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SOME OBSERVATIONS ON THE DROPPING MERCURY ELECTRODE

WM. C. OELKE AND M. SHIELDS

In the course of an investigation of the oxidation reduction potentials of some organic systems, it was found impossible to obtain concordant measurements by the ordinary methods. Accordingly, we turned to the polarographic method first developed by Prof. J. Heyrovsky of the University of Prague and recently gaining favor in this country.

The polarographic method consists of applying, by means of a dropping mercury electrode, a steadily increasing electromotive force to a solution of some substance which can be reduced. Current and voltage are measured and recorded graphically. There is little current increase with respect to voltage until a point is reached where the voltage is sufficient to reduce the substance. The current then rises suddenly until the rate of the reaction becomes steady, when the curve again flattens out to a gentle slope as before. A whole series of reducible substances may be determined from the same solution in this way if their reduction potentials differ by as much as .2 volt.

The reduction potential, measured at a point half the height of the steep part of the curve, is called the half wave potential, and is characteristic of the system reduced. The height of the curve is proportional to the concentration of the substance in solution. Thus the method is not only qualitative but quantitative as well.

Since the purchase of a commercial polarograph was not possible, we were restricted to a system made up of laboratory apparatus. Readings had to be taken by hand and the result was that the work progressed very slowly.

The circuit¹ used consisted of a simple potentiometer circuit which is used both for measuring the potential difference applied to the experimental cell and the current through the cell. The current may be read directly from the potentiometer dial by measuring the potential across a ten thousand ohm resistance in series with the cell.

Fig. I shows the form of cell which we have found quite satisfactory. Instead of employing a pool of mercury as the second

¹ Kolthoff and Lingane. Chem. Rev. 24-12-1934.

² Hohn — Z. Electrochem. 43-127-1937.

Maassen — Angew. Chem. 50-375-1937.

electrode, we have incorporated a calomel electrode directly into our experimental cell² through a KCl salt bridge. Actual junction between the KCl and the solution is through a ground glass joint.

As a rule, polarographic curves plotted by hand on small scale paper are smooth curves with inflection points, but without discontinuity. However, if the curves are recorded continuously as by an automatic apparatus, and plotted on a large scale, they will consist of a series of saw teeth; each saw tooth corresponding to the formation, growth, and discharge of a single drop at the capillary of the mercury electrode. That is, the galvanometer used as a current measuring instrument will show a fluctuation from a minimum point to a certain maximum as a drop grows; the mean position of the indicator determining the curve.

We have found evidence that the flow of current from the growing drop is not as simple a procedure as this would seem to indicate. The current through the cell does not increase smoothly from a minimum to a maximum as the drop grows, but appears to oscillate in some manner.

The effect was first noticed while working with an aqueous solution of 0.001 N. CdCl_2 , NiCl_2 , MnCl_2 , and 0.1 N. Ca Cl_2 . We had had difficulty in obtaining a flow of current through the cell and were making continuity tests by various methods. One of these was a 2200 ohm radio head set connected in series with the cell. It resulted in the following interesting phenomenon.

When the dropping electrode was made positive, the sound in the head phone as each new drop started to form began with a high pitched musical note which rapidly lowered as the drop grew larger until, just before the drop fell, it had fallen to a harsh buzzy rasp. We were able to find no literature mentioning such an effect and so concluded that it had not been previously observed.

We are at present attempting to define the conditions under which the sound phenomenon will take place. A simplified circuit is being employed. (Fig. II.)

We discovered first that when we reversed the polarity of the cell, that is, made the dropping electrode negative, the drops of mercury became extremely minute and fell almost like rain from the capillary. The sound in the head phone was an even, very rapid patter, like hail on a tin roof. Making the mercury electrode positive again caused the drops to return to normal size and dropping rate, and to again produce the musical sequence.

Next we added a rheostat and a volt meter to the circuit and tried changing the applied EMF. The sound faded out when the voltage was decreased beyond 0.5 volt. There was no apparent change in pitch with voltage decrease; the sound merely became so soft that it could no longer be heard.

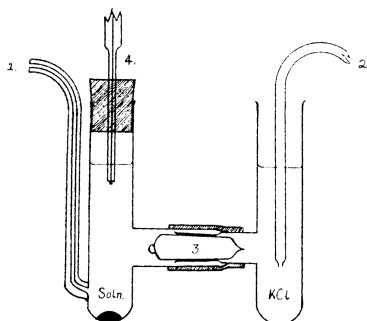


Fig. I.

Cell for polarographic measurements.

1. Arm through which nitrogen is bubbled to expel oxygen from the system.
2. Siphon from calomel electrode.
3. Ground glass plug between halves of cell.
4. Capillary tip of dropping mercury electrode.

