Translated from *Uspekhi Khimii*, **51** 968 - 989 (1982) U.D.C. 543.253:542.97:541.427.2

Catalytic Polarographic Currents of Oxidants

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The state of the theory and practice in an important field of polarography—the catalytic currents of oxidant-substrates—is examined. It has found extensive applications in the last ten years in the development of highly sensitive methods for the determination of a large number of substrates, catalysts, and polarographically inactive ligands. Attention has been given to the problem of the electrocatalytic reduction of molecular nitrogen for its fixation under mild conditions.
A systematic account is given of data for a series of inorganic and organic substrates and catalysts which transfer an electron to the substrate.
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I. INTRODUCTION

Catalytic currents in polarography, due to the regeneration of the depolariser via a chemical reaction, still attract much attention, mainly because they make it possible to increase appreciably the sensitivity of the analytical method and permit the determination of electrochemically inactive substances. However, the importance of catalytic currents goes beyond the analytical applications of polarography. In essence, these phenomena constitute the basis of the coulometric titration method and electrochemical synthetic processes with participation of electron transferring agents[1].

It is very likely that the fixation of atmospheric nitrogen, occurring in plant cells with participation of specific metal-containing enzymes[2,3], as well as many oxidation-reduction reactions constituting the basis of respiration, oxidative phosphorylation, and other processes important to life also occur under the conditions of the catalytic action of micro-elements. For this reason, examination of the available data on the mechanism of the occurrence of catalytic phenomena in polarography, to which this review is devoted, may be of general interest.

The review deals mainly with the reduction of a substrate by variable oxidation state metals; catalytic systems involving the oxidation of the substrate as well as catalysis by ligands (the complex is reduced or oxidised more readily than the aquo-ions) and the catalytic evolution of hydrogen are not discussed, because these two cases have been described quite adequately in other reviews[4,5] and monographs[6,7].

Catalytic currents of the type considered are manifested on polarograms as a rule by an increase of one of the diffusion waves of the catalyst metal and only in systems with hydrogen peroxide as the substrate does a separate reduction wave of the metal peroxide appear.

In the simplest case the mechanism of generation of the catalytic current can be represented schematically as follows:

$$\begin{array}{l} A + ne \rightarrow B \\ \uparrow\!\!_____| \\ B + S \xrightarrow{k} A \end{array} \quad , \qquad (1) \quad (2)$$

where A is the depolariser (the oxidised form of the catalyst), B the reduced form of the catalyst, and S the reagent (substrate or oxidant-substrate) participating in the chemical depolariser regeneration reaction. The catalytic current is determined by the rate of chemical reaction (2).

For a quantitative description of the catalytic currents arising via this scheme, an approximate solution was proposed initially[8,9] and then an exact solution[10], both based on the concept that the chemical depolariser regeneration reaction occurs in a thin layer of solution adjoining the electrode in the presence of an excess of the substrate.

When the reverse reaction (2) is neglected and when $k[S]_0\tau > 10$, the exact solution leads to the asymptotic equation

$$\bar{i}_c/\bar{i}_d = 0.81(k[S]_0\tau)^{1/2} , \qquad (3)$$

in which $\bar{i}_c$ is the average limiting catalytic current, $\bar{i}_d$ the average limiting diffusion current of the catalyst metal, k the rate constant for the forward reaction (2), $[S]_0$ the substrate concentration, and τ the drop period. The expression in square brackets in Eqn.(3) includes the stoichiometric coefficients, which depend on the nature of reaction (2).

A number of reviews have been devoted to the state of the theory and applications of catalytic polarographic currents[4,11-19], but examination of the literature shows that many important factors are still not clear. In particular, the causes of the differences between the rates of reduction of the substrate directly at the electrode and by reaction (2) have not been altogether elucidated. Andrieux et al.[20] considered the quantum-mechanical approach of Hush and Marcus to the relation between the rates of electronic transitions in the heterogeneous and homogeneous reactions. Attention has also been drawn[21] to the electrostatic factor, which increases the rate of interaction of the substrate and catalyst bearing different charges.

Studies have appeared in recent years in which the generation of the catalytic currents of the substrates is attributed to the formation of a complex BS and to electron transfer within the complex from the reduced form of the catalyst to the substrate. Such a mechanism has been proposed for both inorganic catalysts [W(VI)–ClO_3^- [22] and Mo(VI)–ClO_3^-–mandelic acid[23] systems] and for organic catalysts (dithiocarbamate–IO_3^-,[24] haemoglobin–H_2O_2, and iron(III) phthalocyaninetetrasulphonate–O_2 [25] systems), as well as for organic substrates in the Y(III)–L–dimethylformamide (DMF) system[26], which consist of carbonyl compounds: benzophenone, benzaldehyde, and crotonaldehyde.

The so-called coordination mechanism of the generation of catalytic currents has been proposed[16,17,27-30] and developed:

$$\begin{array}{l} A + n_1e \rightarrow B \ , \\ B + S \xrightarrow{k} BS \ , \\ \uparrow\!\!_____| \\ BS + n_2e \rightarrow B + P \ . \end{array} \qquad (4)$$

According to this mechanism the catalyst does not transfer electrons from the electrode to the substrate but merely activates the latter, increasing its reactivity in relation to reduction at the cathode. An equation has been derived for the description of the proposed mechanism[16,27-30]; despite the fundamental difference between the mechanisms, its form is close to that of Eqn.(3).

In order to account for the appreciable change in the catalytic current after the introduction of complex-forming substances into the solution, the formation of a ternary complex of the type BLS has been assumed in the last two concepts. One cannot rule out also another interpretation of this effect. Complex formation frequently accelerates electrochemical reaction (1) in both directions, so that irreversible reactions can actually become reversible. This should lead, in principle, to the acceleration of the homogeneous reaction (2) also.

