Contribution to the Theory of the Discharge of Hydrogen Ions

I. Mercury

By *A. Frumkin*

Before the present war broke out we had accumulated in our laboratory a great amount of unpublished material concerning the process of the discharge of hydrogen ions. Since in the present conditions it is impossible to publish this material fully I considered it reasonable to give the most essential results in the form of a survey. In this survey there are included investigations of other authors published before the end of 1941 and also several of our previous results which, it seems to me, are worthy of a repeated discussion. Unfortunately, more recent literature without a few exceptions was unavailable.

A. Experimental method

1. The rôle of impurities

In many respects the data obtained for mercury even now considerably surpass the results of measurements for other metals in so far as reliability and reproducibility are concerned. However, such data can be obtained only if surface active impurities are carefully removed from the solution; the danger of impurities in the case of mercury, the surfaces being equal, is not less than in the case of other metals, and it cannot be decreased by using electrodes with a large «true surface» as, for instance, is the case for lead. The desorption of neutral molecules from the surface of the mercury takes place only if the cathodic polarization is large. This effect for fatty acids and alcohols is observed in N Na_2SO_4 for a polarization $\sim$1.8 V with respect to the electrode with Hg/Na_2SO_4 saturated Hg_2SO_4, *i. e.* about 1.1 V with respect to the normal hydrogen

potential[1]. In more diluted solutions of electrolytes the range of adsorption becomes still wider. Capillary active cations are not removed by cathodic polarization at all. Thus we should watch out for the influence of impurities which can be adsorbed in the whole range in which the overvoltage on mercury can be measured; when the current density is low (in comparison with the limiting current of diffusion of dissolved traces of oxygen and other oxidants), there is a danger of the experimental data being vitiated by depolarization effects, *i. e.* by foreign electrode reactions. The danger of adsorption of impurities may be decreased by using a dropping cathode, although by doing so we meet new difficulties which we shall speak of further. The contradictions between various data on overvoltage on mercury which exists in literature till now[2] is caused to a great extent by the lack of sufficient attention to this circumstance, especially in the case when the measurements are performed near the electrocapillary maximum, when the conditions for the adsorption of foreign substances on the surface of the metal are especially favourable. In our investigation we used several devices for measuring the overvoltage η in which precautions were taken against impurities in the electrolyte, penetration of oxygen from the air and contamination of the cathode surface by platinum[3]. In one type of apparatus a resting mercury drop with a surface area of about 0.12 cm.^{2} was used as a cathode; in another type use was made of a plane surface of mercury with an area of 10 cm.^{2}. The agreement of the results obtained with the aid of various devices at different time by various observers is the best proof of their correctness. As an example let us compare the data obtained by Jofa for 0.1 *N* HCl[4] with those of Levina and Sarinsky[5] for the same electrolyte. The data of Jofa at 20° within the

[1] Gorodetzkaya and Frumkin, C. R. Acad. Sci. URSS, **18**, 639 (1938); Ksenofontov, Proskurnin and Gorodetzkaya, Acta Physicochimica URSS, **9**, 39 (1938).

[2] See, in particular, the comparison of data in the papers by Jofa, Kabanov, Kuchinsky and Chistyakov, Acta Physicochimica URSS, **10**, 325 (1939) and Levina and Sarinsky, *ibid.*, **6**, 491 (1937).

[3] Levina and Silberfarb, Acta Physicochimica URSS, **4**, 277 (1936); Levina and Sarinsky, *ibid.*, **6**, 494 (1937); Jofa and others, *ibid.*, **10**, 319 (1939).

[4] Jofa and others, Acta Physicochimica URSS. **10**, 325 (1939); Jofa, *ibid.*, **10**, 906 (1939) and also unpublished measurements of Jofa (Electrochemical Laboratory of the Moscow State University).

[5] Loc. cit. and also Sarinsky, «Overvoltage of Hydrogen on Mercury Cathode and ζ-Potential» (Russ.), Môscow, 1938, p. 41.

current density range of from $i = 10^{-7}$ up to 3×10^{-2} are precisely represented by the equation $\eta = 1.442 + 0.12 \lg i$. The measurements of Levina and Sarinsky were performed at a temperature of 22° in the range of i of from 2×10^{-8} up to 2×10^{-4}. After correcting these data for the difference in temperatures the divergence from the values, calculated with the aid of the above mentioned equation, is within the limits from −0.014 to +0.013, the average divergence being 0.009. Therefore, the reliability of these results seems doubtless.

2. Measurement of the volume of hydrogen

As it has been shown in the work of Jofa and others[6], in solutions containing absorbable substances in certain potential ranges

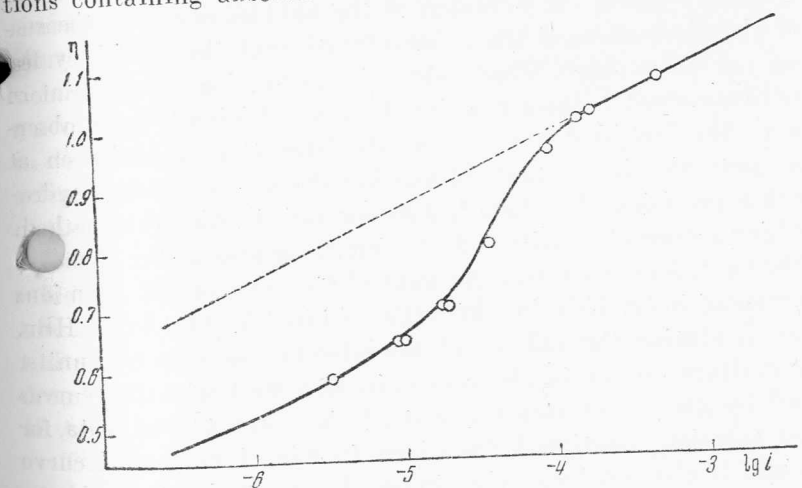

Fig. 1. Comparison of measurements of the overvoltage as depending upon the current intensity and upon the volume of hydrogen evolved in a solution of the 3 g.-eq. KI+0.1 g.-eq. HBr per 1000 g. H_2O (according to Jofa).

Full curve — measurements of current intensity, ○ — measurements of the gas volume.

corresponding to a change in the composition of the surface layer, we note abrupt changes in the slope of the $\eta, \lg i$ curve (Fig. 1). As it is well known, very much similar changes in the slope of the overvoltage curve may be caused by the presence of a small amount of a foreign depolarizer in the solution, for instance, by the presence

[6] Jofa and others, Acta Physicochimica URSS, 10, 323 (1939).

of dissolved oxygen. It is also noted that in these potential ranges the precision of overvoltage measurements is considerably lowered due to the slowness of the process of establishing the equilibrium. Therefore, in order to be thoroughly convinced of the reliability of these data, Jofa performed measurements of the volume of hydrogen liberated on mercury during cathode polarization[7]. This method has already been used previously while studying the mechanism of the liberation of hydrogen on lead[8] and nickel[9] and in the case of lead, the volumetric measurements showed the necessaity of introducing essentia changes in the overvoltage curve taken in the ordinary way.

In the case of mercury the measuring of the volume of hydrogen liberated is complicated by the fact that, when using an electrode with a small surface, the adhesion of the bubbles of gas to the surface of the electrode and the supersaturation of the liquid by the gas can not be avoided. Therefore while measuring every point of the curve we must become convinced by a sufficiently long observation of the fact that the rate o the liberation of hydrogen at a given potential is constant. Measuring the volume of the hydrogen with a precision of 10^{-3} cm.^{3}, Jofa succeeded, using this method, in reaching a current density of 10^{-6} A/cm.^{2}, the area of the electline being 10 cm.^{2}. In such a way the rate of discharge of hydrogen ions was measured in $3N$ HCl, in $2.2N$ HBr and in $3N$ KI $+ 0.1N$ HBr. After recalculating the volume of liberated H_2 into electric units, the overvoltage curves in all cases coincided well with the curves obtained by the direct measurement of the current. The data for the last solution mentioned are given in Fig. 1. The full curve is obtained in the usual way the circles—by measuring the volume; the concentrations were in this case calculated not per litre but per kilogram H_2O.

3. Measurements with high current densities

The question of the dependence of overvoltage upon $\lg i$ at high current densities is of special interest from the theoretical viewpoint, since on definite premises we could expect the appearance

[7] Jofa, Unpublished data.
[8] Frumkin and Kolotyrkin, Acta Physicochimica URSS, **14**, 469 (1941).
[9] Kolotyrkin and Frumkin, C. R. Acad. Sci. URSS, 446 (1941).

of limiting currents of the discharge of hydrogen ions, or, on the contrary, of a limiting value of the overvoltage. As far as the measurements are concerned the possibility of increasing the current is limited, in the first place, by the setting on of concentration polarization. It must be born in mind that we cannot apply an energetic stirring of the solution in the case of a liquid mercury electrode. Consequently, for measurements at higher current densities, we have to make use of amalgamated solid surfaces which always causes some danger of changing the value of the overvoltage, in comparison with pure mercury. When using high current densities, naturally, the danger of depolarization by traces of oxygen falls off, and the possibility of adsorption of capillary active substances is diminished, though not wholly removed (see above). On the other hand, strong stirring, which brings up continually new quantities of the solution to the surface, facilitates at the same time the accumulation of the impurities on the surface of the electrode. Kabanov[10] used as an electrode a short amalgamated silver wire 0.1 mm. in diameter, in a stream of electrolyte ($5N$ H_2SO_4), flowing with a linear velocity of 20 m./sec. Under these conditions the potential of the electrode does not depend upon the rate of the flow; therefore Kabanov came to the conclusion that the conditions were favourable for the vanishing of differences in concentration and temperature arising within the solution. In the measured value of the potential of the cathode a correction was made for the ohmic potential drop in the solution, which reaches 0.1 V for a current density of 10 A/cm.^{2}.

