THE THEORETICAL BASES OF, AND INTERRELATIONS BETWEEN, ELECTROMETRIC METHODS OF CHEMICAL ANALYSIS

(REVIEW)

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In this communication we have attempted, on the basis of existing foreign literature data [1-9 et al.], to describe the theoretical bases, the general nature, and the interrelations of electrometric methods of analysis. In the native literature on this subject, O. A. Songina has published a paper dealing with amperometric titration [10].

It is normal, when using electrochemical methods, to measure one electrical parameter (the current, the emf between electrodes, or the potential on one of them), and to find the relation between the concentration of the component to be determined and this parameter, while keeping the other parameters and the resistance R of the circuit constant.

We will consider only those methods which are related to the process of electrolysis, including phenomena occurring at a metallic electrode immersed in a solution of electrolyte. These are the bases for electrochemical conversions, associated with exchange of electrons at an electrode surface and with transfer of ions and molecules from the solution to the electrode surface and in the opposite direction (diffusion, migration).

The relation between the electrolysis current i and the external voltage V is given by the equation:

$$iR = V - (E_a - E_\kappa) = V - \Delta E, \quad (1)$$

where E_a and E_k are the anode and cathode potentials.

A more rigorous characteristic of the electrochemical reaction occurring at one of the operational electrodes is the relation between i and E_a or E_k.

Most electrochemical reactions proceed at a rate which is more or less restricted, so that problems lying at the base of these methods belong to the domain of kinetics. In the interpretation of electrode reactions considerable importance is attached to graphical and mathematical investigation of the kinetic factor, i.e., to the relation $i = f(E)$. Polarization curves provide the most appropriate characteristics to give a single basis for all electrochemical methods. They give a precise description of the electrochemical reactions which are primarily possible on operational electrodes at a given potential.

An electrically isolated electrode, placed in a redox system solution, acquires, more or less rapidly, a definite equilibrium potential E_{eq}. When a gradual change is made to the potential of an electrode immersed in a solution of only one component of a redox pair, the anode or cathode current increases exponentially after the potential has reached a certain value. Starting at some definite value of the potential, provided that the concentration of the component concerned is relatively small and the electrode is small, the rate of electron exchange increases to such an extent that all the material available to the electrode is subjected to electrochemical conversion. The current then remains constant until a new electrochemical process begins, which leads to a new increase in current. The curve obtained in this way is characteristic for every individual substance which can be oxidized or reduced at an electrode.

It is convenient to denote the current for a cathodic reaction as negative, and for an anodic reaction as positive. An anodic current is then represented on the ordinate axis as above the zero point, and a cathodic current as below the zero. A positive electrode potential (relative to a reference electrode which determines the position of the zero point) is represented by a point on the abscissa axis to the right of the zero, while a negative potential is to the left of zero.

For the components of a given redox system there will be two variants of the relative positions of the polarization curves [11]. The anodic curve will be found at more negative potentials, and the cathodic curve at less negative potentials (Fig. 1). At any potential within the range a to k, oxidation and reduction at the given electrode will take place simultaneously at the appreciable rates i_a and i_k. This means that the resulting curve can be drawn as the sum of the currents, and the position of E_{eq} can be found as the point on this curve at which the anodic and cathodic currents are both considerable and equal in absolute value, and the total current is zero. The slope of the curve is considerable in the region of E_{eq}; in the limiting case, when the electrode processes are extremely rapid, the curve approximates to a vertical line.

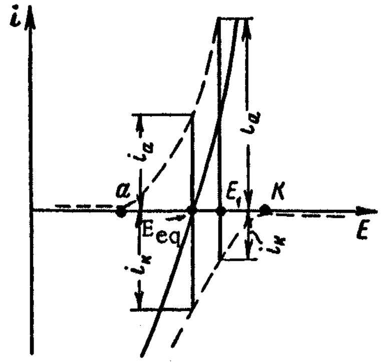

Fig. 1. Polarization curve of a rapid system. Above the abscissa axis equilibrium is shifted to the right, in the direction of oxidation, and below it is shifted to the left, in the direction of reduction.