Electron exchange within the complex is a reasonable alternative to the simple mechanism based on reactions (1) and (2), but we believe that the arguments adduced in its support in relation to the coordination mechanism are weak. Firstly, there is no direct evidence for the reduction of the substrate within the complex at the electrode. Secondly, the majority of substrates interact too weakly with the complex-forming metal to undergo an appreciable alteration in their reactivity. Nor is it clear why the interaction precisely with the reduced form of the catalyst are not with the initial, oxidised form is important for the generation of catalytic currents. Nevertheless, the coordination mechanism does not lack internal logic. Formally, systems with hydrogen peroxide behave seemingly in conformity with the coordination scheme: the metal peroxide compounds are reduced at the electrode.

An invariable condition for the appearance of the catalytic current of the substrate is its high electrochemical overvoltage. Many organic compounds do not exhibit a catalytic effect[21], because the electron transfer stage is in the vast majority of cases rapid (without overvoltage); on the other hand, the reason for the general irreversibility of the reduction of organic compounds is the occurrence of consecutive chemical reactions leading to the formation of covalent, inert C–H, C–C, etc. bonds. In such cases a significant increase of electron transfer to the substrate, with participation of the catalyst acting as an electron transferring agent, is impossible. The catalytic effect in polarography can be produced only by compounds in the electrochemical reduction of which the electron transfer stage is in fact slow. The reduction of the substrate can be accelerated by catalysts with a fairly high reduction potential and the necessary structure. The catalysts (among inorganic substances, these are usually transition metals) exist in aqueous solution in the form of monomeric or polymeric forms with different degrees of hydrolysis, depending on the conditions[31-35]. The activity of the catalyst depends on its state[36-39].

The wide variety of forms of the catalysts and the relatively few substrates make it possible to arrange the available literature data in terms of the nature of the oxidant-substrate.

II. CATALYTIC CURRENTS OF OXIDANTS

1. Catalytic Currents of Hydrogen Peroxide

The catalytic currents of H_2O_2 for the first row of transition metals are represented by the following systems: Ti(IV)–H_2O_2 and Ti(IV)–H_2O_2–L, where L = EDTA, nitrilo- triacetate (NTA), sulphosalicylate (SAL), and 4-(2-pyridylazo)-resorcinol (PAR);[40,41] V(V)–H_2O_2–H_2SO_4,[42] Fe(III)– H_2O_2–H_2SO_4,[43-52] and Fe(III)–H_2O_2–L, where L = bis-salicylidene-ethylenediamine and triethanolamine[53]; Cu(II)–H_2O_2–L, where L = Cl^- and α,α′-bipyridyl[54,55]. The second row of transition metals is represented by the first three numbers: Zr(IV)–H_2O_2,[56] Nb(V)–H_2O_2,[57] Nb(V)–H_2O_2–$H_2C_2O_4$,[58] and Mo(VI)–H_2O_2–L, where L = H_2SO_4 or acetate, phosphate, and hydrogen phthalate buffer mixtures[42,59,60]. The third row of transition metals is represented by the systems Hf(IV)–H_2O_2,[61] Ta(V)–H_2O_2–$H_2C_2O_4$,[62,63] and W(VI)–H_2O_2–L, where L = H_2SO_4, $H_2C_2O_4$, H_3PO_4, and H_3AsO_4,[42,64] and the Os(VIII)–H_2O_2 system[65]. The H_2O_2 catalytic reduction wave has also been observed for La(III).[66]

When the above transition metals are introduced into an aqueous solution of hydrogen peroxide, a catalytic wave appears on the polarogram whose height greatly exceeds the diffusion current of the metal and which is located at more negative potentials than the non-catalytic reduction wave of hydrogen peroxide and the transition metal. Os(VIII), for which the H_2O_2 catalytic wave coincides with its first two-electron reduction wave, is an exception[65]. The H_2O_2 catalytic wave has the form of a sharp or smooth peak, which is not due to adsorption effects, since the introduction of surfactants into the system does not cause the disappearance of the maximum in the polarographic wave[42,61]. The catalytic wave has the normal form without a maximum only for the Fe–H_2O_2 system[45-50]. Therefore the assignment of the M–H_2O_2 systems[67] to the group with a normal form of the limiting catalytic current plateau is incorrect.

A test of Koutecky's theory[10] in relation to the catalytic currents of the Fe(III)–H_2O_2 system demonstrated its validity[46]. The catalytic process in this system is described by the Haber–Weiss scheme[68] in which the rate-limiting stage involves the oxidation of Fe(II) to Fe(III) by hydrogen peroxide with formation of OH· radicals, which also oxidise Fe(II). Subsequently, this mechanism was confirmed also in relation to sulphuric and nitric acid solutions[69]. The presence of OH· radicals in the system was demonstrated by numerous instances of the decrease of the catalytic current in the presence of various organic substances[45,52] and monomers[70-72] which react with OH·.

In order to explain the catalytic H_2O_2 reduction currents in sulphuric acid solutions of the Fe(III)–H_2O_2–L system, investigators[48-50,53] proposed a coordination mechanism of their generation consisting in the fact that the iron(II) obtained at the electrode forms with H_2O_2 or HO_2^- the intermediate complex $[Fe(H_2O)_5(HO_2^-)]^+$, which is rapidly converted into $[Fe(H_2O)_5O]^{2+}$ and the latter is reduced at the electrode with regeneration of the Fe(II) aquo-ion. The slow stage of the process is the formation of the intermediate complex $[Fe(H_2O)_5O]^{2+}$, which is identical with the ferryl ion FeO^{2+}; this complex has properties analogous to those of the OH· radical. As already mentioned, the authors do not present direct evidence for the reduction of the oxygen atom (hydrogen peroxide) in $[Fe(H_2O)_5O]^{2+}$.

