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Oxidation-reduction Measurements and Their Applications in the Study of Interactions in Solutions

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The theoretical principles of oxidation-reduction measurements and their applications in the study of chemical processes accompanied by electron transfer are considered. These include complex formation, protolytic reactions, and association in homogeneous and heterogeneous oxidation-reduction systems.
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I. INTRODUCTION

The oxidation potential, which is a thermodynamic characteristic of a reversible oxidation-reduction system or an oxidation-reduction reaction, is used in many studies among which one can distinguish three main fields.

1. Quantitative determination of the content in solution of one or several components. These must react fairly completely and rapidly with the oxidant or reductant introduced into the solution. This field, established for a long time, constitutes a branch of analytical chemistry[1]. The measurement of the oxidation potential in analytical determinations is carried out either potentiometrically or with the aid of oxidation-reduction indicators[2].

2. Determination of the composition and equilibrium constants for the formation of molecular and ionic forms of substances constituting an oxidation-reduction system.

3. The study of the nature of the chemical bond and of the charge distribution in polyatomic compounds capable of oxidation or reduction. The difference between the oxidation potentials of related compounds, in which the nature of the oxidising (reducing) centre remains unchanged, is interpreted quantitatively. The theoretical methods employed (correlations, quantum-chemical methods) are varied and differ significantly in their validity[3,4]. It is noteworthy that the conversion of the oxidation potential to the molecular orbital energy requires assumptions whose justification is difficult to estimate.

The requirements which must be met by the accuracy of the determination of the oxidation potential in each field differ significantly. They are greatest in the second field, whose establishment and development are associated with the studies of Clark and Michaelis[5,6]. Measurements of the oxidation potential in order to discover the nature of the chemical interaction have been made and are being made on a very wide scale. An appreciable development of the second field has been achieved in the studies of Academician B.P.Nikol'skii. This review deals mainly with the studies carried out by Nikol'skii's school.

II. THE OXIDATION POTENTIAL

Oxidation-reduction measurements constitute a branch of physical chemistry which deals with the study of chemical reactions accompanied by electron transfer[7]. This transfer can take place between the components of two oxidation-reduction systems, where the oxidised form of one system removes electrons from the reduced form of the other, oxidising it and being itself reduced. As a result of such oxidation–reduction reaction, new substances are formed. The transfer of n electrons e also occurs between the components of a single oxidation–reduction system:

$$\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red} \ . \qquad (1)$$

Chemical analysis demonstrates the constancy of the concentrations of Ox and Red subject to the condition that the composition of the solution remains unaltered and the influence of any oxidant or reductant is excluded. In order to characterise the oxidation–reduction system (1), it is necessary to introduce another oxidation–reduction system, the role of which is fulfilled by a plate of an indifferent metal. After the attainment of equilibrium, the plate acquires the equilibrium electrical potential, which ensures the equality of the electrochemical potentials of the electrons in the solution and in the metal in the absence of a potential shift of the equilibrium of reaction (1). Hence it follows that

$$\varphi = \psi^{\mathrm{M}} - \psi = \mathrm{const} - \lg a_e = \overline{\varphi}^0 + \frac{\vartheta}{n} \lg \frac{a_o}{a_r} \ , \qquad (2)$$

where ψ^{M} and ψ are the Galvani potentials of the metal and solution, a_e, a_o, and a_r are the activities of the electrons and the oxidised and reduced forms respectively, and $\vartheta = 2.3RT/F$.

The oxidation potential ϕ, which is equal to the difference between the Galvani potentials of the metals and the solution, includes a constant component $\overline{\phi^0}$—the standard oxidation potential. This constant defines the level of the oxidising capacity of the Ox–Red system and depends on the electron affinity of the species constituting the oxidation–reduction

system as well as their free energies of formation and solvation. Since the absolute value of the standard oxidation potential is unknown, it is assumed that $\overline{\phi^0} = 0$ for the standard hydrogen system, where the activity of hydrogen ions $h = 1$ and the partial pressure of hydrogen is 1 atm (1×10^5 Pa). The oxidation potential of the reversible Ox–Red system is then numerically equal to the e.m.f. of the galvanic cell made up of the oxidation–reduction and hydrogen half-cells.

The oxidation potential, referred to the conventional hydrogen zero, is an electrical measure of the free energy of the oxidation–reduction reaction of the Ox–Red system with the standard hydrogen system[8]:

$$\varphi = -\frac{\Delta G}{nF}, \qquad (3)$$

where F is the Faraday.

The oxidation potentials can vary in a specific manner also under conditions where the effect of the oxidant or reductant is excluded, but the concentrations of the other components of the solution vary. Changes in the oxidation potential are induced by the interaction of the substances constituting the reversible oxidation–reduction system with the solvent and other components of the solution. The appearance of a new species as a result of protolytic, complex formation, and association reactions, as well as other processes leads to an alteration of the activity of the electrons in solution and hence to a change of the oxidation potential. Thus the oxidation potential is not only an electrical measure of the free energy of the oxidation–reduction reaction between the given system and the standard hydrogen system, but is also an electrical measure of the free energies $\Delta G'$ of the chemical reactions between the substances in the oxidised and reduced states, on the one hand, and other components of the solution, on the other, i.e.[9]

$$\varphi = -\Delta G/nF - \Delta G'/nF. \qquad (4)$$

If the first term of Eqn.(4) is kept constant (by protecting the system from oxidation or reduction), the oxidation potential will follow the change in the free energy $\Delta G'$ induced by the chemical reactions occurring in solution.

