

PHYSICAL CHEMISTRY

ON THE INFLUENCE OF STIRRING ON CURRENT VOLTAGE
CURVES OBTAINED WITH A MERCURY CATHODE

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As was shown elsewhere ⁽¹⁾, the maxima on current voltage curves obtained with mercury cathodes are caused by the motion of the mercury surface. This motion, which is especially pronounced with certain polarizations, secures an extra supply of the reducible matter to the cathode, necessary for the maintenance of the maximum current. The parts of the current voltage curves where a limiting diffusion current is observed correspond to a calm state of the cathode. If this explanation be correct, the maxima must

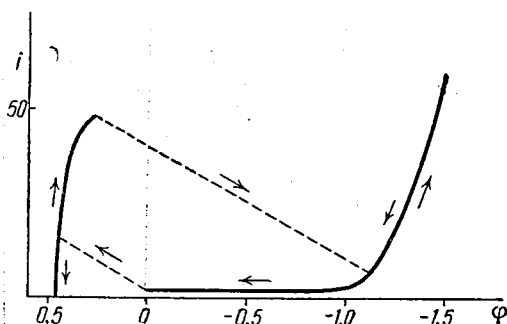


Fig. 1. Current voltage curve with amalgamated platinum cathode in 0.003 norm. $\text{Hg}_2(\text{NO}_3)_2 + 0.003$ norm. HNO_3 . Arrows indicate in what direction the applied voltage is changed. Potentials referred to normal calomel electrode.

disappear in case a strong artificial stirring is applied to the solution. The realization of a strong stirring with a steady cathode presents certain difficulties, since the mercury is thrown out of the enclosing vessel if the motion of the liquid is sufficiently violent. We have overcome this difficulty by using two methods.

1. **Amalgamated Platinum.** A thick strongly amalgamated platinum wire was used as a cathode. If the mercury layer is sufficiently thick, a typical current voltage curve with a maximum and a hysteresis loop can be obtained with a cathode of this kind in $\text{Hg}_2(\text{NO}_3)_2 + \text{HNO}_3$ solutions, as shown by Fig. 1. The diffusion current is very small compared with the maximum current. With the increase of the HNO_3 concentration, the maximum current decreases (the table). If now a strong jet of the solution is directed onto the electrode, the shape of the curve changes completely

(Fig. 2). The jet escapes from an orifice with a diameter of 1 mm situated in the solution close to the electrode, under a pressure of 120 cm of water, and causes a vigorous stirring of the solution. Under the influence of this stirring, both the maximum and the diffusion current increase, the increase of the former being by far smaller. The difference between the maximum current and the diffusion current, as well as the hysteresis loop, nearly disappear.

	0.003 norm. $\text{Hg}_2(\text{NO}_3)_2 + \text{HNO}_3$, saturated with hydrogen					
CHNO_3	0.003	0.006	0.012	0.024	0.048	0.096
i without stirring	45	35	25	16	9	4
i in stirred solution	78	78	73	70	69	70
i diffusion	76	75	68	66	62	63

As shown by the table, the suppressing effect of the foreign electrolyte on the maximum current is no more observed in a stirred solution. Other experiments have shown that the maximum current under these conditions

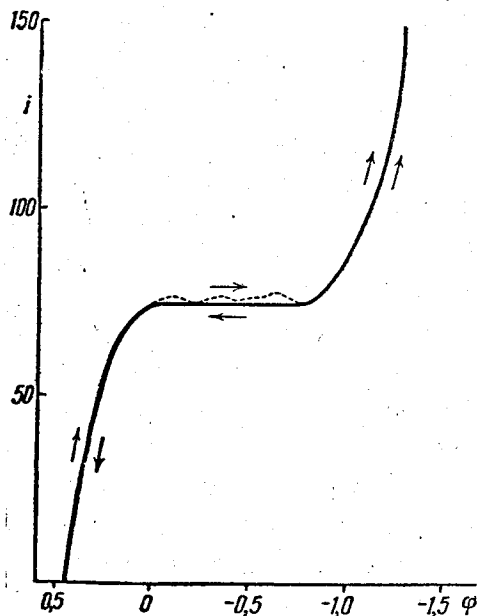


Fig. 2. Current voltage curve with amalgamated platinum cathode in a streaming electrolyte of the same composition.

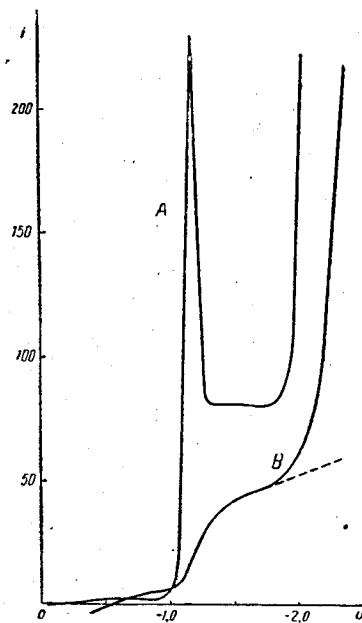


Fig. 3. Current voltage curves of 0.005 norm. $\text{Ni}(\text{NO}_3)_2 + 0.05$ norm. KNO_3 . A—dropping electrode, B—dropping electrode in streaming electrolytes.

is proportional to the concentration of mercury. The cathode behaves now in all respects similarly to an ordinary solid electrode. The decrease of the hydrogen overvoltage due to stirring of the solution has, as shown by Fig. 2, a secondary reason: the strong jet of the solution partly bares the electrode from mercury and the catalytic influence of platinum becomes more pronounced.