Titanium(IV) catalyses the reduction of H_2O_2 but at higher pH values than many other multicharged ions, even when a graphite rotating electrode is used[40]. The catalytic current in the Ti(IV)–H_2O_2 system is described by Koutecky's theory and is limited by the formation of $TiO(H_2O_2)^{2+}$ and the two-electron reduction at the electrode at pH 2–4 of the complex $[TiO(HO_2)]^+$, whose yield increases with pH as a consequence of the increase of the degree of acid dissociation of $TiO(H_2O_2)^{2+}$. The current i_c depends on the nature of the ligand: the presence of EDTA, SAL, and NTA increases i_c, while the addition of PAR decreases it.

The activating effect of ligands is due to the formation of Ti(IV) complexes, which react with hydrogen peroxide faster than the TiO^{2+} aquo-ions[40]. The catalytic activities of ligands increase in the sequence SAL < NTA < EDTA, which can be accounted for by the increasing stability of the complexes formed. Other metals of the titanium subgroup (zirconium[56] and hafnium[61]) catalyse the reduction of H_2O_2; the ease of reduction increases in the sequence Ti < Hf < Zr. As for titanium[40], the catalytic current is limited by the rate of formation of the intermediate complex between zirconyl[56] or hafnyl[61] and hydrogen peroxide. The current i_c in Zr(IV) and Hf(IV) solutions has a maximum (at pH 2.0 and 2.6) under the conditions of the maximum yield of the most active zirconyl or hafnyl ions[73].

Vanadium subgroup metals (vanadium, niobium, and tantalum) are readily hydrolysed[34] and tend to form many peroxide complexes[74] with different catalytic activities. The catalytic currents of the above elements are limited by the rate of formation of the peroxide compound. The vandium(V) peroxide compounds contain between one and four $H_2O_2(O_2^{2-})$ molecules[75]. The catalytic waves of vanadium, niobium, and tantalum have the form of a peak and are observed at less negative potentials than the waves due to metals and the non-catalytic reduction of H_2O_2; $E_{1/2}$ depends on the pH. As was to be expected, there is a complex dependence of i_c on the pH; the catalytic current has a maximum at the following pH:

Element	V(V)	Nb(V)	Ta(V)
pH	5.0	5.2	6.2

This behaviour of i_c for V(V) has been attributed[42] to the presence of its polymeric forms, which manifest different activities, and for Nb(V) and Ta(V) by the change in the composition of their peroxide compounds[56]. Since the vanadium(V) concentration in the above study[42] was very low (8×10^{-8} M), the maximum on the i_c–pH curve is most probably due to the presence in solution of various hydrolysed monomeric forms of vanadium(V) and not polymeric forms. In the presence of oxalic acid, the Nb(V) [58] and Ta(V) [62,63] electrode processes are limited by the formation of the peroxide compound $HMO_3.C_2O_4$, which is reduced to $HMO_2.C_2O_4$ (where M = Nb or Ca) with participation of two electrons.

The Cr(III)/Cr(II), Mo(VI)/Mo(V), Mo(V)/Mo(III), W(VI)/W(V), and U(IV)/U(III) systems, which possess reducing properties, are of greatest interest for the investigation of the catalytic currents of substrates in the presence of chromium subgroup elements (Cr, Mo, W and U). The H_2O_2 catalytic currents are known only for the Mo(VI)–H_2O [45,59] and W(VI)–H_2O_2 [45] systems. The formation of monomeric and polymeric forms of Mo(VI) [31,33,76,77] and W(VI) [31,33,78] in solution as well as a number of peroxides[76, 78,79] and complex compounds having different compositions are responsible for the complex form of the dependence of i_c on the pH and the catalyst concentration. The presence of a maximum on the i_c–pH curve[45], the dependence of its position and intensity on the nature of the buffer solution[45], the presence of a maximum on the i_c–c_{buff} curve for the phosphate buffer solution at pH 4.0,[59] and the decrease of i_c on passing from $HClO_4$ to H_3PO_4 solutions[45] have been explained on the basis of these ideas. The decrease of i_c in the phosphate buffer solution at pH 4.9 [45] on passing from vanadium to tungsten has likewise been accounted for from this standpoint.

The rate-limiting stage is the formation of the peroxide compound, which is reduced with participation of two electrons. The attempt[45] to explain the dependence of i_c on the pH by the presence of different polymeric forms reacting with H_2O_2 at different rates is in our view incorrect, since the Mo(VI) concentration was so low (3.2×10^{-6} M) that Mo(VI) was present only in the monomeric form[33,76]. The dependence of i_c on the pH is therefore associated with the presence of its different hydrolysed forms interacting with H_2O_2 at different rates.

In the manganese subgroup (Mn, Te, and Re) a catalytic H_2O_2 polarographic reduction wave is observed only for Te.[80] It is believed that in the homogeneous catalytic reaction the H_2O_2 oxidises the Te(V) formed to Te(VII).

The metals of the platinum subgroup (Ru, Rh, Pd, Os, Ir, and Pt) are characterised by a high oxidation potential and and extremely high capacity for hydrolysis and complex formation[31,79,81–84], which complicates the observation of the H_2O_2 catalytic currents. Ruthenium(VIII) is a stronger oxidant than osmium(VIII),[85] so that, in contrast to OsO_4, RuO_4 cannot give rise to H_2O_2 catalytic waves. The aquo- and hydroxo-complexes of certain platinum subgroup metals, for example Rh(III) and Ru(IV) (Ginzburg et al.[84] p.99) are extremely inert in processes involving the substitution of water molecules in the inner sphere of the ion by other ligands, which is probably the reason for the small number of examples of catalytic currents in platinum metal–oxidant systems; only two such examples are known: Os(VIII)–H_2O_2 [65,86] and Ru(III)–NH_2OH.[87]

The H_2O_2 catalytic wave in osmium(VIII) solutions[65,86] is observed in the positive range of potentials; with increase of $c_{H_2O_2}$, the current i_c passes through a maximum. The electrode process is determined by the rate of oxidation of Os(VI) to Os(VIII).[65] In unbuffered solutions this process may be limited by the formation of the peroxide compound $OsO_4.H_2O_2$.[86]

The metals of the copper subgroup (Cu, Ag, and Au) exhibit a considerable tendency towards complex formation. Ag(II), Ag(III), and Au(III) compounds show no catalytic activity with respect to the electrochemical reduction of H_2O_2, which can be explained by their high oxidising capacity. The high rate of exchange of water molecules in the first coordination sphere ($k = 8 \times 10^9$ s^{-1}) of copper(II) aquo-complexes (Basolo and Pearson[35], p.138) favours the generation of the catalytic currents of the substrate. The catalytic wave in the Cu(II)–H_2O_2 system[54] at pH < 7 is located in the range of potentials of the first one-electron copper(II) reduction wave and is described by the Koutecky equation[10]. The rate-limiting stage is the oxidation of Cu(I) by hydrogen peroxide with formation of the initial depolariser and the OH· radical, the latter being consumed in the oxidation of Cu(I) and Cl^-.