The correction was calculated without a separate account of the potential drop within the diffusion layer, *i. e.* it was considered that the concentration in all points of the solution is constant. Since we often meet in literature erroneous statements concerning the potential drop within the diffusion layer, although its theory was formulated correctly already by Eucken[11] it is necessary to consider this question here more in detail. In the diffusion layer, when hydrogen is liberated, the anion is not in motion, and, consequently, Boltzmann's formula can be applied to it[12].

[10] Kabanov, Acta Physicochimica URSS, **5**, 193 (1936).
[11] Eucken, Z. physik. Chem., **59**, 72 (1907).
[12] Levich and Frumkin, J. Phys. Chem. (Russ.), **15**, 748 (1941).

Therefore in the absence of foreign ions:

$$\varphi_d = \frac{RT}{n_a F} \ln \frac{c}{c_k} \qquad (1)$$

where φ_d is the fall of the potential in the diffusion layer, c—the concentration of the electrolyte in the bulk of the solution, c_k—the same at the surface of the cathode, n_a — the valency of the anion.

If we designate by i_d the limiting current of concentration polarization, we evidently obtain:

$$\varphi_d = \frac{RT}{n_a F} \ln \frac{i_d}{i_d - i} . \qquad (2)$$

From equation (2) it is seen that in the case of an electrolyte with $n_a = 2$, as H_2SO_4, φ_d reaches the value of 0.01 V only at $i = 0.45\, i_d$ and the value of 0.03 V when $i = 0.9\, i_d$. Since in Kabanov's experiments he failed to observe the appearance of a limiting current of concentration polarization, even if the current density was increased several times, it follows from the above that the quantity φ_d could be neglected in these experiments. The purpose of these experiments was to stine the applicability of the equation of Tafel $\eta = a + b \lg i$ for high current densities and as far as the conditions of keeping up the purity of the solution and of mercury are concerned, they cannot claim a high degree of precision.

Table 1
$5N$ H_2SO_4

lg i	1.396 + 0.116 lg i	Kabanov (interpolated)
$\bar{3}$	1.048	1.00
$\bar{2}$	1.164	1.14
$\bar{1}$	1.280	1.28
0	1.396	1.42
1	1.512	1.56

However it is of certain interest to compare this data with the results of the extrapolation of exact measurements of Jofa[13]. For $5N$ H_2SO_4 the measurements of Jofa in the range of values of lg i from —7 to —1 are expressed by the equation:

$$\eta = 1.396 + 0.116 \lg i.$$

Taking into consideration the fact that the scattering of the points in Kabanov's experiments reached 0.04, we can consider the agreement satisfactory.

Recently a considerable number of measurements for high current densities were performed by Hickling and Salt[14] among them measurements with mercury (apparently, amalgamated copper). According to these authors the ohmic drop of potential vitiates the results of the measurements for high current densities but the calculation of a correction, according to Ohm's law, is impermissible, since it does not take into consideration the fall of the potential in the diffusion layer. In particular, from this viewpoint they consider Kabanov's results incorrect. It was already shown above that they are mistaken in this criticism. In order to avoid the necessity of making the ohmic correction, Hickling and Salt perform the measurement of the potential, as it was previously done in earlier work on overvoltage, a short interval of time after the switching-off of the polarization current, and then extrapolate the curve of the drop of potential with time on the momen of the interruption of the current. The values measured correspond to intervals of time equal to 5×10^{-5}, 7.5×10^{-5}, 10^{-4}... sec. after the switching-off. Overvoltage curves, obtained in such a way, show for several metals considerable deviations of the dependence of η on lg i from the Tafel equation for high current densities. In some cases (Pb, Pt) a maximum η was observed at lg $i = \bar{1}$, in others (Hg, Cu, Cd, Sn, C) only a great slowing down of the increase of η and the approaching of a limit. We shall confine our discussion to the case of Hg. In Table 2 the data of Hickling and Salt for Hg in N HCl are compared with the results of the precise measurements of Jofa. According to the data of the latter for N HCl $\eta = 1.411 + 0.118 \lg i$ for lg $i > -6$; the measurements were brought up to lg $i = \bar{1}$.

Table 2
N HCl

lg i	1.411 + 0.118 lg i	Hickling and Salt	Hickling and Salt (corrected)
3	1.057	1.04	—
2	1.176	1.15	1.145
1	1.293	1.21	1.297
0	1.411	1.24	1.421

For lower current densities the agreement is satisfactory; however when the current density increases we observe a systematic lag in the values obtained by Hickling and Salt.

[13] Unpublished data.

[14] Hickling and Salt, Trans. Faraday Soc., **36**, 1226 (1940); **37**, 224, 319, 333, 450 (1941).

We can suppose that it is caused by the unreliability of the determination of the stationary potential when extrapolating the curve of the decay for high current densities as it was done by Hickling and Salt. For an electrode with a constant capacity C, supposing that the current of spontaneous discharge i_i obeys Tafel's equation with the usual value of b, the curve of the overvoltage decay after the switching-off of the polarization current i_0 is obtained from the equation

$$C\frac{\partial\eta_t}{\partial t} = -i_t = -e^{\frac{(\eta_t - a)}{b}2.30},$$

by integrating which we find

$$\eta_0 - \eta_t = b \lg\left(1 + \frac{2.30 t i_0}{Cb}\right) \qquad (3)$$

where η_0 is the value of η at $t=0$ and η_t—the overvoltage at the moment t. Since for a clean surface of mercury $C = 1.8\times10^{-5}$ farad/cm.^{2}, for $i_0 = 1$ A/cm.^{2} and $t = 5\times10^{-5}$, $\eta_0 - \eta_t = 0.2$V. If we take now the next two intervals equal to 5×10^{-5} the diminishing of the potential within these intervals of time will be correspondingly only 0.034 and 0.02.

It is seen herefrom that the extrapolation on the beginning of the curve on the basis of the measurements started after an interval of time $t = 5\times10^{-5}$ is impossible. In general, we can say on the basis of equation (3) that this extrapolation is admissible only if the interval of time t, elapsing till the first measurement, is small in comparison with $Cb/2.30\,i_0$. Form the relation $t < Cb/2.30\,i_0$ under conditions of Hickling and Salt's experiments, it follows that i_0 should be less than 0.02, at any rate, for an electrode with a purely double layer capacity such as the mercury electrode. Within these limits of current densities the curves of the authors cited really do not show any anomalies. For higher values of i_0 we can attempt to compute with the aid of equation (3) the original value of η_0 from the curves of the decay of overvoltage after the switching-off of the current. Such curves for a mercury electrode are given in a later paper of Hickling and Salt[15]. If we designate by η_* the first value of the overvoltage measured by them, corresponding to $t = 5\times10^{-5}$, and substitute in equation (3) the values of $C = 18.3\times10^{-6}$ and $b = 0.118$ we obtain

$$\eta_0 = \eta_* + 0.118 \lg(1 + 1.07\times10^6 \times 5\times10^{-5} i_0) \qquad (3a)$$

and

$$\eta_t = \eta_0 - 0.118 \lg(1 + 1.07\times10^6\, t i_0). \qquad (3b)$$

We must bear in mind that equations (3a) and (3b) do not contain any arbitrary constants. The values of η_0, given in Table 2 under the heading of «Hickling and Salt, corrected», are calculated with the aid of equation (3a); as it is readily seen, they agree with the results of extrapolation of Jofa's data. Therefore, there may hardly arise any doubt at least in the case of the mercury electrode concerning the correctness of the extrapolation given above in regard to the deviation from Tafel's formulae for high current densities supposed by Hickling and Salt. In order to check the applicability of equation (3) to the curves of the decay of overvoltage obtained by Hickling and Salt, I compared the values of η_t observed by them, taken from the curves in the figure (*loc. cit.* p. 456) with the values, calculated with the aid of equation (3b). The results are given in Table 3.

Table 3

	$i_0 = 1$A/cm.^{2}		$i_0 = 10^{-1}$A/cm.^{2}		$i_0 = 10^{-2}$A/cm.^{2}	
t	η_t obs.	η_t calc. from (3b)	η_t obs.	η_t calc. from (3b)	η_t obs.	η_t calc. from (3b)
0	—	1.421	—	1.297	—	1.145
5×10^{-5}	1.216	(1.216)	1.202	(1.202)	1.123	(1.123)
10^{-4}	1.179	1.182	1.154	1.171	1.105	1.108
2×10^{-4}	1.144	1.146	1.108	1.138	1.084	1.086
6×10^{-4}	1.081	1.089	1.040	1.082	1.026	1.042
10^{-3}	1.067	1.064	1.028	1.058	1.004	1.019

For $i_0 = 1$ and $i_0 = 10^{-2}$ the agreement is quite satisfactory and thus confirms the applicability of equation (3), for $i_0 = 10^{-1}$ it is considerably worse: however, it must be kept in mind that, according to Hickling and Salt's data, the decay of the overvoltage is greater for $i_0 = 10^{-1}$ than for $i_0 = 1$, this probably pointing to some error in the experiment. Fig. 2 shows, how the experimental data

[15] Hickling and Salt, Trans. Faraday Soc., **37**, 450 (1941).

of Hickling and Salt for $i_0 = 1$ fit the curve expressed by equation (3), and also the difference between the graphic extrapolation of Hickling and Salt and the extrapolation with the aid of a theoretical curve (3a).

