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Maxima on Current-Voltage Curves

By *B. Bruns, A. Frumkin, S. Jofa, L. Vanjukova* and *S. Zolotarewskaja*

The maxima on current-voltage curves for mercury cathodes have been first observed and described in detail by Heyrovsky and his collaborators [1]. To explain the appearance of these maxima Heyrovsky introduced the concept of an „adsorption" current which might surpass the ordinary limiting „diffusion" current. The original theory of Heyrovsky was criticized by Bruns and Frumkin [2]. A modified form of this theory was given by Ilkovič [3]. According to Ilkovič, the drop in current after the maximum is caused by the exhaustion of the reducible substance in the neighbourhood of the cathode increasing with time. But it could be shown (see below) that, if the concentration of the solution is kept constant, the maximum current, with a steady mercury cathode, can be observed for a very long time, but suddenly decreases with a slight increase of the applied voltage. Besides, to explain the appearence of a maximum in the case of the reduction of non-electrolytes, like oxygen, Ilkovič assumes that the non-homogeneous electric field surrounding the dropping electrode attracts dissolved molecules possessing a permanent or induced dipole moment. In reality oxygen molecules, in a medium with a high, dielectric constant (like water), will be of course expelled and not attracted by the electric field.

Bruns and Frumkin showed that a steady mercury cathode, as long as the voltage corresponding to the maximum cur-

[1] Summary in Heyrovsky, Adsorption, Electro-Reduction and Over-Potential. Actualités scientifiques et industrielles. 90, Paris 1934.
[2] Bruns a. Frumkin, Acta Physicochimica URSS, **1**, 232 (1934).
[3] Collection, **8**, 13 (1936).

rent is not surpassed, is in a state of violent motion. The stirring of the liquid caused by this motion permits a current to be sent through the cathode which is much larger than the limiting current that would be observed if the same cathode were motionless. The sudden drop in current with an increase of the applied voltage was explained as the result of a sudden change in surface charge, by making certain assumptions about the probability of the adsorption and desorption of ions in the double electric layer.

The motion of a polarized mercury cathode was later described also by Seidell[4] and Antweiler[5]. We shall try to show that a more detailed analysis of the motion of a mercury electrode allows to explain, without any supplementary assumptions, the shape of the current-voltage curves.

Experimental

The experiments described below were performed with steady mercury cathodes of different sizes in solutions of mercurous salts: in this case the maxima of the current-voltage curves are well-pronounced and reproducible.

The maximum current can pass through a cathode of this kind for an indefinitely long time, if the total amount of the mercury salt in the solution is kept constant. Otherwise, with a constant voltage, after a certain lapse of time a sudden drop in current occurs, the value of the maximum current markedly decreasing with a decrease in the mercury concentration and the solution in the neighbourhood of the cathode becoming impoverished in mercury ions with time. With a slowly following electrolyte in a 0,004 N $Hg_2(NO_3)_2 + 0{,}003$ N HNO_3 solution, a current amounting to 96% of the maximum current could be sent for 30 min. through a mercury cathode with a diameter of 7 mm.; but if the applied voltage was increased by 5%, the current intensity at once dropped to 15% of its original value. With cathodes of this kind we investigated the dependence of the maximum current strength upon the concentration of the mercury salt and the electrolyte added to the solution. These experiments will be described in detail elsewhere. We

[4] Seidell, Z. angew. Chem., **48**, 463 (1935).
[5] Antweiler, Z. Elektrochem., **43**, 596 (1937).

shall only mention here that the maximum current i_{max} in a solution $c_1Hg_2A_2 + c_2HA$ or $c_1Hg_2A_2 + c_2MeA$, if c_1 is kept constant and $c_2 > c_1$, is given by the relation

$$i_{max} = b - a \lg c_2.$$

With c_1 equal to 0,00214 N, $a = 0{,}0057$ in the presence of HNO_3 and $HClO_4$, and $a = 0{,}0034$ in the presence of H_2SO_4; b — was equal to — 0,0025 in the first case and to 0,0004 in the second. The value of b, moreover, depends on the nature of the cations;

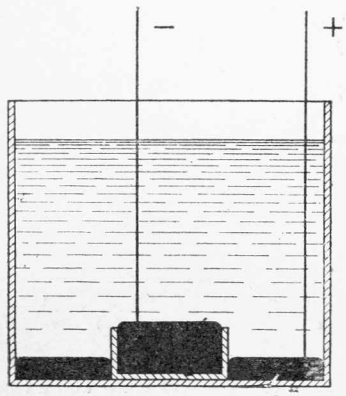

Fig. 1.