In neutral unbuffered chloride media the catalytic wave incorporates both Cu(II) reduction waves[54], which is probably associated with a change in the composition of the layer near the electrode as a consequence of the oxidation of Cu(I). The possibility of the oxidation of the metallic copper formed under these conditions cannot be ruled out either.

In an acetate medium[55] the catalytic wave, having the form of a maximum, arises at potentials more positive (by 0.1 V) than the copper reduction wave (pH 4.6), while in the presence of α,α′-bipyridyl the catalytic wave coincides with the copper reduction wave. A coordination mechanism has been proposed (but not justified experimentally) for the catalytic currents in the systems investigated[55].

The catalytic H_2O_2 reduction current is observed in solutions of copper salts also in anodic processes. It has been found[87] that, at the potential of the anodic peak associated with the dissolution of the copper amalgam (at $E = -0.18$ V), a cathodic current maximum is observed in the presence of H_2O_2 or O_2, which is due to the fact that the catalytic H_2O_2 reduction current is much greater (by a factor of 10–15) than the anodic copper dissolution current. The catalytic reduction current is due to the oxidation of the Cu(I) formed

to Cu(II), which is reduced to Cu(I) at the amalgam dissolution potential. An analogous behaviour has been observed also for lead[87–89], the only representative of non-transition elements catalysing the reduction of H_2O_2. The electrode process generating the catalytic current includes the reaction where the pH(II) at the electrode is oxidised by hydrogen peroxide to Pb(IV), which is reduced electrochemically to Pb(II).[87] The catalytic H_2O_2 current is also observed in the reduction of oxygen at platinum[90] and gold[91] microelectrodes. The exaltation of the limiting current can be explained by the generation of oxygen as a result of the oxidation of the superoxide ion by hydrogen peroxide.

Thus the appearance of i_c in many systems is due to the formation of peroxo compounds (of Ti, V, Mo, W, Nb, Hf, Zr, and Ta) which are reduced at less negative potentials than the metal in the highest oxidation state. The rate-limiting stage is the formation of the peroxo-compound (complex). In many systems incorporating Cu and Pb hydrogen peroxide is reduced by the ion of the catalyst metal.

The catalytic H_2O_2 currents make it possible to detect very low concentrations of catalysts (from 1×10^{-5} to 1×10^{-9} M) and have found extensive applications in the determination of vanadium[42], iron[45,47,50], copper[55,87], zirconium[56], niobium[57,58], molybdenum in soils[59] and granits[60], hafnium[61], tantalum[57,62], tungsten[42], osmium[65,86], and technetium[79]. Molybdenum[92] and titanium[41] (using a graphite electrode), copper[87], lead[87, 89] (in combination with amalgam polarography), and oxygen (using a rotating platinum[90] or gold[91] microelectrode) can be determined with a high sensitivity (to within 1×10^{-6} M). The catalytic H_2O_2 currents have been used successfully also for the investigation of the complex formation reaction between tantalum and oxalic acid[62] and between tungsten(VI) and oxalic, phosphoric, and arsenic acids[64].

2. Catalytic Currents of Hydroxylamine

The oxidising properties of hydroxylamine[93,94] have also been used to obtain its catalytic reduction currents. The first row of transition elements is represented by the systems Ti(IV)–NH_2OH–$H_2C_2O_4$,[95] Ti(IV)–NX_2OH (where X = H or D),[96,97] V(V)–NH_2OH,[98] Fe(III)–NH_2OH–$N(CH_2CH_2OH)_3$,[99] Ni(II)–NH_2OH–CN,[100] and Ni(II)–$NH_2(CH_2)_2NH_2$–CN,[100] the second row is represented by the system Nb(V)–NH_2OH [101, 102] and Ru(III)–NH_2OH,[103] while among the third row elements there are literature data only for tungsten: W(VI)–NH_2OH [104] and W(VI)–NH_2OH–L, where L = ascorbic acid, salicylic acid, catechol[105–107], etc. In the case of titanium-containing systems the catalytic current is limited by the rate of oxidation of titanium(III) ions by hydroxylamine with formation of titanium(IV) and the $NH_2^{\cdot}$ radical and is described by Koutecky's theory[10]. This is proved by the agreement between the rate constants for the oxidation reaction obtained by chemical and polarographic methods. The oxidation rate constants have the following values: 42.0,[95] 41.3,[96] 42,[108] 32.0,[109] and 43.4 litre mol^{-1} s^{-1}.[110] The mechanism adopted is also supported by data for the synthesis of α-aminosuccinic acid from maleic acid under the conditions of electrochemical generation of $NH_2^{\cdot}$ radicals[111].

The catalytic reduction of hydroxylamine in the presence of vanadium(V) in solutions at pH 1–5 is represented by a wave at a potential ~0.3 V more negative than $E_{1/2}$ for the V(V) → V(IV) waves[98]. According to the authors[98], the slow stage of the process is the formation of a complex between polymeric vanadium(V) and NH_3^+OH; the complex $V(V)_n$.NH_2^+OH is then reduced to $V(V)_n$ and $NH_2^{\cdot}$. It is difficult to agree with this, since the concentration at the electrode of the V(V) not bound in the complex at the potentials of the catalytic wave is zero and the mechanism involving vanadium(V) is therefore altogether impossible. We believe that the regeneration of the depolariser is due to the oxidation by hydroxylamine of the V(IV) formed. The introduction of EDTA and *trans*-1,2-cyclohexylenediaminetetra-acetate into the solution reduces i_c as a consequence of the formation of catalytically inactive complexes.