In order to shift the equilibrium in a required direction, it is sufficient to alter the electrode potential by a very small amount relative to E_{eq}. Examples of "fast" systems are I_2/I^-, Fe^{3+}/Fe^{2+}, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$.

For the second variant there is a characteristic location of the cathodic polarization curve relative to the anodic curve in the more negative potential region. In this case, there is no definite value of the potential at which both reactions take place simultaneously at considerable rates. The equilibrium potential for such systems is established slowly and with poor reproducibility, since it depends on kinetic factors as well as on the activities of the components. Both the anodic and cathodic currents are very small close to E_{eq}, so that it is impossible to determine the position of E_{eq} on the curve precisely. In this case, in order to establish the anodic or cathodic process, it is necessary to shift the potential considerably from E_{eq}. In other words, such "slow" systems as $HAsO_4^{2-}/AsO_2^-$ and NO_3^-/NO_2^- show high anodic or cathodic overvoltage.

The concept of a "fast" or "slow" system depends to some extent on the conditions. For example, the redox pair V(V)/V(IV) is fast on a platinized Pt electrode in a perchloric acid medium [11], and slow on smooth platinum in 3 N H_2SO_4 at room temperature [12]. The rates of the electrochemical reactions of the systems Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} are slower in M H_2SO_4 than in M HCl on a smooth platinum electrode [13]. Water as a solvent, and other solvents, at certain values of the electrode potential, are also subject to electrochemical oxidation and reduction ($H_2O \rightarrow O_2$; $H_2O \rightarrow H_2$). This means that it is possible to obtain polarization curves for water and its combined forms. Thus, there is a limit to the potential range in which the electrochemical reactions of components of other redox systems can occur.

Oxidizing and reducing agents, whose polarization curves are within the range of the polarization curves of water, are electrically active and therefore interesting from the point of view of electrometric methods of analysis: e.g. $S_2O_8^{2-}$, VO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, Fe^{3+}, $Fe(CN)_6^{3-}$, I_2, VO_2^+, Fe^{2+}, $Fe(CN)_6^{4-}$, I^-, SCN^-, $S_2O_3^{2-}$, Ti^{3+}, etc. If the oxidized or reduced form of a redox pair is stable in water solution, and is reduced or oxidized at a more negative or positive potential than water, then it becomes an electrically inactive component of the redox system: e.g. $S_4O_6^{2-}$, SO_4^{2-}, Mn^{2+}, Cr^{3+}, etc. It is practically impossible to obtain polarization curves for the latter in an aqueous medium, because the concentration of water is so large that it is impossible to reach its limiting current. Electrical activity is also a conditional concept to some extent, and depends on the experimental conditions.

A proposed distribution for the polarization curves of the components of a redox system, according to their characteristics, is shown diagrammatically in Fig. 2 [14].

Depending on whether both components or only one are electrically active, a redox system is respectively reversible or irreversible from the electrochemical point of view. Reversible systems may be fast or slow; irreversible systems can only be slow, e.g. $S_2O_8^{2-}/SO_4^{2-}$, MnO_4^-/Mn^{2+}, $Cr_2O_7^{2-}/Cr^{3+} + SO_4^{2-}$, CN^-/SCN^-, SO_4^{2-}/SO_3^{2-}, $S_4O_6^{2-}/S_2O_3^{2-}$, $S_2O_6^{2-}/SO_3^{2-}$.

The observed value of E_{eq} at an electrode, immersed in a solution of an irreversible system, depends on the electrically active form of the system and the corresponding form of the solvent, and does not depend on the concentration of the electrically inactive component of the given redox system. Such a potential is known as composite [11].

If a solution contains two irreversible systems which do not interact, then their electrically active forms can give rise to a new redox pair. This pair gives a typically rapid system, whose potential is also considered as composite. For example, the systems $Cr_2O_7^{2-}/Cr^{3+} + SO_4^{2-}$ and CN^-/SCN^- are irreversible, whereas $Cr_2O_7^{2-}/SCN^-$ is a fast system.