III. THEORY OF OXIDATION–REDUCTION MEASUREMENTS

All the interactions accompanied by the transfer of n electrons between p kinds of species in the reduced state and q kinds of species in the oxidised state can be described by a single equation for the oxidation potential:

$$\varphi = \varphi(P, T, c_0, c_r, x_1, \ldots, x_m) = \overline{\varphi}^0 + \frac{\vartheta}{n}\lg\frac{c_0}{c_r} + \frac{\vartheta}{n}\lg\sum_1 \cdots \sum_q K_i^{(o)} \prod_i x_i^{\nu_i} + \frac{\vartheta}{n}\lg\sum_1 \cdots \sum_p K_j^{(r)} \prod_j x_j^{\nu_j}, \qquad (5)$$

where $\overline{\phi^0}$ is the standard oxidation potential, P the pressure, c_0 and c_r are the overall concentrations of the substances in the oxidised and reduced states respectively, x_1, x_2, ..., x_m are the concentrations of substances of m kinds involved in the reaction, $K_i^{(o)}$ and $K_j^{(r)}$ are the equilibrium constants of these reactions, ν_i and ν_j are stoichiometric coefficients, and the subscripts and superscripts o and r show that the given quantities refer to the oxidised and reduced states.

The first sum in the logarithmic term of Eqn.(5) takes into account the formation of species of any composition in the reactions where the system components in the oxidised state are involved and the second takes into account the corresponding interaction of the components in the reduced state.

It is assumed that the following equation should hold for the chemical potential of species of each ith and jth kind:

$$\mu_k = M_k + RT\ln c_k. \qquad (6)$$

The quantity

$$M_k = \mu_k^0 + RT\ln y_k,$$

where μ_k^0 is the standard chemical potential and y_k the activity coefficient, can be regarded as constant under certain conditions. The number of concentration variables in Eqn.(5) is equal to the sum of the concentrations of all the substances present in solution, i.e. $m + p + q + 2$, while the number of independent variables is $m + 2$.

Eqn.(5) can be regarded as a complete mathematical model of all the interactions associated with the given oxidation–reduction system. Interactions of this kind include the stepwise complex formation reactions, comprising mixed, polynuclear, and heteropolynuclear complex formation, hydrolysis (solvolysis), stepwise protolytic dissociation reactions, and the association of the ions and molecules forming part of the oxidation–reduction system investigated or interacting with the latter.

Eqn.(5) makes it possible to obtain any form of the ϕ surface in the space of states (P, T, c_0, c_r, x_1, ..., x_m) by varying the quantities $K_i^{(o)}$ and $K_i^{(r)}$ from 0 to $+\infty$. The determination of the set of the quantities $\{K_i^{(o)}, K_j^{(r)}\}$ compatible with experimental data constitutes the solution of the problem of the quantitative description of reversible reactions in reversible oxidation–reduction systems. The method involving successive sections through the surface in the $\{c_0, c_r, x_1, \ldots, x_m\}$ space with respect to one of the independent concentration variables while all others are kept constant is widely used. This makes it possible to obtain curves representing the partial relations between the oxidation potential and each independent variable. These curves consist as a rule of linear sections joined by smooth bends. The linear sections correspond to the states of the solution in which compounds with specific stoichiometric coefficients predominate. The compositions of the compounds formed can be found from the slopes of the linear sections, which are proportional to the stoichiometric coefficients. The sets of constants $\{K_i^{(o)}, K_j^{(r)}\}$ are determined in simple cases by graphical or computational methods. In the case of chemical interactions leading to the formation of several compounds of complex composition, which are frequently present simultaneously, the above quantities are found with the aid of computers.

In specific cases Eqn.(5) is simplified, because the number of independent concentration variables is reduced and limitations are imposed on the permissible stoichiometric coefficients.

IV. MEASUREMENT OF THE OXIDATION POTENTIAL

The description of interactions in solutions of oxidation–reduction systems is based on the experimental values of the oxidation potential under the conditions of equilibrium at the indicator electrode–solution interface. The correct formulation of the potentiometric experiment involves the establishment of this equilibrium.

The solution of specific problems may be complicated by the low rates of homogeneous and heterogeneous electron transfer reactions, by the breakdown of the condition of the indifference of the electrode owing to the catalytic effect of the material on the processes in solution, including the decomposition of its components, and other causes[7,10–12].

Thus platinum electrodes cease to be indifferent at low oxidation potentials. On the other hand, certain oxidation–reduction systems, for example Ce(IV)–Ce(III), Ti(IV)–Ti(III), V(III)–V(II), and Eu(III)–Eu(II), which should decompose water on the basis of their standard oxidation potentials, actually form stable aqueous solutions. Their stability is associated with the low rates of the reactions of the components of the above oxidation–reduction systems with water. The possibility of the measurement of the oxidation potential depends on the availability of an electrode material with a high oxygen overvoltage (in the region of low potentials) or a high hydrogen overvoltage (in the region of high potentials). Noble metal electrodes are heterogeneous catalysts of reactions involving the decomposition of water and cannot serve as materials for the indicator electrode[13]. On the other hand, when the rate of the homogeneous electron transfer reaction is low, the electrode must catalyse the electron transfer between the oxidised and reduced forms of the system or must catalyse one of the stages of the overall oxidation–reduction reaction.