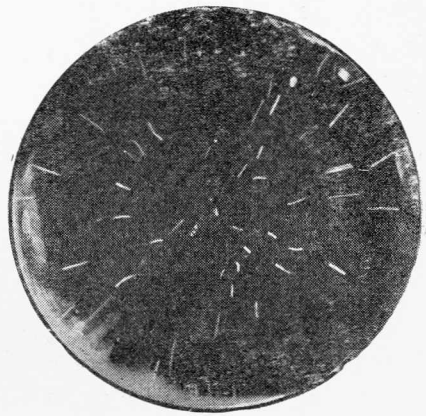

Fig. 2.
Motion of the mercury surface at the beginning of the polarization.

for instance, in nitrate solutions b amounted to 0,0018, 0,0002, — 0,0017, — 0,0019 and — 0,0021, in solutions containing $K^{\cdot}$, $Ba^{\cdot\cdot}$, $La^{\cdot\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$ and $H^{\cdot}$ respectively. The motion of the mercury surface can be most conveniently observed with a very large mercury cathode. In these experiments we used as a cathode a cup (diameter 80 mm.) filled to the rim with mercury. This cup was introduced into a large vessel, as shown in Fig. 1, and the mercury on the bottom of the vessel served as an anode. The solution was 0,02 N $Hg_2(NO_3)_2 + 0{,}002$ N HNO_3. The following three stages of the cathode polarization may be observed.

When the voltage applied to the cathode is increased, motion of the mercury surface from the centre to the periphery sets in with increasing intensity. This motion can be followed by distributing on the central part of the cathode small glass spheres which

can be easily photographed. Fig. 2 gives such a photograph with an exposure of 0,5 sec. As will be shown below, the mercury at the periphery of the cathode becomes polarized with increasing voltage. When the potential at the periphery reaches a value corresponding to the maximum of the electrocapillary curve, there appears on the cathode a distinct ring, which moves to the centre

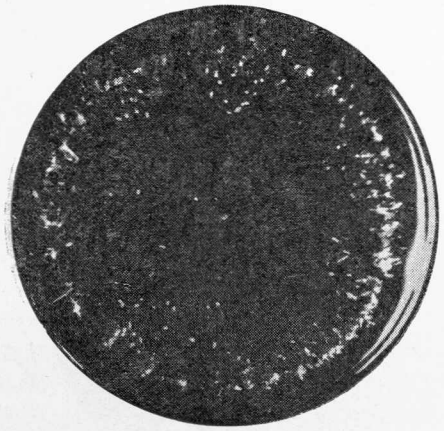

Fig. 3.
Ring on the mercury surface.

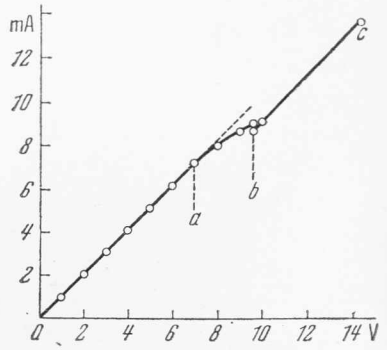

Fig. 4.
Current voltage curve taken with a large cathode.

with a further increase in voltage its diameter steadily decreasing. The ring as is shown by the movements of the mercury surface is that region of the mercury surface, where the polarization corresponds to the maximum of the electrocapillary curve. Everything which falls on the cathode surface as well as particles of dust and other contaminations is concentrated on the ring in this stage.

Fig. 3 reproduces a photograph of the ring taken in the presence of glass spheres. With a further increase in voltage, the ring, after its diameter has reached a minimum value, suddenly shrinks to the centre.