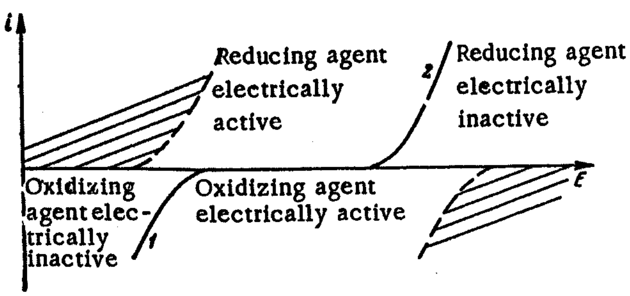

Fig. 2. Distribution of polarization curves of the components of redox pairs relative to the polarization curves of water. 1) Cathodic; 2) anodic.

A compound potential can also arise in a reversible system when the concentration of one of the components is so low that it cannot provide for the electrode process. The potential then depends on the component present at a concentration greater than the limiting value and the component of another redox pair or the solvent. Such a potential is known as limiting [15].

A restricted rate for the electrochemical reaction and its irreversibility have a pronounced effect on the electrode polarization, expressed as the deviation from the equilibrium value of the electrode potential when a relatively small current is passing through the circuit.

There are three possible cases of electrode polarization.

1. The electrode will be ideally nonpolarized if it is immersed in a saturated solution of its sparingly soluble salt in the presence of the solid salt, and if the system is fast. The activity of the metal ion is then maintained constant during the process of electrolysis.

2. There is only slight electrode polarization in solutions of fast redox systems. In consequence of the high current density, and under conditions where the diffusion rate is rapid, an equilibrium potential is established which differs little from the original value, and which depends only on the ratio of the activities of the system's components.

3. The electrode is subject to considerable polarization in solutions of slow and irreversible systems, owing to the slow rate of electron exchange.

Thus, for the same small displacement in electrode potential from the equilibrium value, the change in current for fast systems will be considerably greater than for slow systems. The slope of the polarization at its point of intersection with the zero current axis will be considerably greater in the first case than in the second, i.e.,

$$di/dE\ (\text{fast}) \gg di/dE\ (\text{slow}).$$

In order to give a quantitative characteristic of an electrochemical process, we must consider the mathematical relation between current and electrode potential.

In electrochemical measurements the migration current is eliminated by using a high concentration of electrolyte which does not take part in the electrode process. The equation below is a general mathematical expression for the polarization curve [11], considering only the current resulting from the kinetics of the electrochemical reaction and diffusion:

$$i = \frac{a_{\text{red}} \cdot \exp\left[\frac{\beta n F}{RT}(E - E_0)\right] - a_{\text{ox}} \cdot \exp\left[-\frac{\alpha n F}{RT}(E - E_0)\right]}{\frac{1}{i_0} + \frac{\exp\left[\frac{\beta n F}{RT}(E - E_0)\right]}{K_{\text{red}}} + \frac{\exp\left[-\frac{\alpha n F}{RT}(E - E_0)\right]}{K_{\text{ox}}}}. \qquad (2)$$

In this equation, a_{red} and a_{ox} are the activities of the redox system components in the solution; β and α are the corresponding numbers of electrons transferred; E_0 is the equilibrium potential; i_0 is the absolute value of the current at E_0 when $a'_{\text{red}} = 1$ and $a'_{\text{ox}} = 0$, or when $a'_{\text{ox}} = 1$ and $a'_{\text{red}} = 0$ (a' is the activity of the component in the vicinity of the electrode); K_{red} and K_{ox} are proportionality coefficients, corresponding, respectively, to n, F, $K_{d,\text{red}}$ and to n, F, $K_{d,\text{ox}}$ (K_d is a diffusion coefficient).

Equation (2) clearly illustrates the unity of the bases for electrometric methods of analysis. According to whether the parameter E or i is measured, we are dealing with potentiometry or amperometry in the wide sense of the words.

Although Eq. (2) can be used in principle for the quantitative interpretation of various electrometic methods of analysis, it is difficult to do so in practice. The problem is simplified by consideration of individual cases.

1. In the absence of electrolysis ($i = 0$), i.e., when the electrode is electrically isolated (open circuit), in the case of a reversible system, Eq. (2) acquires the following form:

$$a_{red}\cdot\exp\left[\frac{\beta nF}{RT}(E-E_0)\right]-a_{ox}\times\exp\left[-\frac{\alpha nF}{RT}(E-E_0)\right]=0.$$

Hence we obtain the Nernst formula, based on the equation of classical potentiometry:

$$E=E_0+\frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} \tag{3}$$

(for reversible systems $\alpha + \beta = 1$).