In the presence of the second representative of the vanadium subgroup, namely niobium, the catalytic hydroxylamine waves are observed in hydrochloric acid solutions with high HCl concentrations[101,102], where the catalyst exists predominantly in the monomeric form, which exhibits a higher catalytic activity than the polymeric and colloidal species. The authors[101] explained the generation of the catalytic current in terms of a coordination mechanism in which the rate-limiting stage is the formation of the intermediate complex Nb(IV).NH_3^+OH, which is reduced to Nb(IV) and NH_4^+; proof that the complex Nb(IV).NH_3^+OH is reduced is not presented.

The catalytic hydroxylamine current in the Fe(III)–NH_2OH–$N(CH_3CH_2OH)$ system at the Fe(II) oxidation potential (–1.05 V relative to the saturated calomel electrode) has been studied in 0.01–4.0 M NaOH.[99] The rate-limiting stage is the oxidation-reduction reaction of Fe(II) with NH_2OH. The validity of the mechanism adopted is demonstrated by the agreement between the rate constants for the reaction obtained by the chemical and polarographic methods. At 25 °C in 1 M NaOH they are respectively 205 ± 25 [97] and 198 ± 8 litre mol^{-1} s^{-1}.[99]

The catalytic hydroxylamine current in the Ni–CN–NH_2OH system[100] in neutral and alkaline media can be accounted for by the involvement of Ni(I) and Ni(0). The current i_c is a maximum at pH 8.5–9.5. Under these conditions, the system contains an appreciable amount of the hydrolysed form $NiOH^+$ (pK_1 = 9–9.5).[33] We therefore believe that one cannot rule out the involvement of the above form also in the reactions determining the catalytic current. When hydroxylamine is replaced by ethylenediamine, a catalytic current is also observed, but is smaller[100]. Thus the complexes incorporating elements with the d^8 configuration, which are fairly inert in the ligand exchange reaction in conformity with the crystal field theory[35], exhibit a fairly high reactivity after the introduction of one or even two electrons. Among the elements of the platinum group, the catalytic hydroxylamine current is observed only in the presence of ruthenium(III) [103] and is due to the oxidation by hydroxylamine of the Ru(II) formed and is described by the Koutecky theory; the rate constant for the rate-limiting stage in this process is 3×10^3 litre mol^{-1} s^{-1}. Since the ruthenium(II) aquo-complexes are inert (Cotton and Wilkinson[31], p.42), their observed reactivity is probably associated with the formation of a mixed complex.

A distinctive feature of tungsten, the only representative of the third row of transition elements, is the presence on the polarograms of the test systems of two catalytic hydroxylamine waves and of the catalytic wave of hydrogen ions[104–107]; the authors explained the appearance of the catalytic hydroxylamine waves in terms of a coordination mechanism. The rate-limiting stage for the first catalytic wave is the conversion of the intermediate tungsten(V) complex H_2WO_4.NH_2OH into the activated complex H_2WO_4.NH_3O^-, while for the second catalytic wave the rate-limiting stage involves the conversion of the intermediate tungsten(III) complex HWO.L.NH_3OH^- into the activated complex HWOL.NH_3O.[105,106] The charge of the species involved in the rate-limiting stage was determined using the dependence of the rate of reaction (the current i_c) on the ionic strengths[112]. The authors[105,106] do not present direct evidence for the reduction of the above species. One cannot rule out the possibility that the observed complex pattern may be associated with the presence of polymeric

forms of tungsten in solution, since at the concentrations investigated (5×10^{-4} M) a considerable proportion of the tungsten exists in the polymeric form[78]. This is indicated indirectly also by the decrease of the number of catalytic waves with decrease of the W(VI) concentration[105,106].

The rate constants for oxidation reactions with participation of substrates calculated from their catalytic polarographic currents in the presence of various catalysts and ligands at 20–25 °C.

