THE EXACT DEFINITION OF PEAK POTENTIAL IN OSCILLOGRAPHIC POLAROGRAPHY

A. Ya. Gokhshtein

Scientific Research Institute of Rubber and Latex Materials, Moscow

Analysis of solutions by the method of oscillographic polarography reduces to measurement of the potential and the peak height of the diffusion current. The peak potential depends on the nature of the ion studied, while the height is proportional to its concentration. However, in addition to the electrochemical reactions which take place on the electrode, charging of the electrical double layer occurs. The current which corresponds to this process is proportional to the rate of change of potential and reaches a considerable value. The presence in the electrolysis cell of several substances which participate in the electrochemical reaction, also complicates determination by the method of oscillographic polarography. Usually, to the diffusion current (i_d) of the test ion are added other currents (i_b), so that the total current in the electrolysis cell circuit is determined by their sum [1, 2]:

$$i = i_d + i_b. \tag{1}$$

At the point where the diffusion current passes through its maximum, $di_d/dE = 0$ (E is the electrode potential). Differentiation of (1) at the peak gives

$$di/dE = di_b/dE. \tag{2}$$

Accordingly, the method which has been in use previously (Fig. 1a) for measurement, in which the peak potentials of the total and diffusion current are identified with each other, should be replaced by a more refined method, the principle of which is shown in Fig. 1b. Here the peak potential is defined as the point at which the curves for the total current and for the supporting electrolyte have the same slope. If this technique is not adopted then

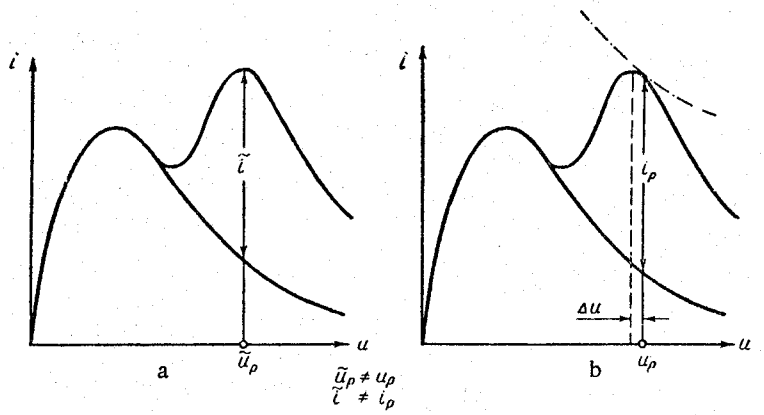


Fig. 1

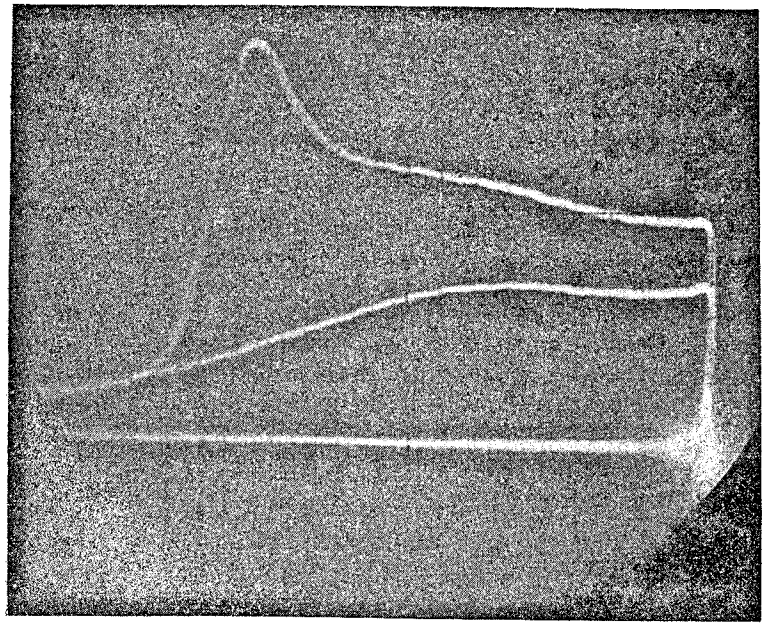


Fig. 2. 20 γ Cd^{2+}/ml in 1 M KCl, α 8.5 volt/second, t = 25°. Dropping mercury electrode, anode polarization with pre-electrolysis.

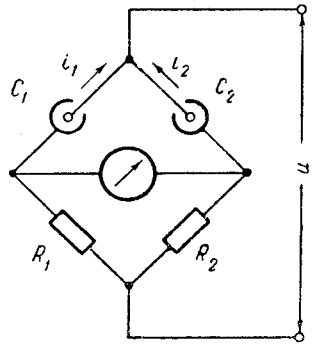


Fig. 3.

has not been established previously.

there will be an error not only in the value of the potential of the maximum, but also in the value of the current which will not be a maximum. The error in the value of the potential is often greater than 10 millivolts in practice, while the rate of change of potential a and the concentration C of the ion participating in the electrochemical reaction will affect its value. The capacity current which makes up part of i_b increases in proportion to a. The curvature of the peak increases with concentration C. Accordingly, the error increases on increasing α and decreasing C. This explains the potential shift on changing the concentration. While the ohmic drop in potential, on increasing the concentration, always shifts the peak towards the higher voltage applied to the cell, the direction of the shift caused by the supporting electrolyte current has not been established previously.

In order to determine the true peak potential on an oscillogram, the curves for total current and supporting electrolyte current are combined. The curves for the test solution, and for the electrolyte serving as the supporting electrolyte, are photographed by successive exposures on one frame of film. In Fig. 2 are shown the anode wave for Cd in 1 N KCl, the supporting electrolyte current, and the zero line. Such a combined photograph makes it possible to carry out a rapid evaluation of the true values of the current and the potential. In the example given, the apparent shift in peak potential was + 10 millivolts. Subtraction of the supporting electrolyte current from the total current on the oscillogram can be substituted by carrying out the subtraction in the electric circuit of the polarograph itself. Electrical circuits for subtracting currents are well known. It should be pointed out that a bridge setup in its original form is not applicable for subtraction of polarographic currents. In actual fact, let U be the potential applied to the bridge, R_1 and R_2 the load resistances, and C_1 and C_2 the electrolyzers containing test solution and the electrolyte used as supporting electrolyte (Fig. 3). Then the potential drop across the electrolyzers C_1 and C_2 will be, respectively:

$$U_1 = U - i_1 R_1; \quad U_2 = U - i_2 R_2.$$

But, since for a given bridge, R_2/R_1 = const, while i_1/i_2 for different solutions can change arbitrarily, then

$i_1/i_2 \neq R_2/R_1$ and $U_1 \neq U_2$. Thus, at the very same moment, different potentials will correspond to the minuend and the subtrahend. This destroys the elementary rule for the subtracting of functions, and in this connection will affect the correctness of the result obtained.

LITERATURE CITED

[1] P. Delahay, New Apparatus and Methods in Electrochemistry, (IL, Moscow, 1957) p. 160.

[2] Ya. P. Gokhshtein, J. Phys. Chem. 32, 1481 (1958).

Received May 5, 1958