From equation (3) it is easy to draw one more conclusion to which, it seems, until now no attention has been paid. Namely, while for an electrode obeying Tafel's equation the stationary over-

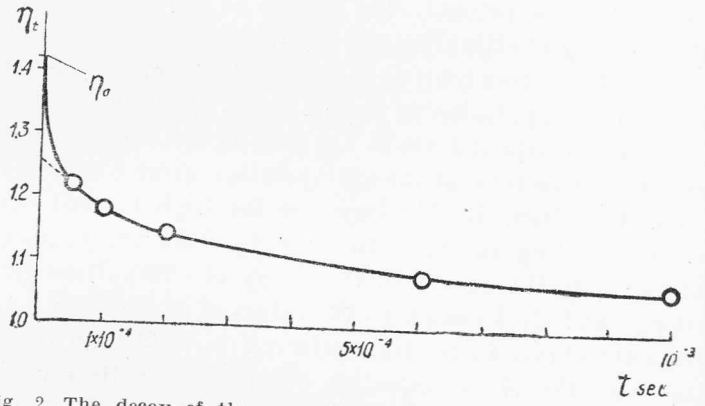

Fig. 2. The decay of the overvoltage after the switching-off of the current for $i_0 = 1$ A/cm.^{2}. ○ — according to experimental data of Hickling and Salt, - - - — — — extrapolated according to Hickling and Salt. Full curve is calculated according to equation (3b).

voltage during the passing of the current increases infinitely as the current density increases, the overvoltage measured after a definite time interval after the switching-off of the current tends to the limit

$$\eta_t = \eta_0 - b \lg \left(1 + \frac{2.30 t i_0}{Cb}\right) =$$

$$= a + b \lg i - b \lg \left(1 + \frac{2.30 t i_0}{Cb}\right) \sim a - b \lg \frac{2.30 t}{Cb} . \qquad (4)$$

Should we take, according to Jofa's data for N HCl, $a = 1.411$ and $b = 0.118$, we will get from equation (4) limit values of η_t equal to 1.214 at $t = 5 \times 10^{-5}$ and 1.179 at $t = 10^{-4}$. These values practically coincide with the values observed by the English authors for $i_0 = 1$A/cm.^{2}. If we should determine from these two quantities the supposed «limit» of η_0 by a linear extrapolation down to $t = 0$, which to a certain approximation corresponds to Hickling and Salt's graphical method, we will get $\eta_0 = 1.25$ (compare Table 2

3rd column). Thus, all the conclusions of Hickling and Salt in the case of a mercury electrode can be predicted, the assumption of the applicability of Tafel's equation for high current densities being taken as a basis.

4. Measurements with very low current densities

In this case the difficulties connected with depolarization by traces of dissolved oxidants are very much increased. Moreover for low current densities for mercury cathodes we go over into the region of potential values near the maximum of the electrocapillary curve, which increases the danger of adsorption of surface active substances. For current densities $\sim 10^{-10}$ a new difficulty arises. The last is caused by the fact that when changing the value of the potential it takes a considerable time to impart the corresponding charge to the double layer of the electrode. For instance, when the potential from one measurement to another is varied by 0.05 V it is necessary to change the charge by 10^{-6} coulomb/cm.^{2}. For a current density equal to 10^{-10} this will take several hours to do so. Therefore, even if the dissolved oxygen is totally removed, this value must be near to the admissible lower limit of current density. The measurements of Levina and Sarinsky were performed down to $i = 2 \times 10^{-8}$; Jofa's measurements down to $i = 10^{-7}$. Apparently, when using ordinary devices with glass joints wetted by the solution or covered by mercury, it is impossible to reach lower values. These measurements did not show any deviations of the overvoltage curve in dilute HCl from the normal curve for low current densities. By using a cathode enclosed in glass and polarizing through it, Bowden and Grew[16] succeeded in reaching values as low as $i = 10^{-9}$—10^{-10}. In doing so they also did not observe any change in the course of the overvoltage curve. The value of the overvoltage for low current densities may be characterized with the aid of i_r—the rate of the discharge of hydrogen ions at the reversible hydrogen potential which we get if in Tafel's equation $\eta = a + b \lg i$ we put $\eta = 0$. According to Bowden and Kenyon's data[17], in 0.2 $N H_2SO_4$, at 25°,

[16] Bowden and Grew, cit. from Bowden and Agar, Ann. Rep. Chem. Soc., **35**, 96 (1938).
[17] Bowden and Kenyon, cit. from Bowden and Agar, loc. cit., 99.

$i_r = 6 \times 10^{-12}$. According to Jofa (unpublished) for 0.1 N H_2SO_4, at 20°, $\eta = 1.427 + 0.113 \lg i$, from which, after making a correction for the temperature coefficient, we get $i_r = 5 \times 10^{-13}$. From the data (unpublished) of Jofa and Mikulin, however, for 0.25 N H_2SO_4, at 25°, we get a higher value of i_r, equal to 1.5×10^{-12}. From Jofa's data for 0.1 N HCl, at 25°, $i_r = 1.8 \times 10^{-12}$, which is in good agreement with $i_r = 1.7 \times 10^{-12}$ extrapolated by Bowden and Agar[17] rom the data of Levina and Sarinsky for 0.1 N HCl, at 25°. In spite of some disagreement in the data obtained in our laboratory for H_2SO_4 we can suppose on the grounds of these results that the values of i_r, obtained by Bowden and Kenyon, are too high, *i. e.* the overvoltage is somewhat lowered (the correct value, is probably about 1.6×10^{-12}); the disagreement with our data is not, however, very great. Altogether different results for low current densities obtained Mituya[18]. His measurements were performed in a soldered glass vessel, filled with hydrogen, in which mercury and a large platinum grid anode were placed. Mituya observed in the range from $i = 1.87 \times 10^{-9}$ to $i = 4.3 \times 10^{-11}$ not only the rectilinear part of the $\eta, \lg i$ curve, but also the approach of the curve to the abscissa axis in the neighbourhood of the reversible hydrogen potential ($\eta < 0.05$). The study of the shape of the overvoltage curve on mercury in the vicinity of the reversible hydrogen potential would be of extraordinary interest from a theoretical viewpoint; however, the reliability of Mituya's data is doubtful for the following reasons. In the rectilinear part of the curve a very unusual value of b for mercury was observed (0.186 at 0° in 0.1 N HCl); for a current density equal to 1.87×10^{-8} (the value up to which the measurements of Mituya were performed) η was found equal to 0.377, while according to the data of Levina and Sarinsky, for $i = 2.2 \times 10^{-8}$, $\eta = 0.505$, at 22°, which would correspond to $\eta = 0.61$ at 0°. Therefore, the value of the overvoltage on the surface of Hg in Mituya's experiments was lowered for some reason by ca. 0.23 V, which enabled him to reach such low values of η. An inspection of the arrangement used by Mituya leads us to the conclusion that platinum from the large surface of the anode could very easily get on the surface of the cathode, the anode being in no way separated from the cathode. This, possibly, was the source of the contamination.

[18] Mituya, Bull. Inst. of Phys. and Chem. Res., Tokyo, 19, 142 (1940).

5. Dropping electrode

In the work of Heyrovsky and his collaborators we find the assertion that the laws of hydrogen overvoltage observed on a mercury dropping cathode differ to a great extent from those obtained with resting mercury; in particular Heyrovsky gives in this case a different value of b in Tafel's[19] equation.

Let us consider two cases separately.

a) Overvoltage on a dropping cathode in the absence of concentration polarization

As it has been shown by Jofa, Kolychev and Shtifman[20], when measuring overvoltage on a dropping electrode, it is necessary to take into account the change in the surface of the drop with polarization and moreover, when $i \leqslant 10^{-5}$, the non-faraday current charging the double layer of the mercury surface also has to be accounted for. Besides that, if we are calculating the current density using the value of the surface area of the drops when detached from the electrode, we must make a correction for the difference between this surface and the mean effective surface of the drops during their growth, this last correction depending upon the experimental conditions. If the measurements are performed for a constant current intensity I, then evidently

$$i = \frac{I}{S} = \frac{I}{S_0} \frac{\tau^{2/3}}{t^{2/3}}$$

where S is the surface of the drop at the moment t, and S_0—the surface at the moment of the detachment of the drop τ.

Hence:

$$\eta = a + b \lg i = a + b \lg \frac{I}{S_0} + \frac{2}{3} b \lg \frac{\tau}{t} = a + b \lg \frac{I}{S_0} + \frac{4}{3} \frac{RT}{F} \ln \frac{\tau}{t} ;$$

$$\bar{\eta} = a + b \lg \frac{I}{S_0} + \frac{1}{\tau} \frac{4}{3} \frac{RT}{F} \int_0^{\tau} \ln \frac{\tau}{t} dt = a + b \lg \frac{I}{S_0} + \frac{4}{3} \frac{RT}{F} . \qquad (5)$$

Therefore, the last correction amounts to $4/3 \times RT/F$, *i. e.* to 0.034 at room temperature. As it has been shown by Jofa, Kolychev

[19] Heyrovsky, Chem. Rev., **24**, 125 (1939).
[20] Jofa, Kolychev and Shtifman, Acta Physicochimica URSS, **12**, 231 (1940).

and Shtifman, after introducing these corrections, in the interval of i from 10^{-5} to 10^{-2} in solutions of HCl and HBr of different concentrations a coincidence within the limits of 0.005 V was observed in the values of overvoltage measured on dropping and resting cathodes. If we perform the measurement not with a constant current, but as it is usually done with the aid of a polarograph, for constant potential, the last term of equation (5) has a somewhat different value. Indeed, in this case

$$\eta = \text{const}, \qquad i = \text{const}';$$

$$I = iS_0\tau^{-2/3}t^{2/3}; \qquad \bar{I} = \frac{1}{\tau}\int_0^{\tau} iS_0\tau^{-2/3}t^{2/3}dt = \frac{3}{5}iS_0;$$

$$\eta = a + b\lg i = a + b\lg\frac{\bar{I}}{S_0} + b\lg\frac{5}{3} = a + b\lg\frac{\bar{I}}{S_0} + 0.026. \qquad (6)$$

Thus, when using a dropping electrode, the measurements performed with a constant current should give a mean value of η by 0.008 higher than measurements with constant η, the mean value of I being the same. Indeed, according to unpublished data, Jofa has succeeded in observing a difference of 0 006 having the correct sign between the overvoltage curves taken according to both methods.

b) Overvoltage on a dropping electrode in the presence of concentration polarization

This case to which apply the statements of Heyrovsky and coworkers as to the existence of essential differences between data obtained with the dropping and resting mercury electrodes is considerably more difficult from the theoretical point of view than the preceding one. Overvoltage in this region of current intensities is characterized in polarographic practice by the half wave potential which corresponds to the fall of the concentration of hydrogen ions at the surface of the dropping electrode to a half of its initial value. As it has been shown by Tomeš[21] it follows from the equations for hydrogen overvoltage in the presence of an excess of an indifferent electrolyte (these equations being obtained from the theory of retarded discharge—see below) that the half wave potential should not depend upon concentration of hydrogen ions, whereas

[21] Tomeš, Collection, **9**, 150 (1937).