Catalytic system	Reaction conditions	k_{tot}, litre mol^{-1} s^{-1}	References
Fe(III)—H_2SO_4—H_2O_2	0.5 *M* H_2SO_4	77.8	[46]
Fe(II)—H_2SO_4—H_2O_2*	0.5 *M* H_2SO_4	60	[45, 46]
Fe(III)—H_2SO_4—H_2O_2	0.0165 *M* H_2SO_4	69	[49]
Fe(III)—H_2SO_4—H_2O_2	0.26 *M* H_2SO_4	54	[49]
Fe(II)—H_2SO_4—H_2O_2*	0.005—2 *M* H_2SO_4	59.0±5.5	[69]
Fe(III)-complexone (IV)-H_2O_2	pH 2—5	10^3	[53]
Fe(III)—H_3Citr—H_2O_2	pH 9	10^3	[53]
Fe(III)—$(NH_4)_2C_2O_4$—H_2O_2	pH 5	10^3	[53]
Fe(III)-PG-H_2O_2	pH 7.6	10^3	[53]
Fe(III)-CA-H_2O_2	pH 9	10^4	[53]
Fe(III)-AA-H_2O_2	pH 9	10^3	[53]
Fe(III)-SAL-H_2O_2	pH 10.7	$(48.00 \pm 1.55) \cdot 10^2$	[40]
Fe(III)-EDTA-H_2O_2	pH 2—5	10^4	[70]
Fe(III)-haemin-H_2O_2	pH 8—12	10^8—10^9	[44]
Fe(III)-catalase-H_2O_2	pH 1—7	10^7	[44]
Fe(III)-BSED-H_2O_2	pH 10	10^7	[44]
Fe(III)-BSED-H_2O_2	pH 6—11	10^6—10^8	[53]
Fe(III)-TEA-H_2O_2	pH 14	10^6	[44]
Fe(III)-TEA-H_2O_2	pH 7—12	10^5—10^6	[53]
Ti(IV)—H_2O—H_2O_2	pH 3.6	53	[40]
Ti(IV)-EDTA-H_2O_2	pH 3.6	$(6 \pm 2) \cdot 10^3$	[40]
Ti(IV)-NTA-H_2O_2	pH 3.6	$(2 \pm 1) \cdot 10^3$	[40]
Ti(IV)-SAL-H_2O_2	pH 3.6	$(3 \pm 2) \cdot 10^2$	[40]
Cu(II)—HCl—H_2O_2	0.1—1 *M* HCl	49	[54]
Cu(I)—HCl—H_2O_2*	0.1—1 *M* HCl	58	[54]
Cu(II)-bipy-H_2O_2	pH 4.6	$4.6 \cdot 10^4$	[55]
Ti(IV)-$H_2C_2O_4$-HA	0.2 *M* $H_2C_2O_4$	42	[95]
Ti(IV)-H_2O-HA	0.1 *M* H_2SO_4	41.3±1.5	[96]
Fe(III)-TEA-HA	1 *N* NaOH	205±25	[97]
Fe(III)-TEA-HA	0.1 *N* NaOH	595	[99]
Fe(III)-TEA-HA	1 *N* NaOH	198±8	[99]
Nb(V)-HCl-HA	4 *M* HCl	1	[101]
Nb(V)-HCl-HA	8 *M* HCl	45	[101]
Nb(V)-HCl-HA	11 *M* HCl	100	[101]
Ru(III)-Britton-Robinson buffer-HA	pH 6.7	$3 \cdot 10^3$	[103]
W(VI)-AA (first wave)-HA	pH 2.0	$4.25 \cdot 10^2$	[105]
W(VI)-AA (second wave)-HA	pH 2.0	$9.3 \cdot 10^3$	[105]
W(VI)-SA-HA (first wave)	pH 2.0	$2.1 \cdot 10^2$	[105]
W(VI)-CA-HA (first wave)	pH 2.0	$4.6 \cdot 10^2$	[106]
W(VI)-CA (second wave)-HA	pH 2.0	$1 \cdot 10^4$	[106]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.4 *M* H_2SO_4 + +0.25 *M* Na_2SO_4	$5.5 \cdot 10^4$	[114]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$5.3 \cdot 10^4$	[115]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.4 *M* H_2SO_4	$4.6 \cdot 10^4$	[116]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* $H_2C_2O_4$	$2.31 \cdot 10^4$	[117]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$5.11 \cdot 10^4$	[118]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$4.35 \cdot 10^4$	[118]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$4.48 \cdot 10^4$	[119]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$4.31 \cdot 10^3$	[120]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.4 *M* H_2SO_4	$2.68 \cdot 10^4$	[122]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* $H_2C_2O_4$	$2.2 \cdot 10^4$	[122]
Ti(IV)—$KClO_3$**	0.2 *M* $HClO_4$	$1.1 \cdot 10^5$	[126]
Ti(IV)—NaSCN—$KClO_3$**	0.2 *M* $HClO_4$	$2.2 \cdot 10^9$	[126]
Ti(IV)—$KClO_3$	0.1 *M* $HClO_4$	$6 \cdot 10^4$	[130, 132]
Ti(IV)-H_3 Trihydrox-$KClO_3$	0.1 *M* $HClO_4$	$6.9 \cdot 10^4$	[130, 132]
Ti(IV)—H_3 Citr—$KClO_3$	0.1 *M* $HClO_4$	$1.4 \cdot 10^4$	[130, 132]
Ti(IV)—H_2 Malic—$KClO_3$	0.1 *M* $HClO_4$	$1.3 \cdot 10^4$	[130, 132]
Ti(IV)—Tartr—$KClO_3$	0.1 *M* $HClO_4$	$1.4 \cdot 10^4$	[130, 132]
Ti(IV)—H_2 Malonic—$KClO_3$	0.1 *M* $HClO_4$	$0.57 \cdot 10^4$	[130, 132]
Ti(IV)—$H_2C_2O_4$—$KClO_3$	0.1 *M* $HClO_4$	$2 \cdot 10^4$	[130, 132]
Ti(IV)-CA-$KClO_3$	0.1 *M* $HClO_4$	$5.2 \cdot 10^4$	[132]
Ti(IV)—H Mandelic—$KClO_3$	0.1 *M* $HClO_4$	$11 \cdot 10^4$	[132]
Ti(IV)-HDPPA-$KClO_3$**	pH 1.6	$(1.5 \pm 0.3) \cdot 10^4$	[135]
Ti(IV)-EDTA-$KBrO_3$	pH 3.3	$6.7 \cdot 10^4$	[133]
Ti(IV)-HDPPA-$KBrO_3$**	pH 2.6	$(1.6 \pm 0.3) \cdot 10^4$	[135]
Mo(VI)—$KClO_3$	0.05 *M* H_2SO_4	$1.5 \cdot 10^3$	[139]
Mo(VI)—$KClO_3$	1 *M* H_2SO_4	$1.3 \cdot 10^3$	[139]
Mo(VI)—H_3 Citr—$KClO_3$	pH 1.1	$1.25 \cdot 10^3$	[144]
Mo(VI)—$H_2C_2O_4$—$KClO_3$	0.5 *M* H_2SO_4	$(7.2 \pm 0.8) \cdot 10^4$	[145]
Mo(VI)-H_3 Glucar-$KClO_3$	pH 1.1	$7.6 \cdot 10^6$	[147]
Mo(VI)—HGl—$KClO_3$	pH 1.7	$1.5 \cdot 10^5$	[148]
Mo(VI)-CA-$KClO_3$	pH 1.7	$8.9 \cdot 10^6$	[149]
Mo(VI)—H_2 Tartron—$KClO_3$	pH 1.7	$(2.0 \pm 0.5) \cdot 10^6$	[153]
Mo(VI)—H_2 Malic—$KClO_3$	pH 1.7	$1.3 \cdot 10^5$	[130]
Mo(VI)—H_2 Tartr—$KClO_3$	pH 1.7	$8 \cdot 10^5$	[130]
Mo(VI)—$KClO_3$—H_2— hydr.	pH 1.7	$7 \cdot 10^6$	[130]
Mo(VI)—$KClO_3$—H Mandelic	pH 1.7	$2.2 \cdot 10^8$	[130]
Mo(VI)—$NaClO_4$	1 *M* H_2SO_4	30	[138]
Mo(VI)—$NaClO_4$	0.05 *M* H_2SO_4	34	[139]
Se(IV)—BrO_3^-***	pH 3.6	$(4.6 \pm 2.9) \cdot 10^5$	[168]
W(VI)—ClO_4^-	12 *M* $HClO_4$	$1.35 \cdot 10^3$	[181]
Cystine-IO_3^-****	pH 9.46	$(1.83 \pm 0.12) \cdot 10^4$	[184]
Cystine-IO_4^-*****	pH 9.46	$(8.8 \pm 1.6) \cdot 10^4$	[184]
Mo(VI)—NO_3^-	0.05 *M* H_2SO_4	$2.5 \cdot 10^2$	[139]
Mo(VI)—NO_3^-	1 *M* H_2SO_4	$2.3 \cdot 10^2$	[139]
Cr(III)—NO_3^-	pH 5.0 at 0 °C	35	[202]
U(IV)—NO_3^-	pH 6	$7.9 \cdot 10^6$	[197]
Cu(II)—$S_2O_8^{2-}$	1 *M* KCl	$1.4 \cdot 10^3$	[206]
V(III)—V(IV)—H_2SO_4	pH 2	19	[209]
Y(III)-benzophenone	0.1 *M* $(C_2H_5)_4NClO_4$ in DMF	$(4.6 \pm 0.2) \cdot 10^3$	[27]
Y(III)-benzaldehyde	0.1 *M* $(C_2H_5)_4NClO_4$ in DMF	$(4.1 \pm 0.1) \cdot 10^3$	[27]
Y(III)-crotonaldehyde	0.1 *M* $(C_2H_5)_4NClO_4$ in DMF	$(2.5 \pm 0.3) \cdot 10^3$	[27]

