic analysis is the back trend to the initial value after the sound has been shut off. Now the question is whether this process is a back diffusion of ions between layers of different concentration, or a restoring of the normal conditions in the electrode double-layer. In the latter case the action of the sound is assumed to be some
influence restricted to the double-layer region itself. In order to decide between these two alternatives it is suitable to deduce theoretical expressions for the kinetics of the two cases.

The following treatment of the kinetics of the electrode reaction is performed in terms of the theory of absolute reaction rates. — At the surface of the electrode two processes occur, the discharge process and the reverse reaction, the ionization process. When the rates of these processes are equal there is no net flow of current and the electrode potential has the equilibrium (static) value. In the case considered here the applied sound has caused the static value to change. After removal of the sound the potential will trend back to its original value. During this change there is a net flow of current between the electrode and the electrolyte but this electricity transport is restricted to this region and serves only to alter the charge density of the electrode capacitor.

The rate of the forward reaction, the discharge process, is given as

\[ k_1 = a_+ \frac{kT}{h} \exp(-\Delta F_1^+/RT) \exp(aVF/RT) \]

and for the ionization process

\[ k_2 = \frac{kT}{h} \exp(-\Delta F_2^-/RT) \exp(-(1-a)V/RT) \]

where \( a^+ \) is the activity of the metal ion in the bulk of the electrolyte, \( \Delta F_1^+ \) and \( \Delta F_2^- \) the activation energies associated with the two processes, \( V \) the electrode potential (the sign of which is chosen in accordance with the Lewis & Randall convention) and \( a \) is the fraction of the electrode potential which will facilitate the forward reaction (a fuller account of this can be found in the literature).

If the sound has caused the electrode potential to be more positive, the resulting process after removal of the sound will be the discharge reaction, \( k_1 - k_2 > 0 \). The potential difference, referred to the normal equilibrium value, \( V_e \), is represented by \( E \), in this case \( E = V - V_e > 0 \). Furthermore the electric current, \( i \) amperes, from the solution to the electrode over 1 cm² of the electrode layer is for the case of univalent ions

\[ i = F \cdot (k_1 - k_2) \]

where \( F \) stands for 1 Faraday.

The electrode layer may as usual be looked upon as a plate condensator with the capacitance \( C \). Accordingly we may write

\[ i = -\frac{\partial V}{\partial t} \cdot C \quad \text{and} \quad \frac{\partial V}{\partial t} = -\frac{F}{C} \cdot (k_1 - k_2) \]

Insertion of the appropriate expressions and rearranging results in

\[ \frac{\partial E}{\partial t} = \frac{F}{C} \frac{kT}{h} \left[ \exp(-FE/RT) - 1 \right] \cdot \left[ \exp(aF(V_e + E) - FV_e - \Delta F_2^-)/RT \right] \]
ULTRASONIC WAVES

Under the conditions that $E < V_0$, the second exponential will vary much less with $E$ than the first one, so we may put approximately

$$\frac{\partial E}{\partial t} \sim c \cdot [\exp(-FE/RT) - 1]$$

(2)

The value of the constant $c$ is inferred from the more general formula. The solution to the simplified equation is

$$c \sim \frac{1}{t_2 - t_1} \left[ E_1 - E_2 + \frac{RT}{E'} \ln \frac{\exp(-FE_1/RT) - 1}{\exp(-FE_2/RT) - 1} \right]$$

(3)

In this case it is justified to use the approximation $e^x \sim 1 + x$, thus

$$c \sim \frac{0.059 \ 10\log (E_1/E_2) + E_1 - E_2}{t_2 - t_1}$$

(4)

At small values for $E$ it is realized that the function will turn into a true exponential one.

$$c \sim \frac{0.059 \ 10\log E_1/E_2}{t_2 - t_1}$$

(5)

The kinetics of the other, above mentioned, alternative, where diffusion is assumed to be the rate-determining stage, is not possible to elucidate in a satisfying way because of the lack of knowledge of the primary concentration distribution. A very approximate treatment, however, yields the result

$$\frac{10\log (E_1/E_2)}{t_2 - t_1} \sim \text{constant} \cdot D$$

(6)

where $D$ is the diffusion coefficient of the dissolved salt.

The two cases yield approximately the same result (first order kinetics). In spite of this it is realized, however, that e.g. by changing the viscosity of the medium and thereby the diffusion coefficient it should be feasible to distinguish between the two treated alternatives.