By virtue of the above complications, the range of systems susceptible to experimental study and the quality of the information obtained depend largely on the extent to which the material of the indicator electrode and the state of its surface satisfy the requirements arising from specific conditions. These requirements can be justified, because, together with the thermodynamic characteristics of oxidation–reduction systems, there are data on the rates of homogeneous[14] and electrode[15] oxidation–reduction reactions. The following postulates have been formulated concerning oxidation–reduction measurements[7,8,10,11]: (1) there can be no universal electrode in oxidation–reduction measurements; a set of electrodes with a wide range of properties is required; (2) in the absence of equilibrium between the components of the solution which are capable of participating in oxidation–reduction interaction, one chooses an electrode whose material ensures reversible electron exchange with one of the oxidation–reduction systems; (3) the agreement between the oxidation potentials measured by different electrodes constitutes an adequate criterion of the attainment of equilibrium in the electrode–solution system.

The choice of the electrode material is based on information concerning the characteristics of the chemical interactions in solution and also on the results of studies designed to determine the limits of the indifference of the electrode materials and the kinetic parameters of electrode processes[8,16–18].

Together with traditional smooth platinum and gold electrodes, iridium and rhodium[7,19–22] as well as mercury[10,23] electrodes are used in oxidation–reduction measurements. The search for new electrode materials and new types of electrodes has led to the development of thin-layer platinum electrodes[8,24,25], electrodes made of semiconducting tin dioxide[26–28], glass electrodes for oxidation–reduction measurements[29,30], electrodes based on polymeric organic semiconductors[31,32], and modified graphite electrodes[33].

Thin-layer platinum electrodes are catalytically active in relation to many oxidation–reduction interactions[8], which permits measurements of the oxidation potential in those cases where homogeneous electron exchange is highly inhibited. However, the high catalytic activity of thin-layer platinum electrodes hinders their use when the stability of individual solution components breaks down and in kinetic studies.

Glass electrodes with an electron response have been developed on the basis of results of systematic studies of the dependence of the electrode properties of glasses on their chemical composition[29,30,34–37]. The possibility of using these electrodes in oxidation–reduction measurements is determined by the chemical indifference of glasses and the high electronic conductivity associated with the introduction of iron or titanium oxides into the composition of the glasses. It has been shown[10,11,38,39] that glass electrodes possess important characteristics such as insensitivity to oxygen and hydrogen, and that they are suitable for the measurement of the oxidation potential beyond the limits of the thermodynamic stability of water. The semiconducting properties of glasses determine their specificity in relation to systems with low oxidation potentials, which provides a basis for further studies on these lines. A semiconductor electrode, reversible in alkaline media, has been developed for the oxygen–hydrogen peroxide system, which is of both theoretical and practical interest[10,39].

The improvement of the experimental formulation of potentiometric measurements is of great importance. Special hermetically sealed apparatus, which eliminate the access of air, have been constructed for the determination of the oxidation potential under the conditions of varying concentrations of individual solution components[7,19,21,40,41].

V. PROTOLYTIC EQUILIBRIA

Clark[6,42] showed that the oxidation potentials of organic reversible oxidation–reduction systems are involved in a complex relation with oxidation–reduction and protolytic equilibria in solutions. In relation to individual examples, Clark formulated the fundamental postulates of the thermodynamic theory of the phenomenon and proposed a graphical method for the determination of the protolytic dissociation constants. During the subsequent development of this research, the study of the protolytic processes occurring in oxidation–reduction systems in a general form was undertaken[7,40,43,44]. Two types of systems were investigated. The first includes systems where the oxidised form is a q-basic acid and the reduced form is a p-basic acid. Regardless of the nature of the protogenic (proton-accepting) groups, their protolytic dissociation takes place as a result of isotypical reactions of the following type:

$$RH_j + H_2O \rightleftarrows RH_{j-1} + H_3O^+ \ . \qquad (7)$$

For systems of the second type, the concluding $(q+1)$th stage of the successive reactions of type (7) consists of the formation of the free base of the oxidised form:

$$R^+ \cdot H_2O + H_2O \rightleftarrows ROH + H_3O^+ \ . \qquad (8)$$

The regions where individual protolytic forms exist in the oxidised and reduced states are determined by the ratios of the protolytic dissociation constants and the pH values. The relation linking the electron transfer processes between protolytic forms and processes involving proton exchange with solvent molecules is reflected in the equations for the oxidation potential ϕ

(a) type I systems:

$$\varphi = \varphi^0 + \frac{\vartheta}{n}\lg\frac{c_o}{c_r} + \frac{\vartheta}{n}\lg\sum_{i=1}^{p} h^{p-1}B_i^{(r)} - \frac{\vartheta}{n}\lg\sum_{j=0}^{q} h^{q-j}B_j^{(o)}; \qquad (9)$$

(b) type II systems:

$$\varphi = \varphi^0 + \frac{\vartheta}{n}\lg\frac{c_o}{c_r} + \frac{\vartheta}{n}\lg\sum_{i=1}^{p} h^{p-1}B_i^{(r)} - \frac{\vartheta}{n}\lg\sum_{j=0}^{q} h^{q+1-j}B_j^{(o)} + \frac{\vartheta}{n}\lg h, \qquad (10)$$

where c_o and c_r are the overall concentrations of all the protolytic forms in the oxidised and reduced states respectively, $B_j^{(o)}$ and $B_i^{(r)}$ are the overall apparent jth and ith dissociation constants, and h is the activity of hydrogen ions. Eqns.(9) and (10) make it possible to predict the properties

of the oxidation–reduction system in the form of its dependence on the oxidation potential and the pH.

The experimental data are thermodynamically highly rigorous and can be very readily interpreted with a consequent high accuracy of the determination of the protolytic dissociation constants when the following oxidation voltage is introduced[7,40,44]:

$$\mathscr{E} = \varphi - \vartheta \lg h. \qquad (11)$$

The oxidation voltage is numerically equal to the e.m.f. of the galvanic cell comprising the hydrogen (glass) and oxidation–reduction half-cells. The properties of the oxidation voltage have been formulated in the following postulates[7,44].