The whole mercury surface is now polarized. In this stage the motion of the surface is less pronounced than in the first and second. Slow and rather irregular movements directed to the centre can be observed. If we compare these observations with the current voltage curve (Fig. 4), we shall find a complete correspondence. A linear increase of the current with the voltage corresponds

to the first stage, when the movements are directed from the centre to the periphery. After the formation of the ring (point *a*), the linear relation does not hold any more, since the outer part of the cathode is already strongly polarized and the current density is smaller here. At the moment of contraction of the ring (point *b*), the current suddenly drops and afterwards increases again (*bc*).

If the voltage is now lowered, the surface remains polarized even when the current intensity is decreased much below the value which corresponded to the complete polarization of the cathode (See Fig. 7). When the anode, instead of being below and around the cathode (as shown in Fig. 1), is situated above it in the form of an amalgamated platinum disc with a diameter of 6 cm., the development of polarization proceeds in a different way. Polarization starts at the centre of the cathode, and in the first stage the movements are directed from the periphery to the centre. Then a ring appears, its diameter increasing with increasing voltage, until at a certain moment it suddenly spreads on the mercury surface. A similar development of polarization was described in the first paper of Bruns and Frumkin. In this case the anode was below the cathode; but polarization was still larger at the centre as the surface of the mercury drop was somewhat below the level of the edges of the enclosing glass tube.

From the description given here, it is obvious, that the reason for the comparatively small polarization in the first stage lies in the violent stirring of the electrolyte caused by the motion of the mercury surface, which supplies $Hg_2^{\cdot\cdot}$-ions to the cathode. To determine the cause of the motion of the mercury surface, we measured its potential at different points. For this purpose a syphon, terminating in a glass capillary, was constructed. The capillary was so fine that it bent when pressed against the mercury, only slightly deforming its surface. In this way the closest approach of the end of the capillary to the mercury surface was secured and a possible error caused by the ohmic drop of potential in the solution was avoided. To keep the distance between the mercury and the capillary constant, the latter was attached to a small cup floating on the surface of the electrolyte. The syphon was connected by a calomel electrode to a Perucca electrometer (sensitivity 0,004 V). By moving the cup we could quickly measure the potential at dif-

ferent points of the electrode. Fig. 5 shows how the potential changes with an increase in distance from the centre of the cathode. In the central region the cathode is practically unpolarized, the polarization increasing quickly as the periphery was approached. To make possible a comparison of the potential distribution at different stages of the polarization, we carried out measurements after the contraction of the ring at the same current strength as before the appearence of the ring. As shown by Fig. 5 the potential gradient on a polarized surface is considerably smaller (by a factor of *ca.* 7) than on an unpolarized one. For this reason the movements of the surface must be much more pronounced in the first period than in the last one.

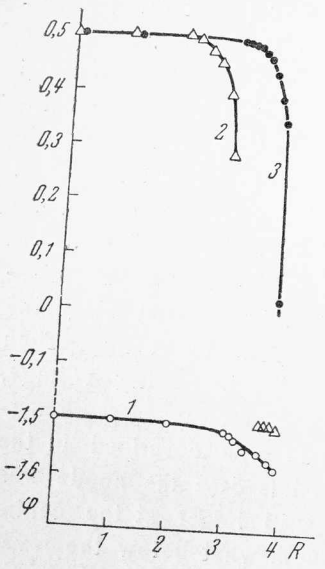

Fig. 5.
Potential at different distances from the centre of the cathode:
● ● ● before appearance of the ring,
△ △ △ in the presence of the ring,
○ ○ ○ after ring contraction.

A similar difference in the distribution of potential between the completely polarized and the slightly polarized parts of the cathode is observed in the presence of the ring. The potential distribution for this case is also given in Fig. 5; the ring was situated within the interval from 2,9 to 3,6 cm. from the centre of the cathode. Fig. 5 shows that the potential gradient in the central region can be observed at a much larger distance from the ring than in the outer, completely polarized part of the cathode.