Tomeš observed a shift of this potential as the solution was diluted. Besides this, it was observed that the shape of the polarographic wave in the case of the evolution of hydrogen also did not correspond to the conclusions drawn from the theory of overvoltage.

It is of certain interest at first to derive from the values of overvoltage measured on a resting electrode the value of the half wave potential for some definite solution. As far as I know, no such computation has as yet been made in literature. As an example let us take N LiCl + 0.001 N HCl. According to the well known equation of Ilkovič, Rideal, McGillavry[22], the intensity of the diffusion current for a univalent ion is equal to

$$I = 4(7\pi)^{1/2}3^{-1/2}FD^{1/2}(c_0 - c)r^2t^{-1/2}$$

where D is the coefficient of diffusion of H^+ ions, $c_0 - c$ is the difference between the bulk concentration of H^+ ions and the concentration at the surface of the drop (g.-eq. per cm.^{3}), r — the radius of the drop at the moment t. The half wave, evidently, corresponds to $c_0 - c = \frac{1}{2}c_0$. For the current density, we get

$$i = 7^{1/2}(3\pi)^{-1/2}FD^{1/2} \times \frac{1}{2}c_0t^{-1/2} = At^{-1/2} \qquad (7)$$

where A is a constant. From equation (7) it follows

$$\eta = a + b\lg i = a + b\lg A - \frac{1}{2}b\lg t,$$

$$\bar{\eta} = a + b\lg A - \frac{1}{2}b\lg\tau + \frac{1}{2}\frac{b}{2.30} = a + b\lg i_\tau + \frac{RT}{F}, \qquad (8)$$

where i_τ is the density of the diffusion current at the moment τ when the drop detaches from the electrode. Let us compute at first the value i_τ, according to equation (7); in doing so let us put $F = 96\,500$, $D = 7.5 \times 10^{-5}$, $c_0 = 10^{-6}$ and $\tau = 5$ sec. Unfortunately, the time of the dropping is not given in the Tomeš paper, but probably the assumed value of 5 sec. will not differ too much from the true one. From equation (7) we get $i_\tau = 1.6 \times 10^{-4}$. Using equation (8) the value of η for a solution of N LiCl + $+5 \times 10^{-4}N$ HCl and a current density i_τ should now be determined. Unfortunately, such measurements have not been made,

[22] Ilkovič, Collection, **6**, 498 (1934); Rideal and McGillavry, Rec. trav. chim., **53**, 1013 (1937).

however Jofa[23] measured the overvoltage in a solution of N LiCl + 0.1 N HCl. For $i = 1.6 \times 10^{-4}$ $\eta = 1.026$. When going over from N LiCl + 0.1 N HCl to N LiCl + 5×10^{-4} N HCl, η should increase (see below) by 0.058 lg 200 = 0.133. Thus we get for the latter solution, i being the same, $\eta = 1.159$ and, according to equation (8), $\bar{\eta} = 1.184$. This value evidently refers to a reversible hydrogen electrode in N LiCl + 5×10^{-4} N HCl, and after recalculating on a normal calomel reference electrode we get for the half wave potential in the usual designation 1.66. Tomeš gives for N LiCl + 10^{-3} N HCl the value 1.63 and for N $CaCl_2$ + + 1.2×10^{-3} N HCl = 1.64. Such an agreement should be considered quite satisfactory. If, however, we shall consider our derivation more in detail, we will note that we made some not quite permissible assumptions. In fact, we have assumed that the concentration of hydrogen ions remains constant during the process the growth of the drop. As well known, it is under this condition, and under this condition only, that the equations of diffusion towards the surface of a growing drop can be integrated and lead to the dependence of current density upon time expressed by equation (7). In reality, during polarographic measurements, it is the potential which remains constant in the course of the growth of the drop, and, consequently, for constant concentration, the current density should be constant which is incompatible with equation (7). Practically, measurements could be effected also for constant I. In this case $i = \text{const} \cdot t^{-2/3}$ which does not agree with equation (7) as well, although the disagreement here is less than in the case when the potential is kept constant. Therefore, the condition of constant concentration of discharging ions cannot be fulfilled in the case of hydrogen ions. In this respect there exists an essential difference between the ion H^+ and, let us say, Hg_2^{++}, for which the constancy of the potential leads directly to the constancy of concentration. Herefrom the impossibility of an exact derivation of the equation of a polarographic wave of hydrogen ions follows directly. To be more exact, in order to do so, we would have to integrate the equations of diffusion towards the surface of a growign drop with the boundary conditions following from the dependence of the cathode potential upon current density and concentration; this

[23] Unpunlished data.

appears, however, to present unsurmountable mathematical difficulties. Thus the measurement of the half wave potential and of the shape of the polarographic wave cannot be used for the precise investigation of the hydrogen overvoltage on mercury. However, we would like to point out that Jofa's experiments (unpublished data) failed to confirm the existence of a shift of the half wave potential when concentration varies as described by Tomeš. In solutions of 0.2 N LiCl + HCl, the concentration of the acid varying from 2×10^{-4} to 10^{-3} N, the half wave potential was equal to 1.65 ($\tau = 2.6$ sec.) and independent of the concentration. A calculation of this potential carried out in the same way as given above, leads to the value 1.66.

6. Adhesion of hydrogen bubbles to the surface of mercury

This phenomenon is especially pronounced when measurements are performed near the electrocapillary maximum, which practically takes place only in strong solutions of acids. Still, for a well purified liquid, the adhesion never reaches such an extent as to alter seriously the results of overvoltage measurements.

7. Slow processes on the surface of the electrode

In the case of a mercury electrode slow systematic changes of overvoltage are, apparently, connected principally with the slowness of adsorption of surface active ions or molecules[24]. These phenomena, which are accompanied by the appearance of hysteresis loops on the overvoltage curve within certain intervals of current densities, are absent in solutions of SO_4'' ions and are especially pronounced in the presence of I' ions. We should admit that the mechanism of these phenomena is not yet quite clear.

Orleman and Kolthoff[25] recently described a new effect, which they call «the anomalous electroreduction of water at the dropping mercury electrode in relatively concentrated salt solutions». What is actually observed is an increase of the diffusion current in some cases of electroreduction, notably of thallium during the electroreduction of TlCl in the presence of a large excess of an indifferent electrolyte. The effect disappears if the drop time exceeds

[24] Jofa, Kabanov, Kuchinsky and Chistyakov, Acta Physicochimica URSS, **10**, 317 (1939).
[25] Orleman and Kolthoff, Journ. Am. Chem. Soc., **64**, 833 (1942).

4.5 sec. and on addition of capillary active substances. It cannot be observed with a stationary electrode. The evidence quoted in favour of the supposition that the effect is due to electrolysis of water seems inconclusive; in fact, as it follows from the data given by the authors, such a reduction at some of the potentials observed is thermodynamically impossible. Orleman and Kolthoff to escape this difficulty admit that no molecular hydrogen, but a dilute hydrogen amalgam is formed during this process. The formation of hydrogen amalgams however until now never could be checked if sufficient precautions were taken to avoid all experimental errors. The effect described by Orleman and Kolthoff is almost certainly a stirring effect caused by the movements of the mercury surface [26]. The character of this movements in concentrated salt solutions needs further investigation.

8. Capacity and structure of the double layer

In order to understand the phenomenon of overvoltage on mercury it is important to know the composition of the double layer within the spatial limits of which the discharge of the hydrogen ion takes place. This knowledge can be obtained both by measuring the dependence of surface tension upon the potential and concentration and by the direct measurement of the capacity of the double layer. The thermodynamical relations which have to be used in the first case for concentrated solutions were deduced by Jofa and Frumkin [27]. The measurements of the recent years have shown unambiguously that there is no disagreement between the direct measurements of the double layer capacity and the results of the computations based on electrocapillary curves [28].

Of considerable interest are the results of direct measurements of the capacity with a mercury cathode in the region of noticeable

[26] Frumkin and Bruns, Acta Physicochimica URSS, **1**, 232 (1934); Antweiler, Z. Elektrochem, **43**, 596 (1937); **44**, 719 (1938); Bruns, Frumkin, Jofa, Vanjukova and Zolotarewskaja, Acta Physicochimica URSS, **9**, 359 (1938).

[27] Jofa and Frumkin, Acta Physicochimica URSS, **10**, 473 (1939).