*The rate constants for reactions involving oxidation by hydrogen peroxide were determined by a chemical method.

**The stoichiometric coefficient of the oxidation reaction was 5.5.

***The stoichiometric coefficient of the oxidation reaction was 6.

****The stoichiometric coefficient of the oxidation reaction was 3.

*****The stoichiometric coefficient of the oxidation reaction was 8. For the calculation of the oxidation reaction rate constant, it was necessary to divide k_{tot} by the corresponding stoichiometric coefficient of the oxidation reaction.

Notation: H_3Citr = citric acid; EDTA = ethylenediamine-tetra-acetic acid; PG = pyrogallol; CA = catechol; AA = ascorbic acid; BSED = bis-salicylidene-ethylenediamine; TEA = triethanolamine; NTA = nitrilotriacetate; SAL = sulphosalicylic acid; bipy = α,α′-bipyridyl; HA = hydroxylamine; SA = salicylic acid; H_2Trihydrox = trihydroxyglutaric acid; H_2Malic = malic acid; H_2Tartr = tartaric acid; H_2Malonic = malonic acid; H_2Glucar = saccharic acid; HGl = glycolic acid; H_2Tartron = tartronic acid; HMandelic = mandelic acid; HDPPA = α-hydroxy-α-dibutylphosphinoylpropionic acid.

Complex formation greatly influences the activity of the catalyst in the reduction processes, which also depends on the nature of the oxidant. Thus the activities of the Fe(II) and Ti(III) aquo-complexes in the reduction of H_2O_2 and NH_2OH are comparable, while the triethanolamine complexes of Fe(II) are more active by three–four orders of magnitude than the Ti(III) complexes (see Table).

The catalytic hydroxylamine waves are used in analytical practice mainly for the analysis of model solutions of niobium[101,102], ruthenium[103], tungsten[104,106], and the polarographically inactive CN^- ions[100].

3. The Catalytic Currents of Chlorate and Bromate Ions

Reactions involving oxidation by chlorates, bromates, iodates, perchlorates, and periodates are catalysed by variable oxidation state elements (molybdenum, osmium, etc.) (Kolthoff et al.[113], pp.97, 607), which can lead to the appearance of the catalytic currents of the above oxidants in the presence of transition elements. The ClO_3^- and BrO_3^- catalytic currents with participation of the transition elements of the first row, i.e. in the systems Ti(IV)–ClO_3^-–L,[114–132] Ti(IV)–BrO_3^-–L,[133–135] V(V)–BrO_3^-–L,[136] Fe(III)–ClO_3^-–L,[137] and Fe(III)–BrO_3^-,[138] with participation of transition elements of the second row, i.e. in the systems Mo(VI)–ClO_3^-–L [23,139–164] and Mo(VI)–BrO_3^-–L,[165,166] and with participation of the elements of the third row, i.e. in the system W(VI)–ClO_3^-–L [167] have been described in the literature. In addition a system involving a non-transition element, namely H_2SeO_3–ClO_3^-–L,[168,169] has also been described.

The catalytic ClO_3^- currents in the Ti(IV)–ClO_3^-–$H_2C_2O_4$–H_2SO_4 system were first investigated by Koryta and Tenygl[114], who established that 5.5 molecules of the titanium(III) complex participate in the reduction of ClO_3^- ions. The oxidation rate constant proved to be 1×10^4 litre mol^{-1} s^{-1}; this value was confirmed by many investigators[115–124].

Since the rate constants for the oxidation with chlorates of Ti(III) in $HClO_4$ and of the Ti(III) oxalate complex in H_2SO_4 are virtually equal (see Table), the Ti(III) aquo-ions are involved in the oxidation reaction responsible for the catalytic polarographic ClO_3^- current[126].