2. In the electrolysis of fast systems, the rate of electron exchange is extremely rapid (i_0 is high), and the limiting factor of the electrochemical reaction is the process of diffusion. In this case,

$$\frac{1}{i_0}\ll\frac{\exp\left[\frac{\beta nF}{RT}(E-E_0)\right]}{K_{red}}+\frac{\exp\left[-\frac{\alpha nF}{RT}(E-E_0)\right]}{K_{ox}}.$$

Replacing a_{red} and a_{ox} in Eq. (2) by the corresponding values from the limiting diffusion current equations ($i_{red} = K_{red}\cdot a_{red}$ and $i_{ox} = -K_{ox}\cdot a_{ox}$), neglecting the value of $1/i_0$, and solving Eq. (2) for E, we obtain the equation of the polarographic wave curve:

$$E=E_0+\frac{RT}{nF}\ln\frac{K_{red}}{K_{ox}}+\frac{RT}{nF}\ln\frac{i-i_{ox}}{i_{red}-i}. \tag{4}$$

3. For irreversible or slow reversible systems the electrochemical process is limited by the rate of electron exchange (i_0 is small), so that:

$$\frac{1}{i_0}\gg\frac{\exp\left[\frac{\beta nF}{RT}(E-E_0)\right]}{K_{red}}+\frac{\exp\left[-\frac{\alpha nF}{RT}(E-E_0)\right]}{K_{ox}}$$

The two last terms in the denominator of Eq. (2) can therefore be neglected. On the other hand, the electrolysis current i may be appreciable if the terms in the numerator of this equation differ markedly in value, which can occur at a high overvoltage ($E - E_0$).

Reduction of the oxidized form occurs when $E \ll E_0$, so that Eq. (2) takes the form:

$$i\approx i_0\left\{a_{ox}\cdot\exp\left[-\frac{\alpha nF}{RT}(E-E_0)\right]\right\}. \tag{5}$$

Replacing a_{ox} by the corresponding value of the limiting diffusion current, and solving for E, we obtain:

$$E_K=E_0-\frac{RT}{\alpha nF}\ln\frac{K_{ox}}{i_0}+\frac{RT}{\alpha nF}\ln\frac{i_{ox}-i}{i}, \tag{6}$$

where

$$E_0-\frac{RT}{\alpha nF}\ln\frac{K_{ox}}{i_0}=E_{1/2,\,K}.$$

If $E \gg E_0$, then, making the same approximations, the equation for oxidation of the reduced form will be:

$$E_a=E_0+\frac{RT}{\beta nF}\ln\frac{K_{red}}{i_0}+\frac{RT}{\beta nF}\ln\frac{i}{i_{red}-i}, \tag{7}$$

where

$$E_0+\frac{RT}{\beta nF}\ln\frac{K_{ox}}{i_0}=E_{1/2,\,a}.$$

A difference from fast systems is that the greater the difference between $E_{\frac{1}{2},a}$ and $E_{\frac{1}{2},k}$ the slower is the system. Thus, the difference $E_{\frac{1}{2},a} - E_{\frac{1}{2},k}$ is a criterion of the rate of an electrochemical reaction.

There is a definite relation between the concentration of a component and the electrical parameters, so that, in order to find the endpoint of a reaction, it is necessary that there should be a sharp change in the observed current or electrode potential in the immediate vicinity of the equivalent point (EP). Graphical and mathematical consideration of the corresponding polarization curves makes it possible to trace the course of a titration curve, with the important object of revealing and giving a theoretical interpretation of the sharp change in the parameters concerned near the EP.

If i is the polarization current, and i_{ox} and i_{red} are the diffusion currents of the component to be determined and its conjugate form in the redox system, then Eqs. (4), (6), and (7) can be used as potentiometric titration equations for various redox systems with one polarized indicator electrode. For example, the change in electrode potential during the process of titration to the EP of the reducing agent of a redox pair can be obtained from the equation

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i + K_{ox} a_0 x}{K_{red} a_0 (1 - x) - i}, \tag{8}$$

which can be derived by transformation of Eq. (4), where x is the proportion of unreacted reducing agent, and a_0 is its original activity.

