Chapter I

Basic Principles of the Polarographic Method

Let us consider the electrochemical process of reduction of compound A to compound B

\[ A + n e^{-} \xrightarrow{k_f} B, \quad (I) \]

where \( n \) is the number of electrons taking part in this process, and \( k_f \) and \( k_b \) are the heterogeneous rate constants of the forward and reverse electrochemical reaction (cm/sec).

The values of \( k_f \) and \( k_b \) are functions of the potential, and on the basis of the theories of slow discharges [7, 8] they can be expressed by

\[ k_f = k_f^0 \exp \left( \frac{-a nFE}{RT} \right), \quad (1) \]

\[ k_b = k_b^0 \exp \left( \frac{(1 - a) nFE}{RT} \right), \quad (2) \]

where \( k_f^0 \) and \( k_b^0 \) are the rate constants of the forward and reverse processes at a potential \( E = 0 \); \( a \) is the transfer coefficient which expresses the fraction of the potential carrying out the cathodic process; \( F \) is the Faraday number; \( R \) is the universal gas constant; and \( T \) is the absolute temperature.

Generally, the current flowing through the electrode \( (i) \) is equal to the algebraic sum of the cathodic \( (i_c) \) and anodic \( (i_a) \) currents, corresponding to the forward and reverse directions of reaction \( (I) \). In the absence of concentration polarization these cur-
rents are

\[ i_c = nFsc_Ak_f, \]  
\[ i_a = nFsc_Bk_b, \]  

where \( s \) is the surface area of the electrode, and \( c_A \) and \( c_B \) are the concentrations of compounds A and B.

If reaction (I) is reversible at the so-called equilibrium potential, \( E_e \), the sum of the values of cathodic and anodic currents taken with the appropriate signs is equal to zero, and it follows from Eqs. (3) and (4), considering Eqs. (1) and (2), that

\[ E_e = \frac{RT}{nF} \ln \frac{k_f}{k_b} + \frac{RT}{nF} \ln \frac{c_A}{c_B}. \]  

Equation (5) is the well-known Nernst equation. The first term of Eq. (5) is very nearly equal to the standard potential (\( E_0 \)) of the oxidation-reduction system (I) and is expressed in this case by the rate constants of the reversible electrode process [9].

It can be shown that at the standard potential, \( E_0 \), the rate constants of the forward and reverse electrode processes are equal [9]: \( k_f = k_b = k_s \), and the value of \( k_s \) can serve as a measure of the reversibility of the electrode process [10]. This will be discussed further.

With concentration polarization the concentration values at the surface of the electrode, \( c_{A,s} \) and \( c_{B,s} \), must be used in Eqs. (3) and (4). If the rate of the electrode process is sufficiently high, the concentration of one of the depolarizers decreases practically to zero at the electrode surface, and the current is determined by the rate of transport of the depolarizer to the electrode. For the case of diffusion transport of the depolarizer to the dropping mercury electrode, Ilković [11] gave an equation that forms the basis for quantitative polarographic analysis. The limiting diffusion current averaged over the lifetime of the drop, at 25°C, according to Ilković's equation is

\[ i_D = 607m^{2/3}t^{1/3}D^{1/2}c_0, \]  

where \( i_D \) is the diffusion current (\( \mu A \)); \( m \) is the flow velocity of mercury from the drop electrode (mg/sec); \( t \) is the drop period (sec); \( D \) is the diffusion coefficient (cm²/sec); and \( c_0 \) is the concentration of depolarizer in the bulk of the solution (mM).