2. Dropping Electrode. If a similar jet of liquid is directed against the end of the capillary of an ordinary dropping electrode (time of drop formation 1 sec.), the dropping mercury is pulverized and is torn of

from the mercury surface in the form of fine droplets. At the end of the capillary there remains a flat mercury surface which can be used as a cathode. It is obvious that very thorough stirring becomes realized in this way. We shall call this electrode «dropping electrode in streaming electrolyte», although there is no regular drop formation in this case. We have investigated with such electrodes the deposition of both Ni- and Hg_2 -ions in solutions saturated with hydrogen. As was shown by Emelianova and Heyrovsky (²), nickel salts give very well developed maxima on current voltage curves.

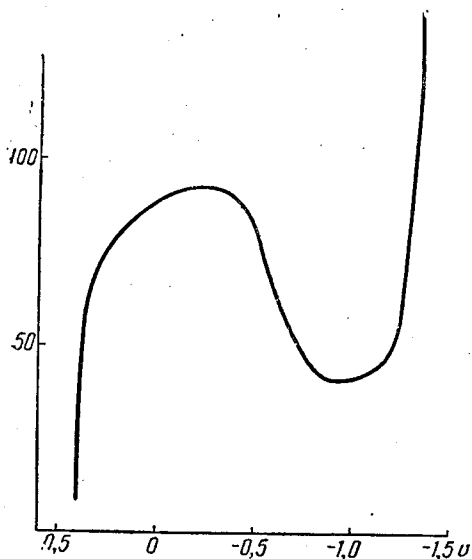


Fig. 4. Current voltage curve of 0.0025 norm. $\text{Hg}_2(\text{NO}_3)_2 + 0.1$ norm. HNO_3 with ordinary dropping electrode.

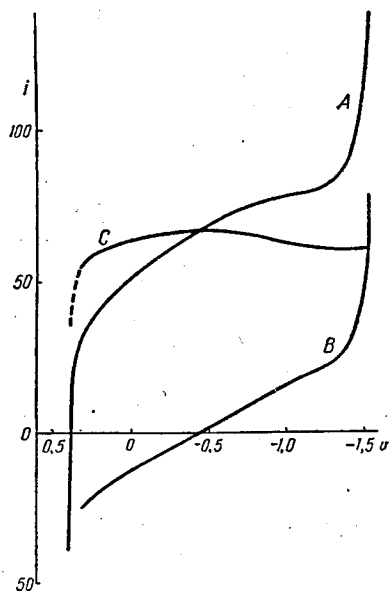


Fig. 5. A—current voltage curve of the same solution with a dropping electrode in streaming electrolyte, B—similar curve in 0.1 norm. HNO_3 , C—curve A corrected for non-faradaic current and depolarization by HNO_3 .

A curve of this kind obtained under ordinary conditions of dropping is given in Fig. 3, A. The same solution under conditions of strong stirring gives a curve without a maximum (Fig. 3, B) which differs from a curve as obtained with a solid cathode only by a certain slope of the part corresponding to the limiting diffusion current of the nickel deposition and at the beginning of the curve, which should be horizontal. As will be shown, this is caused by the non-faradaic current which is very large in this case, since a large number of small droplets are formed. It is interesting to compare the respective influence of Al-ions on curves A and B. As has already been shown by Heyrovsky and collaborators, an addition of a small quantity ($5 \cdot 10^{-4}$ norm.) of an aluminium salt totally suppresses the nickel maximum on curve A, while it has but a small influence on curve B, slightly increasing its slope in the part corresponding to the limiting current of the Ni-deposition.

In a 0.0025 norm. $\text{Hg}_2(\text{NO}_3)_2 + 0.1$ norm. HNO_3 solution with an ordinary dropping electrode a current voltage curve with a well pronounced rounded maximum is obtained (Fig. 4). In a streaming electrolyte (Fig. 5, A) this maximum disappears. The part of the curve corresponding to the limiting current of the Hg_2 deposition has again a marked slope, and a negative current with small voltages is observed. To make clear the reason of these phenomena, we carried out measurements with 0.1 norm. HNO_3 in absence

of mercury salts (Fig. 5, *B*). In this case no electrolytic process is possible until a high cathodic polarization is reached and the whole current up to -1.3 V is a non-faradayic current which is spent on charging the mercury droplets formed. In fact, this current changes its sign from a negative to a positive one, as it should be expected at the electrocapillary maximum -0.48 V. A comparison of curves *A* and *B* shows that our supposition as to the nature of the slope of the middle part of curve *A* was well founded. If we subtract from curve *A* the values given by curve *B*, we obtain curve *C* which represents the part of the current caused exclusively by the deposition of mercury ions. The anomalies of curve *A* discussed above have now disappeared, but a faintly pronounced maximum, evidently a rest of the maximum shown in Fig. 4, becomes visible.

The experiments described in this paper show conclusively that the maxima on current voltage curves obtained with mercury cathodes disappear, if the solution is subjected to vigorous stirring, the influence of auto-stirring caused by the motion of the mercury surface becoming under these conditions negligible.

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