The titration endpoint (TEP) is reached when $i \simeq i_{red}$, so that $K_{red} a_0 (1 - x)/ i \simeq 1$. Hence, $x = 1 - i/ K_{red} a_0$, where $i/K_{red} a_0 = i/i_d$ corresponds to the titration error, expressed graphically by the displacement of the titration curve along the abscissa axis relative to the curve at i = 0, and depending on the anodic or cathodic polarization of the electrode. In order that this titration error should not exceed 1%, not more than 10^{-2} of the original amount of the component to be determined should participate in the electrochemical reaction. This condition dictates the value of the polarization current used, normally about 10^{-6} A.

Classical amperometry also relates to a method in which the titration is carried out with one polarized electrode. In this case, electrochemical conversion of only one component of a redox pair occurs at a selected constant value of the indicator electrode potential. Therefore, when transforming Eq. (2) into an equation for the amperometric titration curve, we can eliminate one of the terms in the numerator. Solving Eq. (2) for i, we obtain a simple relation between the activity a of the component and the diffusion current

$$i = K \cdot a, \tag{9}$$

where the constant K includes all the remaining constant terms in Eq. (2).

When two indicator electrodes are used, with a constant potential difference ΔE maintained between them, a mathematical expression for the electrolysis current can be obtained by combining the relation $f(i, E, a)$ for both electrodes. This relation can be established for the limiting case if it is assumed that, at any instant of the change in concentration of the component, both i and ΔE are very small. Under these conditions,

$$\frac{i}{\Delta E} \approx \left(\frac{di}{dE}\right)_{i=0}, \tag{10}$$

i.e., the current is a linear function of ΔE, with a proportionality coefficient equal to the tangent of the angle of slope of the polarization curve, close to its point of intersection with the potential axis.

If the same electrochemical reaction, $Ox + ne \rightleftharpoons Red$, occurs reversibly at both electrodes, and if the diffusion coefficients for the components are the same K_d, then during the titration $a_{ox} = a_0 x$ and $a_{red} = a_0(1 - x)$. Differentiation of the general equation for the relation $i = f(E)$ gives [11]:

$$\left(\frac{di}{dE}\right)_{i=0} = \frac{(\alpha + \beta)\, nF}{RT} i_0 a_0 \times \frac{\frac{i_0}{K_d} x(1-x) + x^{\frac{\alpha+2\beta}{\alpha+\beta}} (1-x)^{\frac{2\alpha+\beta}{\alpha+\beta}}}{\left[\frac{i_0}{K_d} + x^{\frac{\beta}{\alpha+\beta}} (1-x)^{\frac{\alpha}{\alpha+\beta}}\right]^2}.$$

If α + β = 1, this equation has the simpler form:

$$\left(\frac{di}{dE}\right)_{i=0} = \frac{nF}{RT} i_0 a_0 \frac{x(1-x)}{\frac{i_0}{K_d} + x^{(1-\alpha)} (1-x)^{\alpha}}.$$

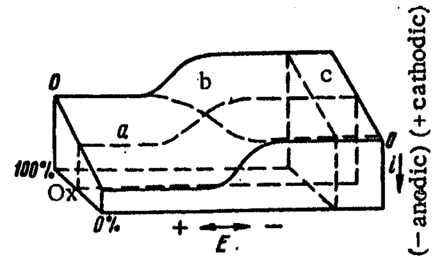

Fig. 3. Three-dimensional model of an electrochemical process.

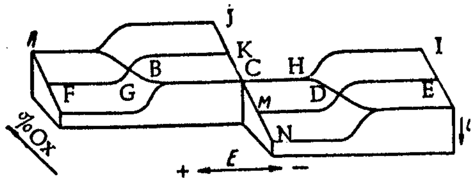

Fig. 4. Three-dimensional model for a mixture of two reversible redox systems.

