The Hydrogen Overvoltage on Lead and the Capacity of the Lead Electrode

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Earlier investigations of the hydrogen overvoltage on lead[2] are not very precise, and the results obtained by individual authors deviate considerably from one another.

In more recent times the overvoltage on lead was measured by Baars[3]. Erdey-Gruz and Wick[4] corroborated his results according to which the dependence of the hydrogen overvoltage on lead upon the current density is anomalous. The semi-logarithmic plot of the overvoltage for the case of lead and also for the case of tantalum gives a straight line which has twice as large a slope as for all the other metals. In order to explain this anomaly, Erdey-Gruz and Wick advanced the hypothesis that the surface of lead and tantalum, even at considerable cathodic potentials, is covered with a layer of oxides which influence the overvoltage of hydrogen. This question was not subjected to further investigation.

Lead oxide or a salt of lead cannot exist, of course, as an individual phase in thermodynamic equilibrium on the surface of a lead electrode at potentials more negative than the potential of $Pb/Pbso_{45at}$, H_2SO_4. On the other hand, the oxides or sulphate of lead may exist on the surface of lead in an adsorbed condition even

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[1] A part of the experimental material included in this paper was obtained by L. V. Vanjukowa and stud. chem. Tichomirov.

[2] Tafel, Z. physik. Chem., **50**, 641 (1905). Glasston, J. Chem. Soc., London, 123. 2926 (1923); **125**, 250. 2414 (1924). Caplan a. Eiseman, Trans. Am. Electrochem. Soc., **43**, 55 (1923) and others.

[3] Baars, Handb. Physik, **13**, 564 (1928).

[4] Erdey-Gruz u. Wick. Z. physik. Chem., **162**, 53 (1932).

at these potentials. The presence of adsorbed lead sulphate or adsorbed anions of sulphuric acid may be expected particularly for those potentials at which the surface of the metal is charged positively. For potentials at which the surface of the metal is charged negatively, the adsorption of anions decreases to zero, and if an increase in the slope of the overvoltage curve is actually due to the adsorption of the SO_4'' ions, then at these (more negative) potentials the overvoltage curve should possess a smaller slope, equal to 0.12, as corresponding to a clean metal surface. Furthermore, in agreement with **Frumkin**'s theory[5], the overvoltage of hydrogen on a clean, negatively charged metal surface should not depend upon the concentration of acid.

Preliminary observations pointed to the fact that, within the limits of current strengths which can be used in practice, we can obtain potentials which correspond to a negative charge of the lead surface. Thus we could count upon obtaining relations for lead which the overvoltage theory requires for a clean metallic surface.

Starting from these considerations we undertook measurements of the overvoltage of hydrogen on a lead surface free from adsorbed salts. In order to obtain comparable data, measurements had to be carried out with lead electrodes having a definite value of the true surface. We prepared electrodes with surfaces as smooth as possible and determined the magnitude of the surface by a method based on the measurement of the capacity of the double layer.

Procedure

The apparatus in which the measurements of the hydrogen overvoltage were carried out was made entirely of glass. Ground-glass joints and stop-cocks were not greased but moistened and covered with a solution of sulphuric acid. The anodic part was separated from the cathodic part by an inside ground-glass stopper. The solution was preliminarily saturated with hydrogen and, in order to purify it, was polarized with the help of an additional lead electrode in a special side vessel. After a few hours the solution was pumped over under pressure of hydrogen into the main vessel which was filled with hydrogen and in which the cathode was located.

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[5] A. **Frumkin**, Z. physik. Chem., **160**, 121 (1933).

The cathode was prepared by shaving off the upper layer of the lead electrode with the aid of a well sharpened chisel of special steel. After the cathodic reduction of the oxide film which had formed in contact with air, the lead electrode assumed a silvery lustre, and after cathodic polarization over a period of a few hours at a current density of about 10^{-4} A./cm.^{2} during which the solution was stirred by bubbling hydrogen through it, the electrode became as bright as a mirror. A measurement of the capacity of the double layer (see below) showed that, during the above procedure, a decrease of the true surface of the electrode takes place. A lead electrode prepared in this way has a double layer capacity equal to 18 μF/cm.^{2}, *i. e.*, the same capacity as a clean mercury electrode. This obliges us to assume that the electrode has now a true surface very close in magnitude to the apparent one.