An interesting relation is observed between the diameter of the cathode and the maximum current. If the experiments are performed keeping the size of the anode and its distance from the cathode constant, the maximum current turns out to be proportional to the radius of the cathode (Fig. 6). This somewhat unexpected relation is to a certain extent explained by the fact that, before the appearence of the ring, polarization is practically concentrated at the periphery of the cathode. The total force causing the motion of

the liquid and determining the supply of the reducible substance is therefore proportional to the perimeter or the radius of the cathode and not to its surface. An increase of the viscosity of the liquid must hinder its motion and therefore lower the maximum current. This conclusion was checked by measuring the maximum current at various temperatures from 0° to 70°C (0,02 *N* $Hg_2(NO_3)_2 + 0{,}002$ *N* HNO_3, cathode diameter 5 mm.). Table 1 shows that the product $i\eta$ changes only by 16%, whereas the viscosity decreases more than four times.

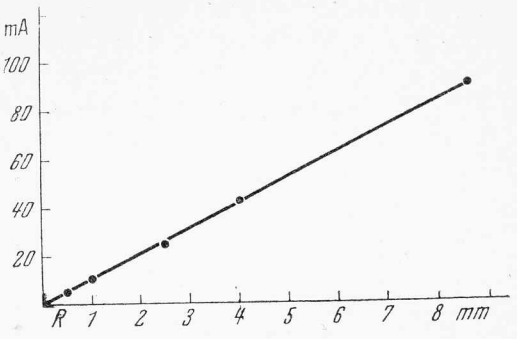

Fig. 6.
Dependence of the current strength upon the radius of the cathode.

Table 1
The dependence of the maximum current upon the viscosity

°C	$i \cdot 10^3$	$\eta \cdot 10^2$	$i\eta \cdot 10^5$
0	13,5	17,9	241
25	25,7	8,9	229
50	39,9	5,5	220
70	49,9	4,1	205

To test the rôle of the motion of the cathode, it was also interesting to carry out experiments with a solid mercury cathode. For this purpose an electrolyte, consisting of 70% CH_3OH and 30% H_2O and containing $Hg_2(NO_3)_2 + HNO_3$, was used. In these experiments the solution was gently stirred. To exclude the influence of other factors besides the solidification of the mercury, parallel experiments were carried out at 1° above and below the melting point of mercury. During the measurements, the temperature was kept constant to 0,1°. Fig. 7 gives the relation between current strength and the applied voltage, as well as the potential at the centre of the cathode for liquid mercury. The diameter of the cathode

was 5 mm. The curves obtained with liquid mercury in $CH_3OH + H_2O$ at — 38°C are similar to the curves obtained under ordinary conditions. The behaviour of solid mercury, as shown by Fig. 8, is quite different; with the smallest voltage applied, the surface becomes polarized; and we get a typical curve with a limiting current which, at a polarization of *ca.* 1,8 V, passes into the curve for hydrogen evolution. The experiments with solid mercury show conclusively that the appearence of a maximum current is connected with the movements of the liquid mercury surface. It must be noted that, with solid mercury at a still higher voltage, a sudden drop of the current is observed which requires further investigations. A similar drop is observed with liquid mercury after the usual drop, if the applied voltage is sufficiently increased further. The change in the state of the current-voltage curve, corresponding to the melting point of mercury, might be observed at ordinary temperatures if 1% gelatine is added to the electrolyte. At a temperature above the „melting point" of gelatine, a curve with a current maximum is obtained, whereas a curve with a limiting current is obtained after the solidification of gelatine.

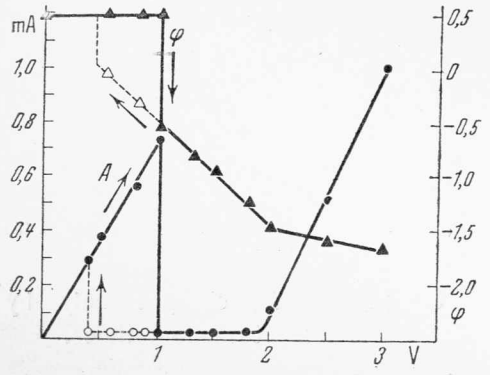

Fig. 7.