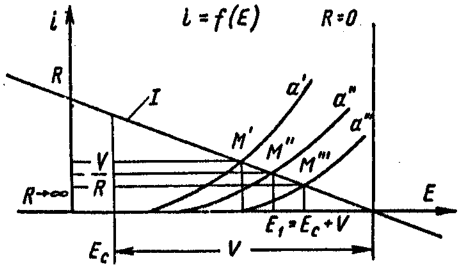

Fig. 5. Titration at constant resistance.

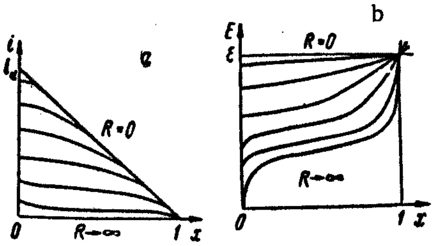

Fig. 6. Deformation curves of a) amperometric, and b) potentiometric titrations, at constant resistance, for R values from 0 to infinity.

For fast systems ($i_0 \gg K_d$),

$$\left(\frac{di}{dE}\right)_{i=0}^{\text{fast}} = \frac{nF}{RT} K_d a_0 x(1-x), \tag{11}$$

and for slow systems ($i_0 \ll K_d$),

$$\left(\frac{di}{dE}\right)_{i=0}^{\text{slow}} = \frac{nF}{RT} i_0 a_0 x^{\alpha}(1-x)^{(1-\alpha)}. \tag{12}$$

Equations (11) and (12) describe the curves for amperometric titration with two polarized indicator electrodes ("dead stop" titration). They show a direct relation between di/dE and degree of conversion x. Starting from Eq. (10), we may therefore write

$$\frac{i}{\Delta E} = f(x). \tag{13}$$

A similar treatment gives the equations of the curves for potentiometric titration with two polarized electrodes ("derivative titration") [12], for fast and slow systems ($x < 1$):

$$\left(\frac{dE}{di}\right)_{i=0}^{\text{fast}} = \frac{RT}{nFK_d a_0} \cdot \frac{1}{x(1-x)}, \tag{14}$$

$$\left(\frac{dE}{di}\right)_{i=0}^{\text{slow}} = \frac{RT}{nFi_0 a_0} \cdot \frac{1}{x^{\alpha}(1-x)^{(1-\alpha)}}. \tag{15}$$

The following relations should apply to titration curves based on Eqs. (11)-(15), as $x \to 1$: $di/dE \to 0$ and $dE/di \to \infty$

However, owing to chemical equilibrium, these differentials have final values depending on the equilibrium constant K_{eq} of the reaction. For example, in the case of titration of a reversible system,

$$\left(\frac{dE}{di}\right)_{i=0}^{\text{EP}} = \frac{RT}{nFK_d a_0} \cdot \frac{1}{\sqrt{K_{eq}}}$$

and

$$\left(\frac{di}{dE}\right)_{i=0}^{\text{EP}} = \frac{nFK_d a_0}{RT} \sqrt{K_{eq}}$$

On this basis the curves for amperometric and potentiometric titrations with two polarized electrodes can be considered as mutually inverse representations.

A three-dimensional model (Fig. 3),* with coordinates i, E, and percentage of oxidized component, has been proposed [12] to visualize the interpretation of electrochemical processes. This model illustrates the relation between oxidized component content and either i or E, when one of them is constant.

Equation (8) provides the basis for constructing this model. Assumming a constant percentage of oxidized component (say 50%), and cutting a section through the solid model, we obtain a surface representing a polarogram of the reversible redox system containing a mixture of equal amounts of the oxidized and reduced forms (the broken line a), which corresponds to Eq. (4).

At constant current (potentiometric titration) we can obtain from the three-dimensional model a surface giving a two-dimensional representation (the broken line b) of the classical Nernst equation. In the case of titration with one

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* Figure 3 preserves the authors' sign convention for current and potential, explained earlier in this paper.

polarized electrode, the previously explained shift of the TEP relative to the EP is confirmed by the corresponding shift of the diagram b.

At constant E, solution of Eq. (8) for i, with further approximations for $E \ll E_0$ and $E \gg E_0$, leads to the equations $i = -K_{red}a_0x$ and $i = +K_{ox}a_0(1 - x)$, respectively. These correspond to a section through the solid model shown in Fig. 3 by the broken line c, representing a typical amperometric titration curve, or to the broken line a, corresponding to the limiting diffusion current in quantitative polarography at a given concentration of the reduced form.