The measurement of the potential of the electrode was carried out with reference to a hydrogen electrode in a solution of the same concentration.

During polarization of the electrode at a current density of 10^{-4} A./cm.^{2}, the potential at first rose somewhat and then remained constant over a period of many hours. During this process not only was the surface of the electrode completely reduced and smoothed out, but also traces of oxygen and lead ions were removed from the solution, which permitted the measurements to be carried out at small current densities (10^{-7} A./cm.^{2} and in dilute acid even at 10^{-8} A./cm.^{2}). The measurements were carried out rapidly, first at current densities ranging from 10^{-3} to 10^{-7} A./cm.^{2} and then from 10^{-3} to 10^{-2} A./cm.^{2}. At large current densities (above 10^{-3} A./cm.^{2}), the solution was stirred by bubbling hydrogen through it during the measurement in order to reduce concentration polarization. A prolonged polarization with a current density of 10^{-3} A./cm.^{2} and larger (at an overvoltage of 1.2 V.) leads to a tarnishing of the lead and to a lowering of the overvoltage. This phenomenon is probably due to the formation of a gaseous hydride of lead at high negative potentials that partly decomposes in the sulphuric acid with the formation of lead sulphate which may be deposited on the electrode anew.

Along with measurements of the overvoltage, we also measured the capacity of the double layer on the surface of the electrode in order to determine the true magnitude of the surface. Determinations of the surface of metals by the capacity method were carried out for the first time by **Bowden** and **Rideal**[6] who made use of an oscillographic method. **Šlygin** and **Frumkin**[7] measured the capacity of the surface of platinized platinum. Owing to the large value of the true surface and precautions taken against depolarization, they could charge the double layer of the surface extremely slowly, which simplified the method of measuring the capacity very much. **Ershler**[8] worked out a method of measuring the capacity using direct current for the case of a smooth surface, employing an apparatus containing an extremely small volume of electrolyte.

In the case of lead, the measurement of the capacity of the double layer in the overvoltage region is complicated by the fact that when charging the double layer, a leakage of current takes place in consequence of the evolution of hydrogen. Calculating the capacity in an analogous case from the oscillographic curve **Volmer**[9] proposed the introduction of a correction for the simultaneous discharge of the ions.

A combined method of determining the capacity of the double layer turned out to be very convenient. This method depends upon the measurement of the rate of charging of the double layer at a given current strength with the introduction of a correction for the rate of the potential drop when the polarizing current is interrupted. It is easy to show that the most exact values of the capacity are obtained for identical rates of charge and discharge of the double layer.

During a measurement of the capacity of the double layer, as well as during a measurement of the overvoltage, the depolarization should be made as small as possible. Therefore, we carried out measurements in a solution saturated with hydrogen using the apparatus described. Special experiments showed that, at potentials more positive than — 0.5 V., the capacity curve rises steeply (Fig. 1), and it is therefore difficult to employ measurements taken in this region

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[6] **Bowden** a. **Rideal**, Proc. Roy. Soc., **120**, 59, 80 (1928).

[7] **Šlygin** a. **Frumkin**, Acta Physicochimica URSS, **3**, 791 (1935).

[8] **Ershler**, Acta Physicochimica URSS, **7**, 327 (1937).

[9] **Volmer**, „Das elektrolytische Kristallwachstum". Actualités Sci. Ind. 373, Paris, 1934.

for a determination of the true magnitude of the surface. Such an increase in the capacity points to the adsorption of anions on the surface of the metal. On the other hand, at very large negative potentials the rate of evolution of hydrogen becomes so large that the accuracy of the determination of the capacity decreases. We therefore measured the capacity within the potential range from — 0.65 to — 0.5 V. with reference to a hydrogen electrode. The potential was determined with the aid of a short-period galvanometer (0.01 sec.) and a one-valve amplifier. The measurements were carried out in the following way. After a definite potential was established (*e. g.*, — 0.65 V.), the polarizing current was interrupted and the drop of potential registered every second (Fig. 2, *I*). After the potential had decreased to — 0.50 — 0.55 V., the polarizing current was switched on and the periodic measurement of the potential was continued until its initial value was established (Fig. 2, *II*).