Dependence of the current strength *A* and cathode potential φ upon the applied voltage with a liquid mercury cathode at — 38° C. Full line — increasing polarization, dotted line — decreasing polarization.

Discussion

The experiments with a large cathode show that the existence of a maximum current for a mercury cathode is connected with a definite state of motion. After the drop of the current intensity, the movements are calmed, and this calm state of the cathode persists if polarization is now decreased. With decreasing polarization an ordinary limiting diffusion current is always observed on a steady cathode. This limiting current corresponding to a motionless state of the surface must be very much smaller than the maximum current, as has already been explained by Bruns and Frumkin.

In another paper it will be shown that the maxima of a current voltage curve disappear when energetic artifical stirring is applied to the solution. All these facts prove in our opinion that, beyond any reasonable doubt, „auto-stirring" is necessary for the appearence of a maximum in current-voltage curves. It is much more difficult to give an explanation of the sudden decrease of the current at a certain value of the voltage applied. We shall here tentatively show that this can be given by an analysis of the relation between „auto-stirring" and polarization of the cathode. Let Fig. 9 represent the usual relation between the polarization of the electrode and the current *i* when two electrolytic processes are possible at the cathode (in our case discharge of $Hg_2^{\cdot\cdot}$ and $H^{\cdot}$-ions)[6], which is observed with constant stirring. The motions of the cathode are caused either by local differences of interfacial tension, or by fluctuations of interfacial tension with time.

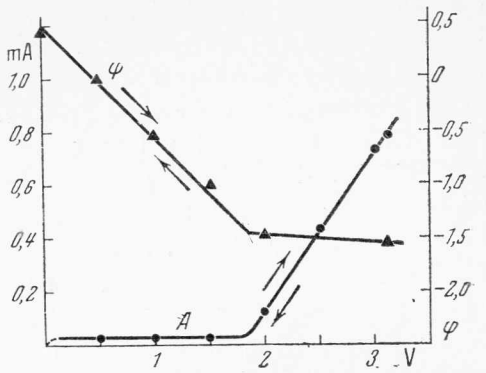

Fig. 8.

Dependence of the current strength and cathode potential φ upon the applied voltage with a solid mercury cathode at — 41°C.

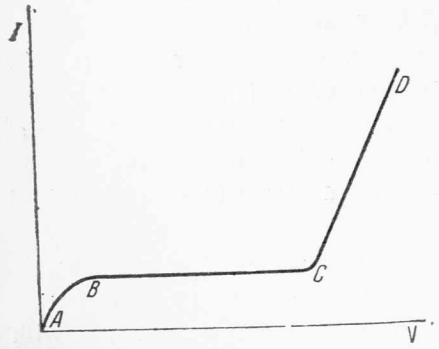

Fig. 9.

With a cathode of definite size, the current density at different points of the cathode will always be different, and this causes

[6] The possibility of a second process, when only one reducible substance is present, is always given by the formation of hydrogen from water molecules.

a difference of tensions and a motion of the mercury. Curve *ABCD* shows that the differences of polarization, which correspond to a small difference in current densities, are small at the beginning of the curve, then rise with rising V, reach a very sharp maximum in the region *BC*, and drop again when the polarization corresponds to the beginning of the second process. There is therefore an optimum region of current values around *BC* where the auto-stirring mechanism will be most pronounced. The influence of the auto-stirring must therefore transform curve *ABCD* into a curve with a maximum and minimum. If we reach, with increasing polarization, a point on the curve where the stirring begins to decrease, this causes a decrease in supply of the reducible substance and in the value of the current; therefore at a given applied voltage further increase of polarization follows and so forth, until a point is reached where a further increase of cathode polarization is stopped by the acceleration of the second electrolytic process. Therefore a part of the current-voltage curve corresponds to unstable states, and this explains the sudden decrease of the current observed at a certain voltage applied. The theory outlined here is in good agreement with the results of the measurements of the potential gradient described above. The local differences of cathode potential reach a maximum value at the current maximum; in the case of a large cathode it could be shown, that this maximum value is determined by the character of both electrolytic processes which may occur at the cathode, a part of the cathode being already completely polarized, while the other part is still practically in an unpolarized state.