If we have two oxidizing agents of two reversible redox systems, then the corresponding location of their models on the potential axis is shown three-dimensionally in Fig. 4, where ABCDE represents the curve for their successive potentiometric titrations. The points B and D represent E_0 for the two systems, and C is the first TEP. This point corresponds to the polarogram curve FGCHI, in which the wave FGC corresponds to oxidation of the component of the redox pair with the higher E_0, and the wave CHI corresponds to reduction of the component of the redox pair with lower E_0. The endpoint of amperometric titration is shown by the point of intersection C of the two straight lines JKC and CMN. The coincidence of the TEP by the amperometric and potentiometric methods indicates their interrelation and the generality of their theoretical bases.

The above considerations are all based on Eq. (8), which is only valid for fast reversible systems. Other approximate equations and another model are required for irreversible systems.

During the titration process i and E (or ΔE) alter simultaneously, but, as is evident from the above equations, not to the same extent. The extents of the changes in each parameter, which control the sensitivity and precision of the electrometric methods, depend on the total resistance R of the circuit, a factor which does not normally receive sufficient attention. Meanwhile, correct adjustment of this parameter makes possible a rational selection of the method by gradually changing from one electrometric method to another, and so determining the most suitable conditions for measurement [1,8,11,16].

Equation (1), with a coordinate system $i = f/(E_a \text{ or } E_k)$, with the potential of one electrode held constant, has the form of a straight line I (Fig. 5) with slope 1/R.

The intersects of this straight line with the polarization curves a', a", a‴, corresponding to different times in the titration of a definite component, give a series of points M', M", M‴, from which titration curves for the various methods can be constructed. Projection of these points on to the abscissa or ordinate axes gives the corresponding changes in potential (potentiometric curve) and current (amperometric curve). It is clear from Fig. 5 that the changes in i and E will differ, depending on the slope of the line I, i.e., on the value of R.

By solving Eqs. (1) and (2) simultaneously we obtain an equation for electrometric titration curves, which allows for a variable value of the resistance. By eliminating either i or E from Eqs. (1) and (4), for the case of titration of one component of a fast system using one indicator electrode, we obtain the following mathematical expressions for $x = f(E_a)$ or $f(i)$, when $x \leq 1$:

$$x = \frac{\exp\left[\frac{nF}{RT}(E - E_0)\right]}{1 + \exp\left[\frac{nF}{RT}(E - E_0)\right]} - \frac{E_1 - E_a}{Ri_d} = f_1(E) - f_2(E) \tag{16}$$

and

$$x = \frac{\exp\left[\frac{nF}{RT}(E_1 - E_0 - Ri)\right]}{1 + \exp\left[\frac{nF}{RT}(E_1 - E_0 - Ri)\right]} - \frac{i}{i_d} = f_1(i) - f_2(i). \tag{17}$$

Here $E_1 = V + E_k$ and $i_d = K_d a_0$, the initial value of the limiting diffusion current of the reducing agent.

A combinations of Eqs. (1) and (13) gives the equations for the titration curves with two indicator electrodes, in amperometry:

$$i = \frac{V \cdot f(x)}{1 + Rf(x)}; \tag{18}$$

and in potentiometry,

$$\Delta E = \frac{V}{1 + R\,f(x)}. \tag{19}$$

These mathematical relations can be used to determine the effect of resistance on the characteristics of electrometric methods.

The effect of including only a small resistance in the circuit is that, in the process of titration with one polarized electrode ($E_a = E_1 - iR$), the electrode potential remains practically constant and equal to E_1. It follows similarly, from Eq. (19), that, in titration with two polarized electrodes, ΔE changes very little and is practically equal to V. The slight changes in E_a, E_k, or ΔE cannot be used for quantitative determinations.

Because of the very small change in electrode potential, Eq. (17) becomes $x = \text{const} - i/i_d$, and, if the voltage V (or E_1) corresponds to the potential of the limiting diffusion current region ($E_1 \gg E_0$), then $x = 1 - i/i_d$ or $i = (1 - x) \cdot i_d$, which is the equation of the amperometric titration curve. Thus, in this case, amperometric measurement is more suitable, as is clearly shown by means of the graph (Fig. 5).