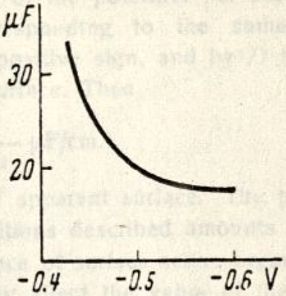

Fig. 1.
The dependence of the capacity of a smooth lead electrode upon the potential.

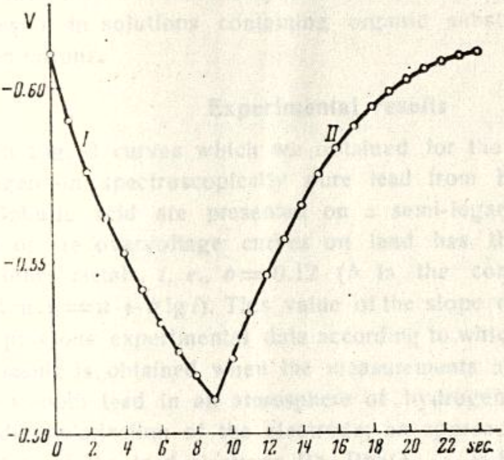

Fig. 2.
Discharge and charge curves of a lead electrode.

For calculation of the capacity, the slope of the curves must be determined at points corresponding to the same potential. Let us denote by Δv_1 and Δv_2 the changes of the potential per second on curves *I* and *II*, respectively, corresponding to the same value of the potential, both taken with a positive sign, and by D the current density per cm.^{2} of apparent surface. Then

$$C = \frac{D}{\Delta v_1 + \Delta v_2}\ \mu\mathrm{F/cm.}^2,$$

where C is the capacity per cm.^{2} of apparent surface. The possible error of the method under the conditions described amounts to 5%.

As is well known[10], the presence of surface active organic substances in the solution may markedly affect the value of the capacity of the double layer of the metal. Therefore, a measurement of the capacity may be used to determine the adsorbability of organic substances on metals. On the other hand, one must keep in mind that a comparison of the true magnitude of the surface of two electrodes may be made only either in the absence of organic substances or in solutions containing organic substances at identical concentrations.

Experimental results

In Fig. 3 curves which we obtained for the overvoltage η of hydrogen on spectroscopically pure lead from Hilger in solutions of sulphuric acid are presented on a semi-logarithmic scale. The slope of the overvoltage curves on lead has the same value as with other metals, *i. e.*, $b = 0.12$ (b is the constant of Tafel's equation $\eta = a + b \lg i$). This value of the slope of the curve contradicts previous experimental data according to which $b = 0.19-0.21$. This result is obtained when the measurements are carried out with pure, smooth lead in an atmosphere of hydrogen after preliminary cathodic polarization of the electrode; an approach to the reversible potential of the lead electrode Pb, $PbSO_{4\,\mathrm{sat.}}$, H_2SO_4 must be avoided. The sulphuric acid was purified by distillation under reduced pressure.

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[10] Proskurnin a. Frumkin, Trans. Farad. Soc., **31**, 110 (1935). Ksenofontov, Proskurnin a. Gorodetzkaja, Acta Physicochimica URSS, **9**, 39 (1938).

Furthermore, from Fig. 3 it is seen that the overvoltage on lead is higher than on mercury (the curve for the overvoltage on mercury is taken from the paper of **Levina** and **Sarinsky**[11]), *i. e.*, higher than on all other metals hitherto measured. According to previous data, lead occupied an intermediate position between silver and copper, *i. e.*, possessed an overvoltage 0.3—0.4 V. lower than the value observed by the present authors. The reasons for this discrepancy will be discussed below.

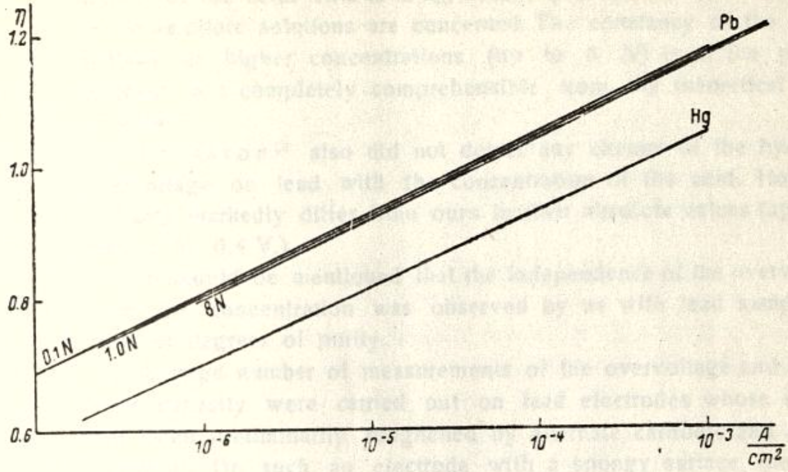

Fig. 3.
Overvoltage of hydrogen on pure lead (0.1 N. 1.0 N and 8 N H_2SO_4) and on pure mercury (0.1 N HCl).