(a) The $\mathscr{E} = \mathscr{E}$ (pH) curve consists of linear sections joined by smooth bends; the number of these sections is equal to the number of all the protolytic forms in the oxidised and reduced states plus one.

(b) The slopes, equal to the partial derivative $(\partial\mathscr{E}/\partial\,\mathrm{pH})_{pc_o pc_r}$, depend on the predominance of one of the protolytic forms in the oxidised state and one form in the reduced state and can be predicted with the aid of Eqns.(9)–(11).

(c) Each bend in the curve and the establishment of a linear section with another slope correspond to a specific stage of the protolytic dissociation; an increase in the slope of the linear section with increase of pH is a sign of the dissociation of the oxidised form and its decrease is a sign of the dissociation of the reduced form.

(d) Each dissociation stage alters the slope of the subsequent linear section of the $\mathscr{E} = \mathscr{E}$ (pH) curve by an amount ϑ/n.

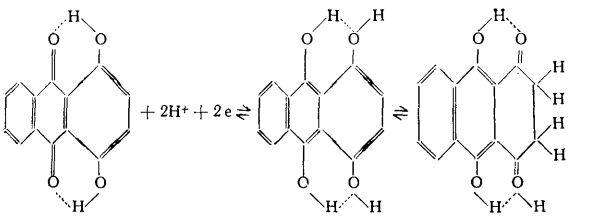
(e) The similarity of two dissociation constants of one of the forms leads to the disappearance of the corresponding linear section; the dissociation of the same protogenic group involved in both the oxidised and reduced forms induces the appearance of an inflection in the $\mathscr{E} = \mathscr{E}$ (pH) curve and a shift of the subsequent linear section parallel to the preceding one; the identity of the dissociation constants should cancel out their influence on the shape of the curve.

(f) The pK for protolytic dissociation is numerically equal to the pH at the point of intersection of the lines obtained by producing two neighbouring sections.

In a consecutive two-stage dissociation of the reduced form the $\mathscr{E} = \mathscr{E}$ (pH) curve becomes concave relative to the abscissa axis, while in the case of the corresponding dissociation of the oxidised form it becomes convex. If the dissociation constants corresponding to these two-stage processes are similar, then the curves pass through an extremum, The appearance of the latter makes it possible to determine stepwise dissociation constants with similar values; the graphical determination with the aid of the $\phi = \phi$ (pH) curve makes it possible to find only their product.

The study of type I systems in relation to the Alizarin C–leuco-Alizarin C system[7,45,46] and of type II systems in relation to the Toluidine Blue–leuco-Toluidine Blue and Methylene Blue systems[7,40,47–49] demonstrated the complete agreement between the theory and experiment. A quantitative characteristic of the oxidation–reduction and protolytic properties, which includes the dependence of the oxidation potential and the oxidation voltage on the pH, the stepwise protolytic dissociation constants, and the distribution of the relative contents of the protolytic forms as a function of pH, has been obtained for the systems investigated.

Since systems formed by quinone or quinone imine and their reduced forms served as prototypes of reversible organic systems, the number of proton-donating (proton-accepting) groups in the reduced state is two greater than in the oxidised state. The study of systems formed by anthraquinone derivatives and their leuco-forms, which contain nucleophilic substituents (OH or NH_2) in the *para*-positions of their aromatic side rings, showed that, on reduction, the number of protogenic groups in these systems does not change or increases by unity[50–56]. The manifestation of these anomalous properties is due to the retention of the quinonoid structure in the leuco-form, which has been shown experimentally[53] to be a consequence of a desmotropic transition; for example, the following transition occurs for quinizarin:



The second stage can be regarded as a result of the partial intramolecular oxidation of the extreme ring by the central ring, which is promoted by strong intramolecular hydrogen bonds.

By comparing the $\mathscr{E} = \mathscr{E}$(pH) relations and the electronic absorption spectra of the six anthraquinone dues investigated and their leuco-forms in CCl_4 and aqueous alcoholic solutions, the sequence of the dissociations of the protogenic groups was established[55]. The OH groups in the β-position are the first to dissociate. Their acid properties are enhanced on conversion into the leuco-form. As a result of the formation of strong intramolecular hydrogen bonds, the acid properties of the OH groups in the β-position are appreciably weakened.

Together with protolytic dissociation, other processes, in the first place association, can occur in organic systems. The study of the Neutral Red–leuco-Neutral Red system[57–59] showed that, in consequence of association, its oxidation potential becomes a function not only of the activity of hydrogen ions but also of the concentration of form RH^+ of Neutral Red, which is capable of association:

$$\varphi = \varphi^0 + \frac{\vartheta}{2}\lg\frac{c_o}{c_r} + \frac{\vartheta}{2}\lg(h^2 + hK_1^{(r)} + B_2^{(r)}) + \vartheta\lg h - \frac{\vartheta}{2}\lg(K_1^{(o)} + Ah), \qquad (12)$$

where

$$A = 1 + 2K_2^{(o)}[RH^+] + 4(K_2^{(o)}K_4^{(o)})^2[RH^+]^3,$$

and $K_2^{(o)}$ and $K_4^{(o)}$ are the formation constants of the dimer and tetramer.