In the limiting case, when R = 0 or is very small, the straight line I becomes vertical, and there are the maximum changes in i, corresponding to the points of intersection of the line I with the polarization curves (Fig. 5).

In the case of two polarized electrodes, the change in i corresponds to $V \cdot f(x)$, because $1 \gg Rf(x)$ [see Eq.(18)], i.e., the conditions for amperometric titration at constant applied voltage are again attained.

Two cases can be considered when a very high resistance is included in the circuit:

A. The second term in Eq. (16) can be neglected if V = 0. In this case the equation transforms into the Nernst equation, and we are dealing with classical potentiometry in the absence of a current. The fact that the greatest change in electrode potential occurs when $R \to \infty$ (open circuit) is shown in Fig. 5 when the line I coincides with the E axis.

B. When V has an appreciable value, i is small, practically constant, and approximately equal to V/R [Eqs. (1) and (18)], and the change in current will be negligible during titration. On the other hand, there will be considerable changes in E_a, E_k, or ΔE [Eqs. (1) and (19)]. Thus, in this case, it is only possible to use potentiometry at constant current with one or two polarized electrodes.

The generality of the above methods is confirmed by the fact that, for a given resistance, the curves for quantitative determination have the same form, dependent on a linear relation between i and E (Ohm's law). In the case of one indicator electrode they retain a logarithmic form for high values of R, since $f_2 \ll f_1$ in Eqs. (16) and (17). For small R values, $f_2 \gg f_1$, and the titration curves are therefore linear in form (Fig. 6).

Thus, when R is increased from zero to infinity, the analytical curves gradually change from one extreme form (linear), which is more suited to amperometric measurements, to another form (logarithmic), which is more suited to potentiometry. Intermediate values of the resistance give less characteristic distorted forms, with a decrease in slope of the line with change in current in the first case, and a jump in potential in the second case; it is difficult to use these forms in practice.

Thus, potentiometry and amperometry are limiting cases of the same method, which may be called voltage-amperometry at constant resistance [1].

The above analysis makes it possible to create the following unique classification of electrometric methods of analysis, based on the phenomena of electrolysis [11,17].

I. All the material to be determined takes part in the electrolytic process. In this case it is possible to use electrolytic analysis in its classical form, or in the more modern form of measuring the quantity of electricity consumed in carrying out the electrochemical reaction (coulometry).

II. A negligible proportion of the material to be determined participates in the electrochemical reaction. In this case it is possible to determine directly the concentration of a substance and the activity of ions by measuring, respectively, the limiting diffusion current (polarography) or the electrode potential (direct potentiometry). The determination may be carried out by using the change in limiting diffusion current (amperometry), or the change in potential of an indicator electrode (potentiometry), to follow the change in concentration of a substance during chemical reaction.

Potentiometry may be divided into the classical (static) form with $i = 0$, and the form in which there is a polarization current, with or without the use of a reference electrode (one or two polarized electrodes). The latter includes both differential and derivative potentiometric titrations. The forms of the curves are completely analogous [12].

Amperometry may be divided into the classical form (one polarized electrode) and "dead stop" titration (with two polarized electrodes).

The choice of one or other variation of the potentiometric method depends on the reversibility or irreversibility of the reacting redox systems. No variant may offer any particular advantage for fast systems, but when irreversible and slow systems are to be titrated it is essential to use polarized electrodes (potentiometry with current flow). This variant forces the electrochemical process and favors the rapid establishment of the equilibrium potential during the titration process, so that it gives a sharp change in potential at the TEP.

The advantages of using two indicator electrodes in amperometry are the simplicity of the apparatus, the elimination of the reference electrode and electrolytic bridge, and the tolerance of a wide variation in applied voltage (10 to 500 mV).

Thus, systematic study of oxidation–reduction phenomena at electrodes and of polarization curves makes it possible to reveal the unity of, and to establish the relations between, electrochemical methods, to make a rational selection of methods, and to make a conscious approach to the development of new electroanalytical methods.

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