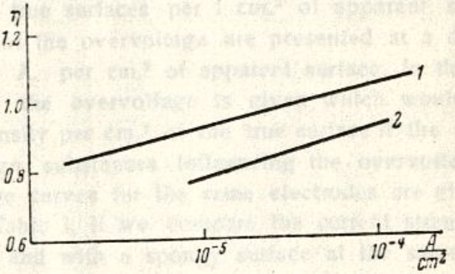

Fig. 4.
Hydrogen overvoltage on lead samples of varios degrees of purity: *1* — spectroscopically pure lead (Hilger); *2* — technical lead.

As was to be expected, the degree of purity of the lead influenced the hydrogen overvoltage (Fig. 4).

The overvoltage was measured using various concentrations of sulphuric acid: 0.01; 0.1; 1.0, and 8 N. The results obtained

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[11] **Lewina** a. **Sarinsky**, Acta Physicochimica URSS, **6**, 491 (1937).

are shown in Fig. 3. From the experimental data it follows that the overvoltage on lead is practically independent upon the concentration of the acid. This is in agreement with Frumkin's theory[12] so far as dilute solutions are concerned. The constancy of the overvoltage at higher concentrations (up to 8 *N*) is at the present moment not completely comprehensible from the theoretical point of view.

Glasston[13] also did not detect any change of the hydrogen overvoltage on lead with the concentration of the acid. However, his data markedly differ from ours in their absolute values (approximately by 0.4 V.).

It should be mentioned that the independence of the overvoltage upon the concentration was observed by us with lead samples of different degrees of purity.

A large number of measurements of the overvoltage and double layer capacity were carried out on lead electrodes whose surface had been preliminarily roughened by alternate cathodic and anodic treatment. On such an electrode with a spongy surface, the overvoltage has of course a lower value than on smooth lead. From the value of the capacity, the true surface was calculated.

Table 1 shows values of the current density per 1 cm.^{2} of apparent and true surface at the same overvoltage (0.7 V.) for electrodes with different true surfaces per 1 cm.^{2} of apparent surface. Furthermore, values of the overvoltage are presented at a definite current density 10^{-4} A. per cm.^{2} of apparent surface. In the next column the value of the overvoltage is given which would exist at a given current density per cm.^{2} of the true surface if the surface were free from foreign substances influencing the overvoltage. In Fig. 5 the overvoltage curves for the same electrodes are given.

As shown by Table 1, if we compare the current strength on lead with a smooth and with a spongy surface at the same overvoltage under similar conditions the increase in current strength per unit area of apparent surface turns out to be approximately equal to the increase in the true surface[6]. Thus, on lead at a con-

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[12] Frumkin, Z. physik. Chem., **160**, 121 (1933); Acta Physicochimica URSS, **7**, 475 (1937). Lewina a. Sarinsky, Acta Physicochimica URSS, **6**, 502 (1937).

[13] Glasston, J. Chem. Soc., London, **125**, 2414 (1924).

stant overvoltage the true current density is almost independent of the structure of the surface. Evidently the evolution of hydrogen does not take place at some special points of the surface, but almost uniformly over the whole surface of the metal. A combined measurement of the capacity of the double layer and of the overvoltage gives the possibility of comparing the overvoltage on electrodes possessing different values of the true surface. For instance, curve *b* (Fig. 5) corresponds to an electrode with an overvoltage

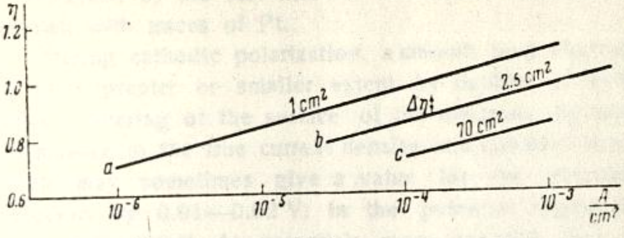

Fig. 5.
The dependence of the overvoltage upon the current density per cm.² of apparent surface for different magnitudes of the true surface per cm.² of apparent surface.