The formation of the associated species was demonstrated and its identification with a specific protolytic form was achieved by analysing the partial relations $\phi = \phi(\lg c_o)$, $\phi = \phi(\lg c_r)$, and $\phi = \phi(\lg c)$, where $c = c_o + c_r$, obtained for the pH ranges corresponding to the conditions where particular protolytic forms predominate. These relations are used to find the compositions and the formation constants of the associated species. Association, taken into account in Eqn.(12) by the quantity A, influences only the protolytic dissociation constant of the associable species RH^+ and does not influence the protolytic equilibria of other forms. Association does not affect the numerical dissociation constants of the forms determined graphically from $\phi = \phi$(pH) relations.

The oxidation of Neutral Red yielded a hitherto unknown compound, which is apparently a charge-transfer complex of the quinhydrone type[60]. It is stable in the crystalline state but in solution it is slowly oxidised by atmospheric oxygen. Its protolytic properties differ from those of the dye and its leuco-form.

VI. COMPLEX FORMATION

In oxidation-reduction systems formed by ions of the same metal in two oxidation states the appearance of complexes of these ions is reflected in the oxidation potential. Two fields differing in their interpretation of the experimental relations are being established[61,62]. In studies on one of them the compositions of the complexes and their stability constants are found with the aid of secondary concentration variables—the formation functions and degrees of formation and complexation (Rossotti and Rossotti[63], chapters 4 and 7). The second field arose and is being developed in the studies of Nikol'skii and his school. In view of the analogy between protolytic process and complex formation, Nikol'skii[64] suggested that complex formation be studied by methods developed for the investigation of protolytic equilibria in oxidation–reduction systems. The experimental study of the iron(III)–iron(II)–acetic acid–water system[65] confirmed the likely usefulness of this approach and initiated the theoretical and experimental studies on complex formation in reversible oxidation–reduction systems consisting of the aquo-complexes of the metal in two oxidation states.

In the course of the development of the thermodynamic theory[7,8,61,62,66], the entire set of reversible reactions leading to the formation of the complexes $M_qH_kA_x(OH)_y \cdot (H_2O)_z^{(qm+k-bx-y)+}$ (oxidised state) and $M_pH_lA_u(OH)_v \cdot (H_2O)_w^{[p(m-n)+l-bu-v]+}$ (reduced state) was taken into account. It is assumed that complexes are formed in aqueous solution of an acid H_bA, with a constant ionic strength, as a result of the substitution by the acido-ligand $H_{b-s}A^{s-}$ of the water molecules coordinated in the aquo-complexes of M^{m+} and $M^{(m-n)+}$, polymerisation, and protolytic reactions including the hydrolysis and protolytic dissociation of the acid and the protonated complexes. The state of the system is described by the equation for the oxidation potential of the type[7]:

$$\varphi = \varphi^0 + \frac{\vartheta}{n}\lg\frac{c_o}{c_r} + \frac{\vartheta}{n}\lg\sum_{p=1}^{P}\sum_{u=0}^{U}\sum_{s=b}^{Bu}\sum_{v=0}^{V} p\,(\beta_{puvl}^{(r)})^{1/p}\,\rho_{puvl}^{(p-1)/p}\,(B_b^{(a)})^{u/p}\times$$
$$\times\, c_a^{u/p} h^{(l-v)/p}\mathcal{H}^{u/p} - \frac{\vartheta}{n}\lg\sum_{q=1}^{Q}\sum_{x=0}^{X}\sum_{s=b}^{Bx}\sum_{y=0}^{Y} q\times \qquad (13)$$
$$\times\,(\beta_{qxyk}^{(o)})^{1/q}\,\omega_{qxyk}^{(q-1)/q}\,(B_b^{(a)})^{x/q}\,c_a^{x/q}h^{(k-y)/q}\mathcal{H}^{-x/q},$$

where β are the overall stability constants of the complexes, $B_s^{(a)}$ and $B_b^{(a)}$ are the overall sth and bth protolytic dissociation constants of the acid, c_a is the overall concentration of the acid, c_o and c_r are the overall concentrations of the complexes including the aquo-complexes, in the oxidised and reduced states respectively, ω and ρ are the concentrations of the complexes, the superscripts o and r show that the given quantities refer to the oxidised and reduced states, while the subscripts $qxyk$ and $puvl$ indicate the compositions of the complexes. The influence of the protolytic dissociation of the acid on the oxidation potential is taken into account by the multiplier

$$\mathcal{H} = \sum_{s=0}^{b} h^{b-s}B_s^{(a)}.$$

It follows from Eqn.(13) that the oxidation potential is a function of four independent variables: h, c_a, c_o, and c_r. In the study of complex formation in mixed solvents and concentrated aqueous solutions, where the activity of water can vary appreciably, this quantity must be introduced into the equation for the oxidation potential.

The partial relations of the oxidation potential, i.e. its dependence on each independent concentration variable while the others are kept constant, are described by curves consisting of linear sections connected by smooth bends. The establishment of a linear section is possible only when complexes of a specific composition, in the oxidised and the reduced states, predominate.

The composition of the complexes, i.e. the sets of values of q, k, x, y and p, l, u, v, are determined by the successive inspection of the curves for all the partial relations of the oxidation potential, starting with the initial linear section of zero slope for each curve, indicating the presence in the system of aquo-complexes alone, or with the section for which the composition of the complexes is known. The slopes of the linear sections and the changes in them serve as a source of the required information.