Besides ultrasonic experiments on this were some other experiments performed for the sake of comparison. Two silver electrodes were arranged in a vessel with silver nitrate solution. (The electrodes had to be wholly immersed in the electrolyte and the connecting wires isolated in order to avoid the simultaneous contact between electrode, electrolyte and air). In the experiment the one electrode was placed in aq. dest. for some 10 minutes and thereafter put back in the electrode vessel. The emf of the cell was then registered in the same way as in the ultrasonic experiments. The kinetics of the emf change was found to be analogous to that which was observed in the ultrasonic experiments.

The mean values for the kinetic constant $c$ that were obtained in these experiments (altogether 60 runs) are given in Table 1; all experiments were performed at $25^\circ$ C. The values are seen to be of the same magnitude throughout, about 0.7, within the limits of experimental error. An important result
**Table 1. Kinetic experiments.**

<table>
<thead>
<tr>
<th></th>
<th>Electrolyte</th>
<th>Type of experiment</th>
<th>( c \times 10^4 )</th>
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<tbody>
<tr>
<td>a</td>
<td>0.1 ( M ) AgNO(_3)</td>
<td>Ultrasonic treatment</td>
<td>0.57 ± 0.11</td>
</tr>
<tr>
<td>b</td>
<td>( \rightarrow )</td>
<td>Immersing in aq. dest.</td>
<td>0.79 ± 0.10</td>
</tr>
<tr>
<td>c</td>
<td>1.0 ( M ) AgNO(_3)</td>
<td>Ultrasonic treatment</td>
<td>0.71 ± 0.08</td>
</tr>
<tr>
<td>d</td>
<td>( \rightarrow )</td>
<td>Immersing in aq. dest.</td>
<td>0.63 ± 0.07</td>
</tr>
<tr>
<td>e</td>
<td>( \rightarrow ) with 50% glycol</td>
<td>Ultrasonic treatment</td>
<td>0.80 ± 0.09</td>
</tr>
<tr>
<td>f</td>
<td>( \rightarrow ) 50%</td>
<td>Immersing in the corresponding solvent</td>
<td>0.72 ± 0.13</td>
</tr>
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is that the process does not seem to behave as to be diffusion controlled, which can be inferred from c) and e). The viscosities of these solutions differ by a factor of \( \sim 4 \) and therefore the diffusion coefficient \( D \) in c) should roughly be one quarter of that in c). The approximate accord between c) and e) therefore proves that the observed kinetics is not dependent on any diffusion process in the solution. This is in harmony with the result of the direct separation experiments reported in \(^2\). — In b), d) and f) the electrode after the treatment with the solvent carried with it a thin film of the pure solvent when it was immersed in the electrode vessel. Even in these experiments there seems to be no influence of diffusion, which, however, must depend on the rough experimental procedure.

Concerning the nature of the ultrasonic influence on the electrode potential it can be concluded that in the studied case the electrode layer after the ultrasonic treatment seems to be rebuilt in much the same way as after treatment with the pure solvent. It may also be added that the accord between a), b) and e), d) is not in harmony with the given theoretical treatment of the electrochemical alternative. The value of the kinetic constant should here be direct proportional to the silver ion activity. As this is not the case one must draw the conclusion that the rate-determining stage is one not involving silver ions but some other species, which are in about the same concentration in all the experiments.

The fact that the electrode potential in the node will be more positive and thus less noble may also be compared with the author's observation \(^12\) that the oxidizing action of the ultrasonic waves is located to the nodal planes. (In the latter case cavitation is held responsible for the effect). However, it does not seem possible at present to draw any firmer conclusions concerning these highly complicated and uncertain phenomena.

The high experimental error was afterwards found to depend on an ageing effect. In Fig. 7 values are given for \( 10^\log c \) as a function of the logarithm of the
time after the cleaning of the electrode with diluted nitric acid. The disturbance of the electrode layer was attained by immersing in distilled water. (This diagram constitutes also another proof that diffusion is not a rate factor in b), d) and f).) Because of the ageing effect, however, some experiments of the type a) and b) have been performed with the same electrode and at about the same time. The accord was now found to be better, within 10% in single determinations.

SUMMARY

The preferred metal ion discharge in electrolysis in a field of stationary ultrasonic waves is found to take place in the antinodes. The potential of a silver electrode is changed so as to be less noble in the nodal position. A kinetic treatment of the phenomenon is performed.

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LITERATURE


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