

PHYSICAL CHEMISTRY

**A METHOD OF STUDYING THE CAPACITY OF ELECTRODES IN  
DILUTE SOLUTIONS**

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By applying the method of studying the capacity of metallic electrodes, various problems on the structure of the double electric layer can be solved. An interesting problem is the study of the degree of diffuseness of the double layer. At the present time calculations after Stern and Gouy can be checked quantitatively and at the same time directly only on the basis of data on the capacity of the electrode. Of course, in view of the fact that the diffuse structure of the ionic layer becomes noticeable only at low concentrations of the electrolyte, it is necessary in order to check in this way to turn to a study of weak solutions.

When the electrode potential is far from the charge's zero point, the electric forces which attract the ions onto the surface of the metal are great, and the degree of diffuseness of the double layer is small. On the contrary, at the maximum of the electrocapillary curve the diffuseness of the double layer increases and, consequently, the capacity should be at its minimum value. Thus, the method of capacity measuring puts into our hands a means of determining the position of the charge's zero points in a way independent of other methods. It is important to note that this method should be especially valuable for solid metals, since no other reliable methods are available here.

It may be considered that of all the methods of capacity measuring, the best one for our purposes is the electric method which consists in measuring the variable polarization component when alternating current is passed through the electrode surface in the solution. This kind of measurement was performed up till now at higher concentrations. One of the variants of such a method is described in the work of Borissova and Proskurnin<sup>(1)</sup>.

For liquid metals the method of calculating the capacity values from the electrocapillary curves is applicable in principle, but when dilute solutions are used the accuracy of the measurements falls, because the mobility of the mercury meniscus in the capillary tube goes down. Up till now it has been possible to reach 0.01 *n* solutions in this manner, but the measurement was not accurate enough to calculate capacities. Philpot<sup>(2)</sup>, who directly determined the charge of falling mercury drops, was successful in reaching a dilution of the order of 0.001 *n* and comparing the data thus obtained with Stern's theory. However, these measurements are also not accurate enough.

In the electric method accepted by the authors in working with very dilute solutions there appear specific difficulties, connected mainly with the low electroconductivity of the solutions.

The polarization component variable  $p_{\sim}$  consists of two terms, one of which depends upon the capacity of the double layer, and the other on the ohmic resistance:

$$p_{\sim} = \sqrt{\frac{i^2}{\omega^2 C^2} + r^2 i^2} \quad (4)$$

where  $\omega$  is the cyclic current frequency;  $C$ , the capacity in farads;  $r$ , the resistance of the solution between the two electrodes;  $i$ , the current strength.

The value  $ri$  which determines the «ohmic correction» increases greatly when the solution is diluted and may be somewhat decreased by moving the auxiliary electrode nearer to the one being measured. A decrease in the frequency of alternating current results in the capacity resistance increasing in comparison with the ohmic resistance of the solution.

On the basis of these considerations we used one-period alternating current and had the possibility of reaching a 0.001  $n$  concentration for salt solutions and 0.0001  $n$  for hydrochloric acid. In order to study even more dilute solutions, it is necessary to use current of even longer period, besides purifying the water, used in preparing the solution, more thoroughly.

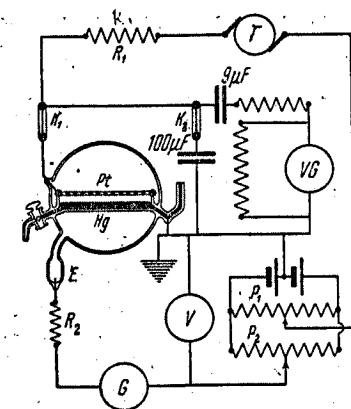


Fig. 1.

In the work referred to above Proskurnin and Borissova applied the «parallel feeding diagram» which is well-known in electrotechnics. They diverted the direct and alternating components of the polarizing current from generators joined in parallel, using separating and blocking condensers and throttles.

Since the blocking apparatus for one-period current are very cumbersome, we used the series feeding system represented in Fig. 1 in this work. The generator  $I$  is a small alternator, whose rotor does 1 revolution per second. Its rotation velocity is stabilized by means of a synchronic motor. The one-period alternating current passes through a limiting resistance and through the switch into an apparatus, in which there are two electrodes: the auxiliary one of platinum gauze ( $Pt$ ) and the one to be measured of mercury in a glass dish ( $Hg$ ). Then it goes through a battery of accumulators, a potentiometer  $P_1$  and then back to the generator  $I$ .

The potentiometer  $P_1$  makes it possible to set a constant polarization on the mercury. The potentiometer  $P_2$  is included in the circuit of the compensation apparatus in order to measure the potential ( $\varphi$ ) of the mercury electrode.  $E$  is a calomel electrode;  $G$ , a zero instrument;  $R_2$ , a resistance ( $10^5 \Omega$ ) which keeps the alternating polarization current from branching.

If switch  $K_1$  is turned off and  $K_2$  turned on, it is possible to direct the alternating current through the capacity standard ( $100 \mu F$ ) instead of the mercury electrode.

A short-period galvanometer  $VG$  furnished with a high series resistance serves as a millivoltmeter for the alternating current, and the value of alternating polarization is measured by means of it. The locking condenser  $9 \mu F$  does not let the direct component of the polarizing current through the galvanometer  $VG$ .

Comparing the polarization values  $p_{\sim}'$  and  $p_{\sim}''$  when the switches  $K_1$  and  $K_2$  are turned on respectively, we get:

$$\frac{p_{\sim}'}{p_{\sim}''} = \frac{\sqrt{\frac{i_1^2}{\omega^2 C^2} + r^2 i_1^2}}{\frac{i_2}{\omega \cdot 400 \mu F}}$$

where  $i_1$  and  $i_2$  are the current strengths when the switches  $K_1$  and  $K_2$  are turned on.

If the switching resistance  $R_1$  is high, it can be taken that  $i_1 = i_2$  and then  $i$  can be cancelled respectively in the formula. Thus, it is not necessary to know the magnitude of the alternating current. In some cases, namely in the region of minimum capacity, it was sometimes necessary to take into account the change in current and to introduce the corresponding small correction in calculating the capacity.

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#### REFERENCES

- <sup>1</sup> Borissova a. Proskurnin, Acta Physicochimica, 4, 819 (1936).
- <sup>2</sup> Philpot, Phil. Mag., 13, 775 (1932).