The nuclearity of the complexes is determined from the slopes of the linear sections of the partial relations $\phi = \phi(pc_o)$ and $\phi = \phi(pc_r)$, since

$$\left(\frac{\partial\varphi}{\partial\, p\, c_o}\right)_{p\,c_r,\,p\,c_a,\,pH} = -\frac{\vartheta}{nq}, \qquad (14)$$

$$\left(\frac{\partial\varphi}{\partial\, p\, c_r}\right)_{p\,c_o,\,p\,c_a,\,pH} = \frac{\vartheta}{np}. \qquad (15)$$

The number of groups A^{b-} in the complexes can be found from the slope of the curve for the partial relation $\phi = \phi(pc_a)$, because

$$\left(\frac{\partial\varphi}{\partial\, p\, c_a}\right)_{p\,c_o,\,p\,c_r,\,pH} = \frac{\vartheta}{n}\left(\frac{x}{q} - \frac{u}{p}\right). \qquad (16)$$

The nuclearity (the numbers q and p) and the number of the groups A^{b-} in the complexes (the numbers x and u) can be determined fairly reliably and simply.

The $\phi = \phi$ (pH) curve depends in the general case on the activity of hydrogen ions in a complex manner. Owing to the protolytic dissociation of the acid, linear sections may not appear, or their slopes can be distorted, since

$$\left(\frac{\partial\varphi}{\partial\,pH}\right)_{p\,c_o,\,p\,c_r,\,p\,c_a} = -\frac{\vartheta}{n}\left[\frac{l-v}{p} - \frac{k-y}{q} + \left(\frac{u}{p} - \frac{x}{q}\right)\sum_{s=0}^{b}(b-s)\,h^{b-s}B_s^{(a)}/\mathcal{H}\right]. \qquad (17)$$

The differences k–y and l–v in such systems can be determined with the aid of Eqns.(17) by substituting in the latter the values of the derivative found graphically at selected points. In the analysis of the $\phi = \phi$ (pH) curves one must take into account the intramolecular neutralisation reactions[7], because the differences $k-y$ and $l-v$ indicate either the basicity of the complex, when $k > y$, and $l > v$, or the number of its OH groups, when $y > k$ and $v > l$. Intramolecular neutralisation reactions apparently involve proton transfer from the protonated ligand to the OH group with conversion of the latter into a water molecule. The proton transfer is facilitated by the presence of intramolecular hydrogen bonds in the complex.

Complex formation in oxidation–reduction systems containing metal ions in two oxidation states and two different ligands—the anions of the acids H_bA and $H_\beta L$, includes competitive and mixed complex formation and hydrolysis. The oxidation potential becomes a function of five independent concentration variables, including the overall concentrations of the two acids c_a and c_α:[67]

$$\varphi = \varphi^0(c_o,\, c_r,\, c_a,\, c_\alpha,\, h). \qquad (18)$$

Analysis of Eqn.(18) together with the study of the characteristics of the mixed complex formation made it possible to determine the conditions under which a quantitative investigation of the formation of simple and mixed complexes becomes possible.

The formation of heteropolynuclear complexes containing the ions of two metals is no less complex. A thermodynamic description of heteropolynuclear complex formation has been

achieved in relation to the Fe(III)–F(II)–M(III) system in an aqueous solution of an acid HA, where M(III) is not involved in oxidation–reduction interactions with bivalent and tervalent iron[7,68].

The equation of the oxidation potential expresses the dependence of the latter on five independent variables, namely the overall concentrations of tervalent and bivalent iron, the ions of the metal M(III) and the acid HA, as well as the activity of hydrogen ions. The slopes of the linear sections of the partial relations $\phi = \phi(pc_O)$ and $\phi = \phi(pM)$ make it possible to determine the nuclearity of the heteropolynuclear complex with respect to Fe(III) and M(III) respectively. Information about the number of anions A and hydroxy-groups in the heteropolynuclear complex can be obtained with the aid of partial relations between the oxidation potential and pc_a and pH subject to the condition that the composition of the coexisting complex of the M(III) ion is known.

The reactions involving the formation of complexes in heterogeneous oxidation–reduction systems metal ion (solution)–metal[7,69] and complex formation with ligands constituting an oxidation–reduction system[7,70] have also been examined theoretically.

In oxidation–reduction measurements the necessary condition for the determination of the composition and stability constants of ionic and molecular forms of the oxidation–reduction system is the validity of Eqn.(6) for all the types of species whose concentrations vary in the solution composition ranges investigated. This is usually achieved either by employing fairly dilute solutions with respect to electrolytes at a constant ionic strength or by using a constant and high concentration of a supporting salt, which is an indifferent and strong electrolyte, for example, sodium or lithium perchlorates, etc.

In the latter case the compositions of the complexes are determined without taking into account their association with the cation or anion of the supporting salt. The study of the association of the components of an oxidation–reduction system with the ions of the supporting salt therefore constitutes an independent problem, the solution of which must be obtained at a variable ionic strength. A method has been developed for the investigation of complex formation (ionic association) between ferrocenium cations and Cl^- and ClO_4^- anions, under conditions where the concentration of the main electrolyte (HCl, $HClO_4$) varies within wide limits (0.01–3 M).[71]

A characteristic feature of the method is that the concentration variable employed is a function of the concentration of the acid and the mean activity coefficient of the main electrolyte ($\lg c_a$, $\lg c_a y_\pm$, or $\lg c_a y_\pm^2$) such that the effects of the "non-ideality" of the test system are compensated to the maximum extent in the partial derivative of the oxidation potential. The study of the complex-forming capacity of the ferrocenium nucleus in relation to the Cl^-, SCN^-, ClO_4^-, SO_4^{2-}, NO_3^-, and Br^- ions by various methods[7,72–74] confirmed the reliability of the proposed procedure.