[28] Experimental data on capacity; Proskurnin and Frumkin, Trans. Faraday. Soc., **31**, 110 (1935); Borissowa and Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936); **12**, 371 (1940); Barclay and Butler, Trans Faraday. Soc., **36**, 128 (1940); Frumkin, *ibid.*, 117; Grahame, J. Am. Chem. Soc., **63**, 1207 (1941); Philpot, Phil. Mag., (7), **13**, 775 (1932).

evolution of hydrogen, when it is already impossible to obtain an electrocapillary curve experimentally. In doing so we must keep in mind, however, that the possible range of measurements is limited here also. Having a relation between overvoltage and current, expressed by the equation $\eta = a + b \lg i$, while measuring the capacity with the aid of an alternate current we will observe in the system, besides capacity, a conductivity $Fi_0/2RT$, which increases with cathodic polarization. Indeed, if on a direct current i_0 a weak alternate current I is superimposed, then

$$\eta = \frac{2RT}{F} \ln (i_0 + I) + \text{const} = \frac{2RT}{F} \ln i_0 + \frac{2RTI}{Fi_0} .$$

The appearance of this «conductivity» of the electrode limits the range of applicability of alternate current. In using currents of comparatively high frequency we have to take into account also the ohmic resistance of the solution when measuring the capacity of the mercury electrode [29]. In this case with mercury it is difficult to give to the electrode an advantageous shape in the sense of lowering the ohmic resistance, while in the case of solid metals, such as platinum, this can be done. That is why up to now we did not succeed in raising the frequency above 3500 c. p. s. While measuring capacity up to this limit we did not observe a considerable change in its value; the reality of a small decrease which has been observed has still to be checked. It will be seen below that the study of the capacity of the double layer is especially important for the explanation of the influence of adsorption of ions upon overvoltage. Here it is necessary to consider only several general conclusions to which the study of the capacity of the double layer leads.

a) The absence of atomic hydrogen on the surface of mercury. While the discharge of hydrogen atoms on nickel or platinum takes place on a surface covered to a considerable extent by adsorbed hydrogen, on the surface of mercury in the potential region of hydrogen overvoltage no measurable quantities of atomic hydrogen could be observed. This is seen best of all from a comparison of electrocapillary curves of an acidulated and an alkalized neutral salt. It is evident that, electric potentials being the same, the chemical potential of

[29] Borissowa and Proskurnin, Acta Physicochimica URSS, **12**, 371 (1940).

hydrogen in an acid solution is considerably higher and in the presence of adsorbed hydrogen the surface tension in an acid solution should be lower. Meanwhile the electrocapillary curves, for instance, of N Na_2SO_4 + $+0.01N$ KOH and N $Na_2SO_4 + 0.01N$ H_2SO_4 coincide within the limits of some tenths of dyn/cm. (the electrocapillary curve of the alkalized solution lies even a few tenths of an unit lower [30]; the measurements were performed up to $\varphi = -1.5$ with respect to a normal calomel electrode). In view of the excess of the common electrolyte present in both solutions we can suppose that the ionic composition of the double layer is the same; then for the surface densitiy of the atomic hydrogen Γ_H we get from Gibbs' formula

$$\Gamma_H = -\left(\frac{\Delta\gamma}{\Delta\mu_H}\right)_\varphi \qquad (9)$$

where μ_H is the chemical potential of the hydrogen and γ — the surface tension at the mercury-electrolyte boundary. Considering that the change in the boundary tension in going over from one solution to another is in any case less than 0.5 dyn/cm., while μ_H when the concentration of the hydrogen ions in the solution changes by $\sim 10^{10}$ for constant electric potential φ, should change by $RT \times 10 \ln 10$, *i. e.* by 5.5×10^{11}, we get from equation (9) that

$$\Gamma_H < 10^{-12} \text{ g. atom/cm.}^2.$$

Meanwhile, as it is known, concentrations of ions in the double layer are of the order of 10^{-10} g. ion/cm^2. The total covering of all the atoms of mercury on the surface by hydrogen would give us $\Gamma_H \sim$ $\sim 2 \times 10^{-9}$. Therefore, atomic hydrogen surely cannot be present on the surface of mercury in concentrations exceeding 0.05% of that corresponding to the saturation of all surface atoms or 1% of the concentrations of ions in the double layer; in reality it is probably still less. Therefore theories of overvoltage allowing any considerable saturation of the mercury surface by adsorbed discharged hydrogen atoms should be discarded [31]. Concerning the absence of atomic hydrogen on the surface of mercury see also Barclay and Butler [32] and Frumkin [33].

[30] Unpublished data.
[31] Hirota and Horiuti, Bull. Chem. Soc. Japan, **13**, 228 (1938); Heyrovsky, Chem. Rev., **24**, 125 (1939).
[32] Barclay and Butler, loc. cit.
[33] Frumkin, Scient. Pap. Inst. of Phys. and Chem. Res., Tokyo, **37**, 473 (1940).

b) This comparison of the properties of the double layer in two solutions with different pH, but practically identical in composition in other respects, is of interest from another point of view too. It shows that the structure of the double layer, the composition of the solution being unchanged, is not connected with the value of overvoltage. In fact, should a comparison be made, for instance, for $\varphi = -0.72$ (with respect to a normal hydrogen electrode) the overvoltage in the alkalized solution will equal zero while in the acidulated one it will amount to about 0.58 V. As the measurement of the surface tension shows, the double layer in both cases has exactly the same structure. In the theory of overvoltage which has recently been developed by Kimball, Glasstone and Glassner [34] the supposition is made that the double layer consists of two spatially separated parts and that the potential drop in one of them (namely the one adjoining the electrode) is equal to the value of the overvoltage, while the remaining portion of the potential drop lies in the outer part of the double layer. On the basis of such a conception one would expect a very different structure of the double layer in the acidulated and the alkalized solutions, the total potential drop being equal. As we see, this is in contradiction with experimental data.

c) The measurements of the capacity of the double layer may in certain cases give a very detailed picture of its structure. Of special interest is the case when in the double layer we have polyvalent cations (Al^{+++}, La^{+++}, Th^{++++}) which, as it is known, increase the overvoltage [35]. In Fig. 3 are shown the curves of the capacity of a 10^{-3} N HCl solution with additions of $LaCl_3$ (based on data of Vorsina [36]). The potentials are given with respect to a normal calomel electrode. From these curves it is seen that when going over from a positive charge of the surface of the mercury to a negative one, there is observed a pronounced maximum of the capacity, *i. e.* a rise of the absolute value of the charge within a comparatively narrow potential range. This rise is connected with the penetration into the surface layer of polyvalent cations whose electric field forces out

[34] Kimball, Glasstone and Glassner, J. Chem. Phys., **9**, 91 (1941).
[35] Herasymenko and Šlendyk, Z. physik. Chem., (A) **149**, 123 (1930); Frumkin, Z. physik. Chem., (A) **164**, 121 (1933); Levina and Marinsky, Acta Physicochimica URSS, **7**, 485 (1937).
[36] Vorsina, unpublished data (Karpov Institute of Physical Chemistry).

hydrogen ions from the surface layer thus leading to an increase of the overvoltage.

B. The results of overvoltage measurements on Hg

1. Dilute solutions. Experimental data

Let us conventionally define as dilute the solutions in which the concentration of H^+ does not exceed $0.1-0.2\,N$. Let us consider at first solutions of pure acids, containing no foreign cations.

a) Concentration. In dilute acid solutions the overvoltage does not depend upon concentration. The data of Levina and Sarinsky[37] show that the curves for $0.001\,N$ and $0.01\,N$ HCl coincide, the curve of $0.1\,N$ HCl lies, apparently, somewhat lower; the difference, however, does not exceed 0.005.

b) The shape of the curves. The η, $\lg i$ relation is linear, the value of the coefficient α ($b = \frac{RT}{\alpha F} \times 2.303$) being very near to 0.5 (see below). On the curve of $0.2\,N$ HBr for $\lg i < -6$, according to Jofa's data, a decrease of the overvoltage as compared with the linear relation is observed. This phenomenon, connected with the adsorption of the anion, would undoubtedly be better expressed in solutions of HI, but for low concentations there are no corresponding measurements.

c) Influence of the anion. Even though between different acids small individual distinctions are observed, yet a definite influence of the nature of the anion in dilute solutions cannot be established. The most reliable data of Jofa can be expressed by the following relations:

Table 4

Acid	η at 20°
$0.1\,N$ HCl	$1.439 + 0.119 \lg i$
$0.2\,N$ HBr	$1.420 + 0.114 \lg i$
$0.1\,N$ H_2SO_4	$1.426 + 0.113 \lg i$
$0.1\,N$ $HClO_4$	$1.393 + 0.106 \lg i$

The value for $0.1\,N$ $HClO_4$ are perhaps somewhat less reliable than the others. The mean value for the remaining three curves is $1.428 + 0.115 \lg i$. In the range of $\lg i$ from -6 to -1 individual curves differ from this average not more than by 0.013, which is close to the limits of experimental error. Therefore in these conditions the influence of the anion may be practically neglected.

[37] Acta Physicochimica URSS, **6**, 491 (1937).

d) The temperature coefficient. According to Jofa and Mikulin[38] for $0.25\,N$ H_2SO_4, at 0.3° $b = 0.107$, at 20° $b = 0.116$, at 60° $b = 0.130$ and at 80° $b = 0.135$, *i. e.* b is almost proportional to the absolute temperature.

e) Let us turn now to solutions containing either an excess of a foreign electrolyte or polyvalent cations in a small concentration, which from a theoretical viewpoint must give the same results. This case is of particular interest for the theory of overvoltage. Unfortunately, the experimental data in this case are considerably less numerous. In literature it is often asserted that in this case overvoltage also does not depend on the concentration of H^+ ions[39]. However, the measurements of Levina and Sarinsky[40] demonstrate clearly that in the presence of $LaCl_3$ overvoltage increases by 0.105—0.110 when going over from $0.1\,N$ HCl to $0.001\,N$ HCl, while according to Herasymenko and Šlendyk[41] the cathodic potential of hydrogen at a given current density in $N\,BaCl_2 + x$ HCl solutions becomes in the average by 0.112 more negative when the concentration of HCl is decreased tenfold, *i. e.* the overvoltage increases by about 0.055. The measurements of Levina and Sarinsky cover a too narrow range of $\lg i$ values to allow a sufficiently exact calculation of the quantity b in Tafel's equation, but these measurements seem to show a considerable increase of b (up to 0.142) in $0.001\,N$ HCl in the presence of $LaCl_3$. This phenomenon requires additional checking. In $0.25\,N$ $H_2SO_4 + N\,Na_2SO_4$ solutions Jofa and Mikulin found the normal value $b = 0.116$.