Table 1

Curve	Electrode	True surface in cm.² per 1 cm.² of apparent surface	Current density at an overvoltage of 0.7 V.		Overvoltage measured at a current density of 10^{-4} A. per cm.² of apparent surface	Overvoltage calculated from the true current density for a clean surface	Difference Δη
			per 1 cm.² of apparent surface	per 1 cm.² of true surface			
a	Smooth lead (Kahlbaum)	1	1×10^{-6}	1.0×10^{-6}	0.965	0.965	—
c	Electrode with spongy surface .	70	80×10^{-6}	1.1×10^{-6}	0.71	0.72	−0.01
b	Electrode with spongy surface contaminated by traces of Pt . .	2.5	8×10^{-6}	3.2×10^{-6}	0.84	0.91	−0.07

which is 0.07 V. lower if we compare the overvoltage with curve *a* at identical true current densities. This decrease in the overvoltage is explained by the fact that the surface of electrode *b* was contaminated with traces of Pt.

During cathodic polarization, a smooth lead electrode is covered to a greater or smaller extent by bubbles of hydrogen. This partial covering of the surface of the electrode by bubbles causes an increase in the true current density at a constant current strength, which may sometimes give a value for the overvoltage that is increased by 0.01—0.02 V. in the potential region ranging from —0.7 to —0.8 V. At potentials more negative than —0.9 V., the bubbles adhere to the electrode markedly less strongly than at less negative potentials: at a potential of —1.076 V., the diameter of bubbles breaking away from the electrode was *ca.* 0.1 mm., at a potential of —0.96 V. *ca.* 0.2 mm. and at a potential of —0.89 V. *ca.* 0.7—0.8 mm. A comparison with experiments carried out on mercury, platinum and other metals[14] shows that the maximum of the contact angle corresponding to the zero value of the surface charge lies in the case of lead in an 8 *N* solution of sulphuric acid at potentials less negative than —0.8 V.

It was pointed out above that the capacity of the double layer of a lead electrode depends upon the potential, increasing for potentials more positive than —0.6 V. (Fig. 1). As is known, the increase of the capacity is especially pronounced in that region where the metal is charged positively. Thus, comparing the data for the capacity of the double layer and for the adhesion of bubbles, one may suppose that in an 8 *N* solution of sulphuric acid the point of the zero charge of the lead electrode lies in the potential region between —0.6 and —0.8 V. with reference to a hydrogen electrode. This conclusion is confirmed by unpublished measurements of the electrocapillary curves of molten lead and of mercury in molten KCl + LiCl by S. W. Karpatschef who found that the maximum of lead is shifted with respect to the mercury maximum by 0.37 V. to more negative potentials. As the overvoltage at the electrocapillary maximum of mercury in 1 *N* sulphuric acid amounts according to our measurements to 0.195 V., the potential at the point

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[14] Gorodezkaja a. Kabanov, Sow. Phys., **5**, 418 (1934).

of zero charge of lead may amount to $-0.195-0.37=-0.565$ V., referring to a hydrogen electrode in normal sulphuric acid, or to *ca.*—0.62 V., referring to a hydrogen electrode in 8 *N* sulphuric acid. The overvoltage on lead at the point of zero charge in 8 *N* acid must therefore slightly exceed 0.62 V., as the point of zero charge with increasing concentration is probably somewhat shifted to more negative potentials due to the small adsorption of the SO_4'' anion. In more dilute solutions the overvoltage corresponding to the potential of zero charge must be still lower. From this it follows that our measurements of the overvoltage were carried out mainly on a metal whose surface was charged negatively.

The overvoltage curve with a small slope as shown by Fig. 3 is obtained only after complete reduction of the lead surface and under the condition that the measurements are not extended to potentials more positive than —0.65 V., or that in the region of small overvoltage they are carried out rapidly. Otherwise at more positive potentials in 8 *N* acid the slope of the curve increases assuming values between 0.12 and 0.22. If the measurements are carried out slowly, but in all other respects the conditions are the same as described above, a bend in the overvoltage curve appears in 8 *N* acid between — 0.6 and — 0.7 V.