By analogy with the oxidation voltage [Eqn.(11)], the following quantity was introduced[7]:

$$\mathscr{E}_A = \varphi + \vartheta \lg[A]. \qquad (19)$$

The quantity $\mathscr{E}_A$, called the oxidation voltage on the ligand scale, is numerically equal to the e.m.f. of a galvanic cell consisting of an oxidation–reduction half-cell and a half-cell reversible with respect to the anion A. The properties of the partial relation $\mathscr{E}_A = \mathscr{E}_A(pH)$ resemble those of the oxidation voltage. The use of the oxidation voltage on the ligand scale is limited by the restricted set of reversible electrodes. The complex formation reactions in the Fe(III)–Fe(II)–HCl–water system have been investigated with the aid of the function $\mathscr{E}_A$.[75–77]

The stability and hydrolysis constants in relatively simple systems are determined graphically or by simple computational methods[7]. A quantitative description of the chemical interactions, leading to the formation of complex compounds having an involved composition and frequently present simultaneously, is achieved with the aid of computers[7,72–82]. In this case the stability constants of the complexes are regarded as parameters of a regression relation, which is expressed by the equation of the oxidation potential [Eqn.(13)]. The above parameters are found by the method of least squares using a program for the direct minimisation of the sum of squares of deviations of the experimental oxidation potentials from the theoretical values. A combination of random search and coordinate-by-coordinate procedures is useful as a minimisation method.

The set of complexes which is sufficient for the description of all the partial relations between the oxidation potential and independent concentration variables, i.e. the entire set of experimental data, can be refined by comparing the content of a particular complex and the overall error referred to as the limit of sensitivity[7,78]:

$$\delta = |10^{\pm n\tau/\vartheta} - 1| \cdot 100\%, \qquad (20)$$

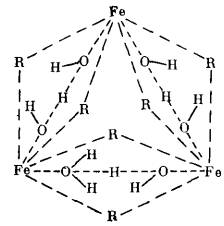
where τ is the accuracy of the potentiometric measurements. If the maximum content of the complex is less than δ, then its presence is undetectable and it can be disregarded. In general, one should bear in mind that the set of the stability constants of complexes obtained with the aid of the most sophisticated programs can be regarded as compatible with the available experimental data.

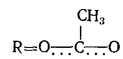
The experimental study of complex formation in systems formed by metals in two oxidation states and various ligands promoted the development of a theory of oxidation–reduction measurements and the elucidation of the fundamental characteristics of the reactions occurring in inorganic–reduction systems.

The complex formation reactions have been studied in particular detail in the Fe(III)–Fe(II) system in aqueous solutions of aliphatic acids (in the formic acid–valeric acid series), chloroacetic, aminoacetic, and hydroxyacetic acids, acrylic acid[7,19,21,65,83–106], dibasic aliphatic acids[107–110], aromatic acids[111–115], and strong inorganic acids (hydrochloric and sulphuric)[75–77,116]. The iron complexes were studied in aqueous solutions containing the anions of two acids (acetate ions and those of salicylic and sulphosalicylic acids or thiocyanate ions, ethylenediaminetetraacetate anions, and thiocyanate ions)[72,73,117–121]. The hydrolysis of tervalent iron has been studied in detail[122–128]. The formation of heteropolynuclear hydroxoacetato-complexes of tervalent iron and chromium has been investigated in aqueous acetic acid solutions[129–134].

Appropriate treatment of the experimental data made it possible to obtain the quantitative characteristics of the reversible complex formation reactions which include information about the compositions of the complexes, their stability constants, and the regions where they exist. The influence of temperature and ionic strength on the above characteristics was investigated for the Fe(III)–Fe(II) system in aqueous solutions of acids in the formic acid–valeric acid series[89,90,92] and in perchloric acid (hydrolytic reactions)[124,128]. The thermodynamic formation functions of the complexes of bivalent and tervalent iron were found from the results of these investigations by the temperature coefficient method. Direct calorimetric determinations of the enthalpy of formation were carried out for a number of complexes[85] by thermodynamic titration[135].

The quantitative study of the reversible formation of complexes of bivalent and tervalent iron in aqueous solutions has led to the following conclusions. The stability of the complexes increases with increase of temperature, ionic strength, and acid concentration. These factors are manifested particularly clearly in the case of the trinuclear complex having the composition $Fe_3A_6(OH)_2^+$, which predominates over a wide range of compositions; this has been explained by the conversion of the complex into a cyclic structure as a result of ring closure by linkages between coordinated aliphatic acid anions via iron atoms[7]:

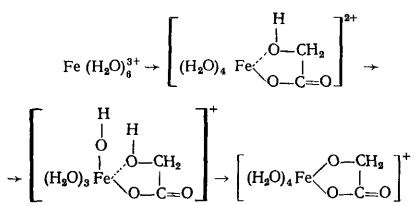




(21)

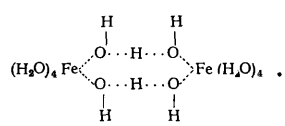
The cyclic structure is supported by the thermodynamic functions for the formation of the above complex and the ease with which it is converted into mono- and di-nuclear complex species and is formed from them. On crystallisation, structure (21) is apparently converted into an Orgel structure[136], according to which three metal atoms are combined via a single oxide ion and the formula $M_3OA_6(H_2O)_3^+$ must therefore be attributed to the complex.