The addition of electrolytes with an adsorbable organic cation, such as N $(C_4H_9)_3H^+$ causes a strong rise in the overvoltage[42].

2. The slow stage of discharge

It is scarcely reasonable to give here again the theory of overvoltage for a mercury cathode in details. I will consider only those

[38] Unpublished data.
[39] Bowden and Agar, Ann. Rep. Chem Soc., **35**, 97 (1938).
[40] Levina and Sarinsky, Acta Physicochimica URSS, **7**, 485 (1937).
[41] Herasymenko and Šlendyk, Z. physik. Chem., **149** 26 (1930).
[42] Jofa, Kabanov, Kuchinsky and Chistyakov, Acta Physicochimica URSS, **10**, 327 (1939).

points which recently have been discussed in literature or those which it seems desirable to elucidate from the point of view of new experimental results.

Since for a mercury cathode the practical absence of H atoms on the surface of the electrode can be demonstrated unambiguously (see above), the recombination theory or any theory according to which the velocity of hydrogen evolution is determined by some reaction with the participation of an atom and an ion of hydrogen, as, for instance, $H + H^+ + \ominus \rightarrow H_2$ or $H_2^+ + \ominus \rightarrow H_2$ cannot explain the experimental value of the coefficient $\alpha \sim {}^1/_2$. Indeed, all the corrections proposed recently by Horiuti and collaborators[43], based on the account of the repulsive forces of interaction between adsorbed atoms and molecular ions H_2^+ of hydrogen, and also between these particles and the activated complex of reaction, determining the rate of the evolution of H_2, become meaningless and the elementary method of calculations according to which for a recombination mechanism $\alpha = 2$, while for a mechanism where an atom and an ion of hydrogen participate $\alpha = 1$[44] remains valid. While in the presence of noticeable quantity of hydrogen on the surface we can get from these theories, as has been shown by Horiuti, fractional values of the coefficient α as well, in the case when there is a low saturation with adsorbed hydrogen they necessarily give values of $\alpha \geqslant 1$.

Therefore, the author concludes that for the case of an Hg-electrode the only permissible supposition is that the initial process of discharge, which leads to the appearance of the adsorbed atom of hydrogen is the slow stage of the whole reaction. This supposition, as it is known, was formulated in a quantitative way for the first time by Volmer[45]. It enables us to consider Tafel's relation as a particular case of kinetic regularities which are observed in the process of proton transfer[46]. What happens farther to the atom of hydrogen — whether it leaves the surface of the mercury because of its reaction with a

[43] G. Okamoto, Journ. Fac. Sci. Hokkaido University, **2**, 116 (1938).

[44] Or more than unity, if we consider not only the increase of the surface concentration of H, but the accelerating action of the field upon the reaction $H + H^+ + \ominus$ as well.

[45] Erdey Gruz u. Volmer, Z. physik. Chem., (A) **150**, [illegible] (1930).

[46] Frumkin, Z. physik. Chem., (A) **160**, 116 (1932).

second ion or because of its recombination with another atom— we can not judge on the basis of the available experimental data.

There were several considerations put forth in order to explain the appearance of a fractfonal coefficient α within the scope of the theory of retarded discharge.

According to Polanyi[47], of basic importance is the weakening of the bonds between the atom of hydrogen and the surface of mercury in the transition stage of the discharge reaction as the overvoltage increases, due to which not all the accelerating action of the field on the reaction of the discharge can be utilized. It would be very important, for the sake of testing this theory, to know the energy of adsorption of a hydrogen atom on the surface of mercury. When this theory is critically examined the supposition is usually expressed that this energy is very small. The latter is based, however, [illegible]n data concerning the binding energy of isolated molecules HgH; the identification of this binding energy with the energy of adsorption of an atom H on a metal surface seems arbitrary. Eyring and collaborators[48], following Erdey Gruz and Wick[49] suppose that the discharge of an activated complex takes place ap[illegible]oximately in the middle of the Helmholtz layer; correspondingly it [illegible]lows herefrom that only a half of the potential drop is utilized. Finally, the interaction between a hydrogen atom after discharge and molecules of water which formed the hydration shell of the hydrogen ion, also affects the value of α. This has been pointed out for the first time by Gurney[50].

However, we must admit that none of the theories proposed can explain the remarkable fact that α retains a constant value very close to 0.5 within a great range of current density — from 10^{-8} and probably even 10^{-9}—10^{-10} till 1 or even till 10 A/cm.^{2}, which corresponds to a change of the energy of reaction by 22—26 Cal. It is as yet a problem of the future to set up a truly quantitative theory of the hydrogen ion discharge.

[47] Horiuti and Polanyi, Acta Physicochimica URSS, **2**, 505 (1935).

[48] Eyring, Glasstone and Laidler, J. Chem. Phys., **7**, 1053 (1939).

[49] Erdey Gruz u. Wick, Z. [illegible]physik. Chem., (A), **162**, 53 (1931).

[50] Gurney, Proc. Roy. Soc., (A) **134**, 137 (1931); Butler, Proc. Roy. Soc., (A) **157**, 423 (1936); see also Essin and Kozheurov, Acta Physicochimica URSS, **16**, 169 (1942).

3. The reacting particle

In most of the theories which have been proposed till now, it was supposed that in acid solutions it is the hydrogen ion which is the reacting particle. According to Eyring and his collaborators [51], however, even in acid solutions it is not a H^+ ion that reacts, but a molecule of water. In this case, however, the cathodic potential of mercury in the course of hydrogen evolution would not depend upon the concentration of H^+, *i. e.* overvoltage would decrease with dilution, which contradicts all experimental data [52]. In order to avoid this difficulty Kimball, Glasstone and Glassner [53] tried to divide the potential drop in the Helmholtz double layer into two parts; of these two parts only one corresponding to the overvoltage is effective during the discharge of hydrogen ions. As it has been shown above, this supposition, however, is not confirmed by experimental data concerning the double layer.

4. The structure of the double layer

If we are assuming that the hydrogen ions are the reacting particles and only those hydrogen ions which come into direct contact with the surface of mercury, then in the expression of the rate of the discharge reaction there must enter along with the cathodic potential φ the value of the potential at a distance of one ionic radius from the surface of the mercury [54]. This value has been designated by Stern [55] in his theory of the double layer by ψ_1.

If the surface of separation of a moving liquid would pass at a distance of one molecular diameter from the surface of the mercury, then the last quantity could be identified with the ζ-potential as determined from electrokinetic data. A number of facts, however, make us think that the thickness of the layer of liquid held by the molecular forces of the metal exceeds one molecule, and at such conditions the quantities ψ_1 and ζ do not coincide; their difference must increase with the concentration of the solution.

[51] Loc. cit.
[52] Frumkin, Acta Physicochimica URSS, **12**, 481 (1940).
[53] Loc. cit.
[54] Frumkin, Z. physik. Chem., (A), **164**, 121 (1933).
[55] Stern, Z. Elektrochem., **30**, 508 (1924).

From the point of view of the double layer theory, the simplest case is the one in which there is an excess of an indifferent electrolyte in the solution; then the concentration of H^+ in the double layer must be proportional to the concentration in the solution. In this case it is easy to show that the overvoltage must increase with dilution like the quantity $(-RT/F)\ln[H^+]$.

As it has already been pointed out the existence of this effect was some times disputed in literature. However I see no possibility of escaping from this conclusion, unless we are to assume a large specific adsorption of the H^+ ions, which, however, would contradict the experimental data relating to electrocapillary curves.

In the general case it follows from the theory, that

$$\varphi = \frac{RT}{\alpha F}\ln[H^+] - \frac{RT}{\alpha F}\ln i - \frac{1-\alpha}{\alpha}\psi_1 + \text{const}, \qquad (10)$$

$$\eta = \frac{1-\alpha}{\alpha}\psi_1 + \frac{RT}{\alpha F}\ln i + \left(1-\frac{1}{\alpha}\right)\ln H^+ + \text{const}, \qquad (10a)$$

and if $\alpha = 1/2$

$$\varphi = -\psi_1 + \frac{2RT}{F}\ln[H^+] - \frac{2RT}{F}\ln i + \text{const}, \qquad (11)$$

$$\eta = \psi_1 - \frac{RT}{F}\ln[H^+] + \frac{2RT}{F}\ln i + \text{const}. \qquad (11a)$$

As it has been shown by the present author [56] under the condition that the surface of mercury is charged negatively and that the concentration of anions in the surface layer can be neglected in comparison to the concentration of cations, in solutions of acids without foreign electrolytes the quantity $\psi_1(-RT/F)\ln[H^+]$ is constant when η is constant and, consequently, η does not depend upon the concentration of the acid. The last conclusion can be considered well confirmed by experiment; however, from the viewpoint of the checking of the theory it is of less interest since the independence of the overvoltage of concentration might be deduced on other theoretical bases too, as for instance, from the recombination theory. In the latter, however, this independence has to hold also when foreign electrolytes are added, which is not confirmed by experiment. In order to check equation (11a) it would be very important to pro-

[56] Acta Physicochimica URSS, **6**, 491 (1937).

long the measuremens of η in dilute solutions of acids up to the point of zero charge near which the quantity ψ_1 changes markedly. At $[H^+]$ and i constant, equation (11a) turns into

$$\eta = \psi_1 + \text{const.} \tag{12}$$

5. Polyvalent cations

Equation (12) was used to explain the increase of the overvoltage under the action of polyvalent cations [57]. The measurements of the capacity of a mercury cathode in dilute solutions carried out by Vorsina[58] enable to check equation (12) more directly. In fact, if we admit the basic assumption of Stern for the case of a negatively charged surface of mercury, *i. e.* if we consider the layer adjoining the electrode as a condenser of constant capacity C, with the potential in each point depending only on its distance from the surface of the mercury, then, according to Stern, the charge of the surface ε is equal to

$$\varepsilon = C(\varphi - \psi_1). \tag{13}$$

The cathodic potential φ here, naturally, is counted off from the point of zero charge (in the absence of a specific adsorption of ions, *i. e.* when $\psi_1 = 0$).