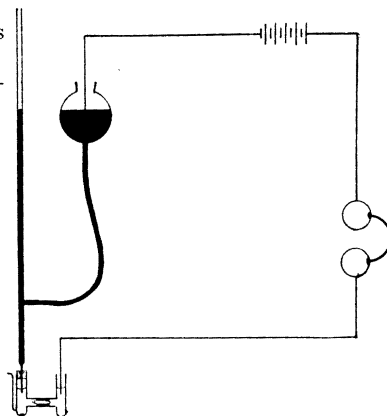


Fig. II.

Circuit used in observing current irregularities produced by growing drop.

Solutions of 1 N. HCl and 1 N. NaOH were tried in the cell with the following results. In the acid solution the lower limit of audibility of the sound was 0.2 volt. It could still be heard when all 6.6 volts of the battery were applied.

In the alkali solution the phenomenon occurred only between 0.4 and 1 volt. Above this voltage, the high pitched portion of the sequence ceased and merely an irregular rattle remained. The mercury drops became heavily coated with a brown compound, possibly mercuric hydroxide. Dropping rate decreased and finally no more drops fell. Current through the cell ceased.

An RCA 151 cathode ray oscillograph was connected in parallel with the working cell. With maximum gain and sweep frequency, we were able to get some picture of the phenomenon. Frequent current displacements were observed which rose rapidly to a peak but dropped off more slowly. Most interesting was the fact that they were all direct current displacements, for at no time were there displacements below the median or 0 voltage line of the instrument.

The frequency of the displacements was greatest at the start of the drop, corresponding to the high pitched note in the phones, but decreased as the drop grew larger. The amplitudes of the displacements were least at the beginning of the drop and gradually increased until the drop fell.

An attempt was made to photograph the image as it appeared on the screen, but the effect was too transient to catch with a 3.5 lens.

Our observations so far would seem to indicate that the current changes heard as sound in the head phones are a result of potential changes produced between the mercury drop and the conducting solution by the process of drop formation; the same sequence of events occurring in the course of each drop. Whether this be a surface tension phenomenon or something more obscure, we are not prepared to say without a great deal more investigation. Although of undoubted theoretical interest, it is highly unlikely that the phenomenon has any effect at all upon the use of the dropping mercury electrode in polarographic determinations. The period of even the most sensitive galvanometer is so slow that the effect is not recorded. Indeed, this probably accounts for the fact that it has not been observed before. (Fig. III.)

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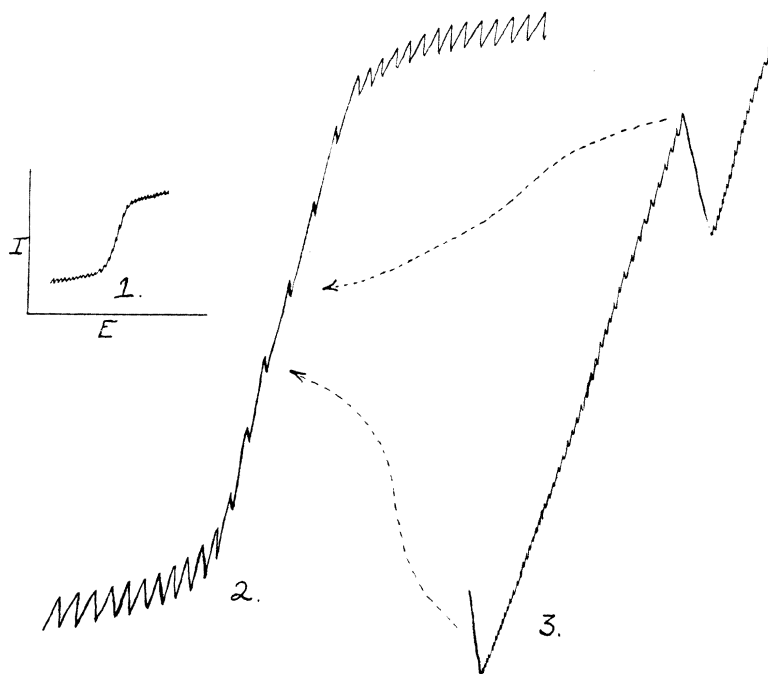


Fig. III.

Sketched curves of current displacements.

1. Small scale reproduction of a typical polarographic curve corresponding to the discharge of a single ionic species.
2. The same enlarged to show the current fluctuations produced by single drops.
3. Enlarged section of curve No. 2 showing current fluctuations during the growth of a single drop as the authors believe they would appear if they could be recorded by a sufficiently sensitive instrument.

Note: Observations of growing drops by means of a microscope plainly show irregularities in the rate of growth.