The shape of the current voltage curve observed is largely determined by the magnitude of the ohmic drop of potential in the solution at the moment when the current begins to decrease with increasing voltage. If the ohmic drop is fairly large there must be at a given applied voltage a strong increase of polarization even with a slight decrease of the current, as shown by Fig. 4. With a small ohmic drop a large increase of polarization is impossible as with increasing polarization the current soon becomes very small; in this case a curve of the form shown in Fig. 7 can be obtained, and a limiting current can be observed with increasing polarization. If the $i\varphi$ curve has a maximum and a minimum, but the quantity $i - \frac{\varphi}{w}$ (w — total resistance of the circuit, φ — potential of the cathode) changes monotonously with increasing polarization, the current-voltage curve will show a maximum and a minimum but no sudden drop of the current will appear (rounded maximum).

Since motion of the cathode is very irregular, the stirring must change with time. For this reason the potential at a definite point of the cathode changes with time too; and this circumstance again contributes to the movements of the cathode. It is obvious that temporary changes in the rate of stirring will cause much larger changes of potential in the *BC* region of the current-voltage curve than in the *AB* or *CD* region; and the influence of this factor will, therefore, as well as the influence of local potential differences tend to transform curve *ABCD* into a curve with a maximum and a minimum. We have shown therefore that auto-stirring of the cathode will always be impeded when polarization of a part of the cathode reaches values which make a second electrolytic process possible. This gives a general explanation of the appearance of maxima of current-voltage curves with a mercury cathode. We do not pretend, however, that the decrease of auto-stirring cannot be caused by other reasons. For instance just in the case of the reduction of mercury ions in an acid solution, when the two processes correspond to different branches of the electrocapillary curve, auto-stirring might decrease due to purely hydrodynamic reasons, when polarization corresponding to the maximum of the electrocapillary curve is reached in a certain part of the cathode. In fact, with smaller mercury cathodes, the drop in current, as shown for instance in Fig. 7 might be observed at voltages which appear too low to cause a noticeable evolution of hydrogen. It will be very important to study in detail the distribution of potential on the cathode surface and its motion in this case. The surface tension of mercury does not change with small changes of the potential at the maximum of the electrocapillary curve. The movements of the cathode, therefore, cannot appear if the initial polarization corresponds to this point. This explains, as was already mentioned by Frumkin and Bruns, the disappearance of the maximum of the current-voltage curve if the potential of the reduction process corresponds to the maximum interfacial tension of mercury, discovered by Heyrovsky and Vascaut-

zanu[7]. Heyrovsky himself assumes that this disappearance is caused by vanishing of the electrokinetic potential at the electrocapillary maximum which, according to this theory is necessary for maintaining the "adsorption" current; but the disappearance of the current maximum at the „electrocapillary zero" is observed in the presence of iodides and thiocyanates also. As it is well known, the anions of these salts are strongly adsorbed on the mercury surface, and therefore the electrokinetic potential in solutions containing these salts does not vanish at the electrocapillary maximum.

Adsorbed substances exert a calming action on the motion of a liquid surface. The theory of this effect was recently developed by R. Ivanov and W. Shoulejkin [8]. They could show that the calming action is a result of an absorption of energy caused by the irreversibility of the changes of surface tension, occurring when the film is expanded and compressed. It seems probable that a suppression of the maximum current in the presence of capillary active substances [9] is a similar phenomenon and must be explained by the damping action of the adsorbed film on the movements of the mercury cathode. A similar explanation can be proposed for the suppressing action of polyvalent anions when the maximum occurs at a potential corresponding to a positive charge of mercury and for the action of polyvalent cations in the opposite case [10]. When the surface expands, ions with a charge opposite to the charge of the surface are adsorbed; and on contraction of the surface they are desorbed. As the equilibrium between the surface layers and the bulk of the solution cannot be established momentarily, expansion and contraction of a charged surface will be to a certain extent practically irreversible, and the charge must exert a damping action like a film of a capillary active substance. The irreversibility, and therefore the damping action, will be most pronounced if the charge is high at a low volume concentration of the electrolyte, as will be the case with polyvalent ions. There is still another reason for the suppressing action of electrolytes. The motion of the mercury