Since the measurements of capacity give directly the quantity $\partial\varepsilon/\partial\varphi$, we can find from these measurements the quantity ε if the position of the point $\varepsilon = 0$ is known and, consequently, according to equation (13) the quantity ψ_1 as well[59]. In practice most difficulty in doing so is caused by the insufficient precision of the determination of the quantity C. The value of ψ_1 found in this way can be compared with the values obtained from the increase of the overvoltage in dilute solutions, when polyvalent cations are added. In earlier works[60] it was supposed that, when polyvalent cations are added the quantity ψ_1 falls down to zero, since the layer looses its diffuse structure. Basing on this assumption the quantity ψ_1 may be found directly from the increase of η of the initial solution.

[57] Frumkin, Z. physik. Chem., loc. cit.; Levina and Sarinsky, Acta Physicochimica URSS, **7**, 485 (1937).
[58] Proskurnin and Vorsina, C. R. Acad. Sci. URSS, **24**, 915 (1939); Vorsina and Frumkin, *ibid.*, 918.
[59] Frumkin, Trans. Faraday. Soc., **36**, 126 (1940).
[60] Frumkin, loc. cit.; Levina and Sarinsky, loc. cit.

However, later measurements of Vorsina[61] showed that in reality the problem is more complicated. For instance, if the quantity ψ_1 is determined for the solutions $HCl + LaCl_3$ with the aid of the curves of Fig. 3, then it turns out that if a sufficient amount of $LaCl_3$ is added, ψ_1 first reaches a zero value and then changing its sign becomes positive. As it has already been shown the determination of single values of ψ_1 is not exact, because of a certain arbitrariness in choosing C. Experimental data vary within the limits of 17—20 microfarads per cm.^{2}. We shall use the value of 19 microfarads. Supposing the capacity of the Helmholtz layer to be approximately independent of the nature of the cation the average of Vorsina's numerous measurements for the value of the capacity at negative surface charges in a region of potentials, where the capacity almost does not change with polarization, is equal to 18.3 microfarads per cm.^{2}. However, it is sound to suppose that the true value of C lies somewhat higher, since by making use of the last value one would conclude that the diffuse structure completely disappears in a double layer at a concentration of 0.1 N. This, as it can be shown, is incompatible with other observations.

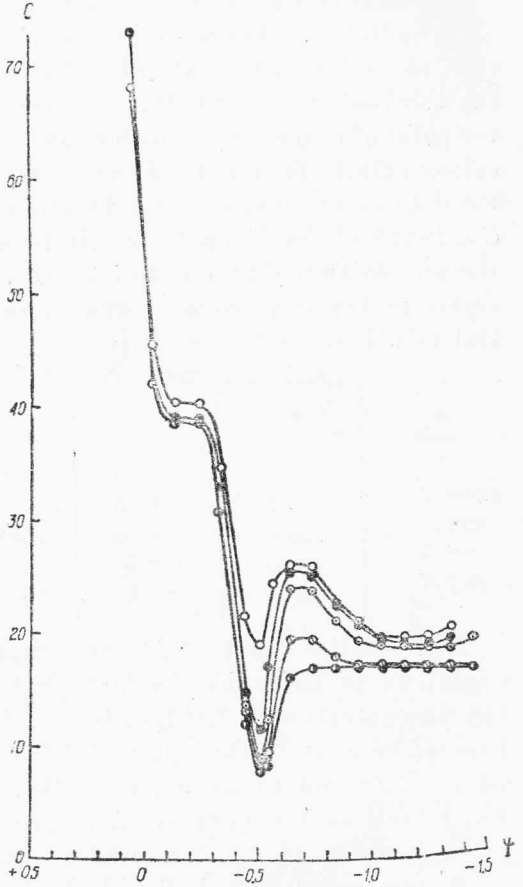

Fig. 3. The dependence of capacity (in microfarads/cm.^{2}) upon the potential of the electrode in solutions 10^{-3} N HCl + $x N$ $LaCl_3$ (according to Vorsina). x (reading up): 0; 10^{-5}; 10^{-4}; 10^{-3}; 10^{-2}.

[61] Vorsina, Acta Physicochemica URSS (in press).

The absolute values of ψ_1, especially at large negative potentials, are very sensitive to the choice of the value of C. However for the checking of equation (12) it is necessary to know only the difference of the values of ψ_1 for various solutions which depends upon C to a considerably smaller extent. The results of such a calculation are given in Table 5. The second column contains the values of overvoltage, according to the data of Levina and Sarinsky, for $\lg i = \overline{8}.35$, the third — the corresponding cathodic potentials φ calculated from the point of zero charge, which lies at —0.5 with respect to a normal calomel electrode, and the fourth — the values of ψ_1, calculated from the data of Vorsina, with the help of equation (13), using the value $C = 19 \times 10^{-6}$. In brackets are given the ψ_1 values calculated upon the supposition that $C = 18.3 \times 10^{-6}$. The quantities $\Delta\eta$ and $\Delta\psi_1$ represent the increase of η and ψ_1 in comparison with the initial solution.

Table 5

x	η	φ	ψ_1	$\Delta\eta$	$\Delta\psi_1$
0	0.520	—0.47	—0.09(—0.07)	—	—
$10^{-5}N$	0.597	—0.54	—0.05(—0.03)	0.077	0.035
$10^{-4}N$	0.606	—0.55	0.03(0.06)	0.086	0.13
$10^{-3}N$	0.610	—0.56	0.09(0.11)	0.090	0.18
$10^{-2}N$	0.606	—0.56	0.13(0.16)	0.086	0.22

The smaller value of $\Delta\psi_1$ as compared with $\Delta\eta$ at $x = 10^{-5}$ is explained probably by the fact that in Vorsina's experiments the concentration of $LaCl_3$ in the weakest solutions was markedly lowered because of the adsorption on the walls of the apparatus. At $x = 10^{-4}$ and above $\Delta\psi_1$ exceeds $\Delta\eta$ considerably. At higher concentrations the quantity $\Delta\eta$ approaches a limit in spite of the rapid increase of $\Delta\psi_1$. In order to explain this phenomenon we must reconsider Stern's double layer theory [62]. If the increase of $\Delta\eta$ lags behind that of $\Delta\psi_1$ this means that in the layer adjoining the surface of the electrode the concentration of the ions H^+ exceeds the quantity $[H^+]e^{-\psi_1 F/RT}$; we can easily see this by considering the derivation of equation (10). Such an excess would be impossible if the potential at a distance of one ionic radius from the surface of the electrode would have a constant value ψ_1

[62] Compare Essin and Markov, J. Phys. Chem. (Russ.), 1[illegible]18 (1939).

in all points. In reality, in the vicinity of polyvalent cations at any moment more positive values will be observed, while in the interstices between them—more negative ones. In these points a considerably higher concentration of ions H^+ should exist. As yet, there is no double layer theory which would consider the potential not only as a function of the distance from the surface, but also as depending upon the location of the particular point with respect to the ions of the double layer. However, it seems quite plausible to suppose that the last effect will be especially pronounced in the presence of polyvalent cations.

The increase of the overvoltage due to adsorption of organic cations, which has been mentioned above, in many ways resembles the effect of polyvalent cations. When interpreting the action of cations with a large radius such as $N(C_4H_9)_3H^+$ along with the change of the ψ_1 potential, the blocking of the surface by the organic ions has to be taken into account.

6. Adsorption of anions

According to equation (11) and (12) adsorption of anions must cause a lowering of η. Unfortunately, there were performed no measurements of η in dilute acid solutions with strongly adsorbable anions, such as HI. On the overvoltage curve of $0.2N$ HBr a lowering of η for $\lg i < -6$ is observed. Jofa, Kabanov, Kuchinsky and Chistyakov [63] measured the overvoltage in solutions of $0.1N$ HCl with additions of N KCl, N KBr and N KI. They observed at low current densities deviations from Tafel's formula, the overvoltage being lower as calculated from the linear relation. The lowering increased with the increase of the adsorbability of the anion. Since the penetration of the anion strongly influences the capacity of the double layer, the value of ψ_1 can not be computed for every value of the potential as it was done in the case of cation adsorption. The only exception is the potential corresponding to $\varepsilon = 0$, *i. e.* to the maximum of the electrocapillary curve, since in this case $\varphi = \psi_1$. The latter assertion holds strictly for a model of a surface layer which treats all ions as spheres of equal radius over which the charge is distributed with spherical symmetry. On the other hand, if, for instance, the centre of gravity of the charge

[63] Loc. cit.

of deformed anions is nearer to the surface of the mercury than is the centre of gravity of the cation charge, then between the surface of mercury and the plane surface in which the centres of hydrogen ions are located there will exist a negative potential difference and the value of ψ_1, as deduced from the position of the maximum of the electrocapillary curve, will be more negative than that one, which has to be taken into account when calculating the overvoltage (see also next paper of this series).