Protolytic processes determine the characteristics of the complex formation in solutions of acids containing two and more protogenic groups. The deprotonation of the alcoholic group in the coordinated ligands (hydroxyacid anions) is due to the weakening of the O–H bond as a result of the polarising effect of the metal atom and, what is most important, as a result of the intramolecular neutralisation reaction. Here one takes into account the fact that the hydroxy-group is coordinated via the oxygen in the deprotonated state and its dissociation strengthens the corresponding chelate. In conformity with the hypothesis of the intramolecular neutralisation reaction, the formation of the deprotonated iron(III) glycolate complex FeA^+ can be represented by the following scheme[106]:



(22)

The formation of hydroxo-complexes of tervalent iron is promoted by the increase of the concentration of metal ions, temperature, and the concentration of the supporting electrolyte. It is suggested that iron(III) ions in the complex are linked via OH groups and water molecules[128]:



(23)

Hydrolysis and complex formation are in general competing processes. In solutions of weak monobasic organic acids, mixed di- and tri-nuclear complexes incorporating the OH group are formed.

New results have been obtained in a study designed to discover chemical interactions by oxidation–reduction measurements in Ce(IV)–Ce(III) systems[137,138] and in the heterogeneous cadmium ion–cadmium amalgam[69,78,81,139] and indium ion–indium amalgam[140] systems. The influence of the relatively unstable species on the nature of the partial relations of the oxidation potential has been demonstrated for these systems and those mentioned above. The study of the cadmium ion–cadmium system is of fundamental importance, since it confirmed experimentally the applicability of oxidation–reduction measurements in the study of chemical interactions in heterogeneous oxidation–reduction systems and hence greatly extended the scope of such measurements.

Complex formation with ligands constituting an oxidation–reduction system was first investigated for the Alizarin C–leuco-Alizarin C–M(III) systems (M = Al, Ga, or In).[141–143] Joint consideration of the partial relations between the oxidation potential and the concentration parameters together with the results of a spectrophotometric study made it possible to establish the sequence of reversible processes occurring in the system and to determine the compositions of the Alizarinate and leuco-Alizarinate complexes, their stability constants, and the protolytic dissociation constants of the ligands in the coordinated state. The acid properties of the latter are enhanced owing to the polarising influence of the metal atom.

VII. REDOXITES

By a redoxite we understand a homogeneous variable-composition phase whose components form a reversible oxidation–reduction system and can be involved in reversible oxidation–reduction interaction with aqueous solutions and oxidation–reduction systems[7]. It is necessary that, when the redoxite comes into contact with aqueous electrolyte solutions, its oxidised and reduced forms should not dissolve appreciably in the aqueous phase.

It is possible to distinguish three classes of redoxites: redox polymers[144,145]; ion exchangers saturated by variable-valence metals[146,147]; solutions of hydrophobic oxidation–reduction systems in solvents immiscible with water–liquid redoxites[7]. The properties of liquid redoxites have been studied mainly by Nikol'skii's school.

A characteristic feature of liquid redoxites is that the equilibrium between the redoxite and the aqueous solution is established rapidly, the measurement of the oxidation potential does not require the introduction of a mediator into the equilibrium aqueous solution[148], and the measurements of the potentials themselves are carried out using an indifferent electrode in the redoxite phase[149]. Under the conditions of the redoxite–aquoues solution phase equilibrium and when fairly dilute aqueous solutions are used, the chemical potentials of water and the non-aqueous solvent hardly change under isothermal-isobaric conditions. Therefore, in the determination of the state of the components of the oxidation–reduction system in the redoxite phase the involvement of the solvent species and water in the corresponding processes is not observed. The relation between the composition of the phases of the heterogeneous redoxite–aqueous solution system and the oxidation potential of the redoxite has been studied theoretically using as the independent variables the concentrations of the substances in the phase where they are largely concentrated[150–153]. This choice of

variables makes it possible to characterise the phase compositions solely in terms of the macrocomponents, which significantly facilitates the experimental study and the oxidation–reduction reaction consequently involves extraction of substances from one phase to the other.

It has been shown experimentally[154,155] and proved theoretically[7,156] that a fundamental characteristic of liquid redoxites is that it is always possible to specify a region in the aqueous solution where an indifferent electrode combined with the redoxite phase constitutes an ion-selective electrode for one of the ions of the aqueous solution. Borate[157], perchlorate[158], bromide, and iodide[159] ion-selective electrodes have been proposed on the basis of redoxites.

The oxidation–reduction and other properties of redoxites have been studied in greatest detail on the basis of the following reversible oxidation–reduction systems: (a) alkylferrocene–alkylferrocenium[7,149]; (b) quinone–hydroquinone and their derivatives[160]; (c) Alizarin–leuco-Alizarin[154,161]; (d) Nile Blue–leuco-Nile Blue[162]. In the determination of the state of the components of the oxidation–reduction system in the redoxite phase, it was found that 1:1 and 1:2 ionic association reactions between the ferrocenium cation and anions develop in system (a) and that protolytic dissociation coupled with the formation of ionic associated species with the cations of quaternary ammonium bases takes place in systems (b) and (c).

The study of solid redoxites is complicated by the low rate of the oxidation–reduction reaction between the redoxite and aqueous solution[144]. It has been found that protolytic and ion-exchange processes involving the redoxite are fairly rapid and their study is therefore not difficult, provided that electron exchange equilibrium has been established beforehand in the redoxite–solution system[163]. This permitted extensive experimental studies on redoxites of the phenothiazine type on the basis of polyene fibres[163–168]. The representation of the experimental data by the dependence of the oxidation potential of the redoxite on the pH makes it possible to find separately the number of protogenic groups due to the dye- and leuco-dye in the redoxite and to determine their dissociation constants. On the basis of the proton-donating groups manifested, it is possible to discover whether the bond formed by the dye and the leuco-dye is chemical or covalent[164]. The relation between the oxidation–reduction and protolytic properties of redoxites has been proved theoretically[150].

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