Complete reduction of the lead surface, leading to a decrease in the slope of the overvoltage curve, takes place only at more negative potentials. At a potential more negative by 0.2 V. than the potential corresponding to the bend, reduction of the surface occurs only after more than an hour from the beginning of the polarization. The change in the slope of the curve does not take place gradually but by a jump. During this time a quantity of electricity passes which is thousand times as large as that which is required to reduce the sulphate which could be present on the surface.

In some experiments[15], after a previous prolonged polarization at a potential more negative than — 0.7 V., an overvoltage curve was obtained with a small slope up to a potential of — 0.5 V. Then for a short time the current was interrupted, and the potential of the electrode approached that of $Pb/PbSO_{4\ sat.}$, H_2SO_4, after which, in the potential interval from —0.55 to —0.75 V., an over-

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[15] Carried out by J. Kolotyrkin.

voltage curve was obtained with an increased slope. From this, one may assume that the increased slope of the overvoltage curve is caused by the presence of adsorbed lead sulphate on the surface of the lead electrode, and that the adsorption equilibrium is not reached instantaneously.

As has been pointed out above, the capacity of the double layer of the lead electrodes (both with smooth and spongy surfaces) increases if the potential is made more positive than —0,6 V. (Fig. 1).

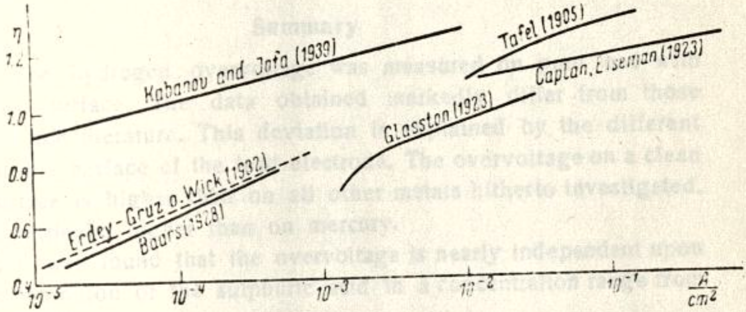

Fig. 6.
Overvoltage curves obtained by different authors.

This rise of the capacity indicates an adsorption of SO_4'' ions, *i. e.*, the formation of a surface layer of $PbSO_4$. In the same potential region one should expect the appearance of the catalytic effect of the adsorbed layer of lead sulphate on the hydrogen evolution, and this is approximately what was found by experiment.

On the basis of what has been stated above, the deviations between the results of our overvoltage measurements and the results of the work of previous authors, may be explained. In the first place in previous investigations insufficient attention was paid to the smoothness of the lead surface; as a result, lowered overvoltage curves were obtained (Fig. 6) lying almost entirely below the potential at which reduction of the surface of the lead takes place. The curves had therefore an increased slope (Baars, Erdey-Gruz and Wick). Furthermore, measurements were apparently carried out with insufficiently pure lead and with solutions not subjected to preliminary purification by electrolysis. Traces of impurities may likewise lower the overvoltage of hydrogen and increase the slope of the curve. Only Tafel obtained data which, in the narrow interval of current densities ranging from 0.05 to 0.15 A./cm.[2], give a curve with a slope close to 0.12 and lying only 0.1 V. lower in absolute value than the curve which we obtained. At small current densities the results of Tafel and of other authors seem to be vitiated by the depolarization of the electrode.

In conclusion we wish to express our deep gratitude to Prof. A. Frumkin who proposed this problem and gave valuable advice.

Summary

1. The hydrogen overvoltage was measured on pure lead with a smooth surface. The data obtained markedly differ from those given in the literature. This deviation is explained by the different state of the surface of the lead electrode. The overvoltage on a clean lead surface is higher than on all other metals hitherto investigated, and in particular higher than on mercury.

2. It was found that the overvoltage is nearly independent upon the concentration of the sulphuric acid in a concentration range from 0.01 to 8 *N*.

3. A method of obtaining a smooth lead surface is described.

4. A simple method of determining the true surface of the lead electrode was worked out which is based upon the measurement of the capacity of the double layer. The dependence of the capacity upon the potential of the electrode was determined.

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