In solutions containing KCl and KBr the overvoltage could not be measured at the maximum of the electrocapillary curve, but in a solution of $0.1N$ HCl$+N$ KI such a measurement is possible. If we admit that the point of zero charge of mercury in the absence of specific adsorption of the anion lies at -0.50 with respect to a normal calomel electrode then in this solution at the maximum $\psi_1 = 0.32$. The decrease of the overvoltage as compared wiht the valu which would be observed at the same i and $[H^+]$ in the absence of adsorption and which can be obtained by extrapolation of the rectilinear part of the η, $\lg i$ curve (Fig. 1) to this potential equals -0.23. While according to equation (12) the relation $\Delta\eta = \psi_1$ should hold, in reality $\Delta\eta \sim 0.7\psi_1$, *i. e.* we get a result similar to the case of polyvalent cations. Thus the experiment confirms a qualitative parallelism between the absorbability of the anions and the lowering of the overvoltage, but for a quantitative theory the scheme of the double layer proposed by Stern is too rough an approximation.

As it is pointed out in the paper referred to above, when comparing electrocapillary and overvoltage curves, our attention is called to the following circumstance: the deviation of the latter from the rectilinear course begins at potentials considerably more negative than it could be expected according to the electrocapillary data. The overvoltage is already markedly lowered at such values of φ at which the adsorption of the anion does not yet have any effect upon the value of the boundary tension. The reason for this disagreement is not clear, but possibly it is connected with the difference of conditions of the formation of the mercury surface in both cases. As it was pointed out in the beginning of this paper, the establishing of adsorption equilibrium in the region of the transition from the rectilinear part of the η, $\lg i$ curve to the lowered values of η sets in with considerable delays, while the values of the surface tension are always measured on a fresh surface. It would be very desirable to perform

measurements of overvoltage and of boundary tension (or capacity) in these solutions on the same mercury electrode.

When salts are added to $0.1N$ HCl and $0.1N$ HBr we observe for more negative potentials not a fall, but an increase of η of the order of 0.035—0.040 V. This increase is similar to the results of the

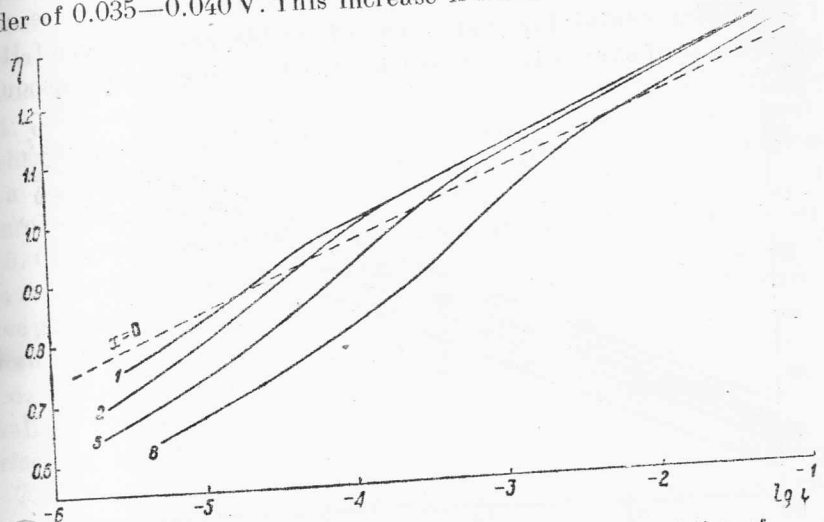

Fig. 4. The dependence of the overvoltage upon $\lg i$ in solutions of 0.1 g.-eq. HBr + x g.-eq. LiBr + 1000 g. H_2O. Dotted curve 0.1 HBr without Li Br.

action of polyvalent cations at low concentrations (the addition of $LaCl_3$ to $0.1N$ HCl increases the overvoltage by 0.026 V), and may be explained by the transition of ψ_1 from the initial negative to a zero value, or (this being more probable) to a small positive one. The possibility of such an increase points to the existence of a diffuse structure of the double layer at this concentration. As the concentration of the salt increases the region of the anion adsorption widens, and the lowering of the overvoltage and the «anionic» effect overlap the «cationic» one, spreading gradually over the whole curve as is seen from Fig. 4, where the η, $\lg i$ curves for mixtures of $0.1N$ HBr$+$LiBr are given. The dotted curve refers to pure HBr[64]. Similar relations are observed in mixtures of $0.1\ N$ HCl$+$LiCl and $0.1N$ HBr$+$LiI. When adding Na_2SO_4 to $0.1N$ H_2SO_4[64], *i. e.* a salt the anion of which is not adsorbed on mercury, up to a concentration of $5N$, the slope of the η, $\lg i$ curves remains invariable and

[64] Unpublished data of Jofa.

only a progressive increase of the overvoltage is observed. This last might depend upon the binding of H^+ ions by SO_4^{--} ions with formation of HSO_4^- ions and with a corresponding lowering of the concentration of H^+ and also upon the disappearance of the initial negative value of the ψ_1-potential (Fig. 5). For instance, in the case of a solution containing one g.-eq. of Na_2SO_4 per 1000 g. of H_2O the increase of overvoltage caused by the lowering of $[H^+]$should

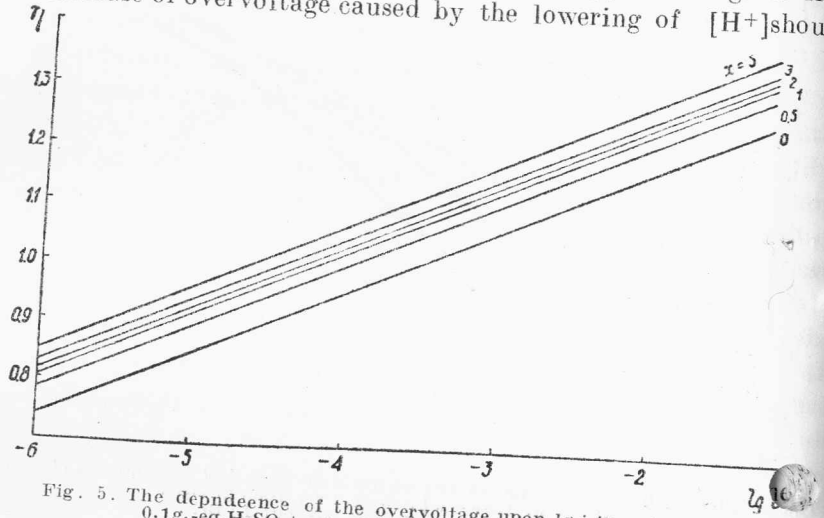

Fig. 5. The depndeence of the overvoltage upon lg i in solutions of 0.1g.-eq.H_2SO + xg.-eq. Na_2SO_4 + 1000 g. H_2O.

be, according to equation (11a), equal to 0.026, and with 5 g.-eq. Na_2SO_4 — to 0.054. The increase of η observed at $i = 10^{-4}$ A/cm.^{2} is equal to 0.061 and 0.105 respectively. The computation of the quantity $(RT/F) \ln [H^+]$ which enters into equation (11a) was carried out using the measurements of Harned and Akerlöf[65] on the supposition that all changes in the activity of H_2SO_4 in these solutions are caused by changes in the concentration of H^+ ions when adding Na_2SO_4.

Summary

1. Measurements of the hydrogen volume evolved confirm the correctness of the dependence of the overvoltage upon the current density as determined by the usual method.

2. Tafel's formula holds for the process of hydrogen evolution in the case of a mercury electrode up to the highest current densities used ($i = 1$ and 10 A/cm.^{2}). Deviations observed by Hickling and Salt were caused by an incorrect extrapolation of the curves of the overvoltage decay on the moment of interrupting the current.

3. When using a dropping electrode, the mean current intensities being equal, measurements for constant current intensity should give a mean value of the overvoltage by 0.008 exceeding the value at constant potential.

4. The half wave potential for the process of hydrogen ion discharge, calculated from the results of measuring the overvoltage on a resting electrode, is in good argeement with data obtained polarographically.

5. Quantitative analysis of phenomena taking place at the surface of a mercury dropping electrode shows that the measuring of the half wave potential and the shape of the polarographic curve cannot be used for an exact determination of the hydrogen overvoltage on mercury.

6. The comparison of electrocapillary curves of acidulated and alkalized solutions proves the absence of atomic hydrogen on the surface of mercury.

7. The mean value of the overvoltage on mercury, according to the most reliable data of Jofa for 0.1 N HCl, 0.2 N HBr and 0.1 N H_2SO_4 at 20° is $1.428 + 0.115 \lg i$.

8. The computation of the ψ_1-potential from the capacity curves measured by Vorsina shows that when salts of polyvalent cations (La^{+++}, Th^{++++}) are added to dilute solutions of acids the negative values of the ψ_1-potential go over into positive ones (a phenomenon similar to the reversion of the charge of negative colloids).

9. The increase of the overvoltage observed when polyvalent cations are added is less than the simultaneous increase of the ψ_1-potential. This phenomenon can not be explained if we admit that the potential in the double layer depends only upon the distance from the surface of the mercury.

10. When salts with a common anion are added to solutions of HCl or HBr a decrease of the overvoltage is observed for low current densities and a certain increase for high current densities.

11. When adding Na_2SO_4 to a dilute solution of H_2SO_4 only an increase of the overvoltage is observed, this increase being connected partly with a change in the structure of the double layer, partly with the decrease of the activity of hydrogen ions.

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[65] Harned and Akerlöf, Physik. Z., **27**, 414 (1926).