[7] Collection, **3**, 418 (1931).
[8] Ivanov a. Shoulejkin Bull. Acad. Sci. URSS, Série Georg. 325, 345 (1937).
[9] Rasch, Bull. Acad. Sci. Bohême (1929); Rayman, Collection, **3**, 314 (1931); Hamanoto, Collection, **5**, 427 (1933).
[10] Heyrovsky a. Dillinger, Collection, **2**, 626 (1930).

surface caused by local differences of interfacial tension will always be directed from points with a higher absolute value of the electric charge to points with a lower one, and therefore will tend to equalize the local differences of charge and of potential, the primary cause of the motion. In this respect the interface behaves as if it had a very high surface conductivity. This effect will increase when the charge of the mercury per unit surface *ceteris paribus* increases. It follows from the double layer theory that, at a certain distance of the electrocapillary maximum, the charge ε at constant potential is in a first approximation a linear function of the log of the concentration $|\varepsilon| = \text{const.} + \frac{RT}{nF} \log c$, n being the valency of the ion attracted by the mercury surface. Our measurements, as presented above, show therefore that the decrease of the maximum current caused by an increase of the concentration of the indifferent electrolyte is proportional to the increase of the charge, the proportionality factor being roughly the same for uni- and bivalent anions.

The complete dependence of the maximum current upon the charge must be, however, more complicated, as the motions of the cathode cannot arise with an uncharged surface, and the presence of an electrolyte is necessary to build up a surface charge. In fact, when the reduction proceeds at potentials close to the electrocapillary maximum, as in the case of oxygen and mercuric cyanide, a certain increase of the maximum current with an increase of electrolyte concentration is observed at a very low concentration, which is followed by the usual decrease [11]. However this phenomenon requires a detailed study, before definite conclusions can be reached, and the explanation given here is presented only in a hypothetic form. The influence of the charge on the elastic properties of the mercury surface not only plays a rôle in the suppressing action of electrolytes, but might be also one of the causes of the appearance of maxima; namely, if the charge of the polarized surface exerts a stronger damping action on the surface movements than the charge of the unpolarized one. The difference might be related to the absence of equilibrium between the metal surface and the sur-

[11] Dillinger, Bull. Acad. Sci., Bohême 1929, Varasova, Collection, **2**, 8 (1930).

rounding solution in the first case. Considering the whole problem of the phenomena on a polarized mercury cathode, we do not try to give at the present moment a quantitative theory on the basis of the "auto-stirring" mechanism outlined here in a qualitative form, as we think that it would be first necessary to carry out measurements of local potential differences and of potential variations with time under different conditions of polarization. But it appears that the most striking phenomena observed with mercury cathodes might be explained in this way. With a dropping electrode still other complications arise, owing to the important fact that, with a given voltage applied, the mean current density does not remain constant during the formation of a drop. We shall not discuss here the particular development of the theory which must be given in this case. We should only like to point out that the movements of the mercury surface make it impossible to draw conclusions from drop-weight measurements on the mercury — solution tension in the maximum current region, which is a probable explanation of the so called "anomalies of the electrocapillary curve" discovered by Kučera and investigated by Heyrovsky and Simunek [12].

Summary

A theory of the maximum of current-voltage curves is outlined, which is based mainly on experiments carried out with large mercury cathodes and with solidified mercury. This theory explains the appearance of maximum by the "auto-stirring" caused by the movements of the mercury surface. These movements are related to local difference of interfacial tension or to variations of interfacial tension with time and it is shown that these movements must be most pronounced under definite conditions of polarization. The decrease of the auto stirring when polarisation exceeds a certain limit might be caused by the beginning of a second electrolytic process or by a less favourable distribution of surface tension differences on the surface or at last by an increase of the damping action of the surface charge.

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[12] Heyrovsky a. Simunek, Phil. Mag., **7**, 951 (1929).