In the presence of an excess of oxalic (H_2Ox), citric (H_3Citr), and tartaric (H_2Tart) acids, EDTA, and CNS^- ions, titanium(IV) is reduced with a single reversible one-electron wave at less negative potentials than in the absence of the above ligands[39]. At low ligand concentrations a Ti(IV) reduction prewave is observed (catalysis by the ligand). In the presence of $KClO_3$ the height of both the aquo-ion wave and the prewave increases[124–126]. Among other acids, dicarboxylic acids comprising malonic acid (H_2Malonic) and carboxylic hydroxyacids comprising malic, trihydroxyglutaric (H_2Trihydrox), and glucaric (*d*-saccharic) acids also exhibit a catalytic activity (ligand catalysis). In the Ti(IV)–$KClO_3$–L systems the catalytic ClO_3^- current is superimposed on the Ti(IV) → Ti(III) reduction wave[127–132]. The current i_c is a maximum at pH 1–1.1, which can be explained by the involvement of the $Ti(OH)^{3+}$ species[127]. With increase of the $KClO_3$ concentration, the current i_c also increases and reaches a constant value, while with increase of the ligand content it passes through a maximum[124,125,127,128]. The catalytic waves in Ti(IV) solutions have the usual form with a distinct limiting current plateau and are described by the Koutecky theory[10].

The rate-limiting stages in the processes are the oxidation of $Ti(OH)^{3+}$ [125–127,130,132] or of its complex[128] by chlorate ions. At low ligand concentrations, where a prewave is observed, the mechanism of the generation of the catalytic current involves the oxidation of both the titanium aquo-ion and its complex ion[124,126], in which the organic ligands investigated exist in the form of uncharged species[125,132]. The ligands (see Table) can be arranged in the following sequence in terms of their increasing influence on the catalytic ClO_3^- current in the Ti(IV)–ClO_3^-–L system: H_2Malonic < H_2Malic < H_2Tart < H_2Citr < HDPPA < H_2Ox < Ph < H_2O < H_2Trihydrox < HMandelic ≪ CNS^-. The appreciable increase (by approximately four orders of magnitude) of the rate of oxidation of Ti(III)L on passing from an organic to an inorganic ligand (CNS^-) is probably associated with the faster formation of the complex $Ti(CNS)^{2+}$.[126]

The current i_c in the Ti(IV)–$KBrO_3$–EDTA system diminishes with increase of pH and at pH ≥ 3 reaches a constant value which is independent of the acidity of the solution[133].

As a representative of the titanium subgroup, zirconium does not give rise to a catalytic BrO_3^- wave in the presence of EDTA.[133]

In an acetate buffer solution at pH 5.0 the polarogram of vanadium(V) shows the catalytic BrO_3^- wave with a sharp maximum at $E = 0$ V,[136] which hardly changes after the introduction into the solution of 0.05 M resacetophenone oxime (2,4-dihydroacetophenone oxime), which forms a complex with V(V). The appearance of this wave is probably associated with the oxidation of the V(IV) formed by BrO_3^- ions to V(V), since it is located at the potentials of the V(V) → V(IV) reduction wave. The catalytic ClO_3^- and BrO_3^- currents in the Fe(III)–KCl system[137,138] are due to the interaction of ClO_3^- and BrO_3^- with the colloidal hydroxide $Fe(OH)_2$.

A large series of studies on the catalytic ClO_3^- currents in the presence of Mo(VI) have been carried out[23,139–164]. The first catalytic chlorate currents in the presence of Mo(VI) were investigated by Kolthoff and Hodara[139] at various sulphuric acid (0.01–2 M), sodium chlorate (0.2–1.2 M), and molybdenum(VI) concentrations. In weakly acidic H_2SO_4 solutions (up to 0.1 M) in the absence of chlorate, a single wave corresponds to the reduction of Mo(VI) to Mo(V) and two waves correspond to the reduction of Mo(V) to Mo(III). On the other hand, in strongly acid solutions ($c_{H_2SO_4} > 1$ M) the reduction of Mo(VI) to Mo(V) is characterised by two waves, while the reduction of Mo(V) to Mo(III) is characterised by a single wave, which can be explained by the reduction of various hydrolysed Mo(VI) and Mo(V) forms[140]. Two catalytic waves, due to the reduction by the Mo(V) and Mo(III) species of the chlorate ions formed at the electrode, are observed in the presence of chlorate. The rate of oxidation of Mo(III) to Mo(V) by chlorate, calculated from the data of Delahey and Stiehl[141], is independent of $c_{H_2SO_4}$.

In the presence of organic compounds (malic, tartaric, trihydroxyglutaric, mandelic[130], citric[144], glucaric[147], glycolic[148], tartronic[153], oxalic[145], and malonic[143] acids and catechol[149]), the Mo(VI) polarogram at pH 1.7 in the 0.1 M H_2SO_4 + 0.2 M Na_2SO_4 system consists of two or three waves. The catalytic wave in the form of a peak is located at the potentials of the first[143,144,147,149,153] or second[148] reduction wave of Mo(VI) and in oxalic acid solutions two peak-shaped catalytic waves, corresponding to the Mo(VI) and Mo(V) regeneration processes, are observed. In all cases the current i_c passes through a maximum with increase of the ligand concentration and the pH of the solution (pH_{max} 0.9–1.0). In the case of oxalic acid the heights of the first and second catalytic waves are maximum in 0.1 and 0.5 M H_2SO_4. With increase of c_{KClO_3} the current i_c increases in all cases and reaches a limiting value. The dependence of i_c on the acidity of the medium and other parameters can be explained by the different catalytic activities of the hydrolysed forms of molybdenum[23,145,161]. Many investigators[143–145,147–149,151–153] believe that the rate-limiting stage in the generation of catalytic currents is the oxidation of the molybdenum(V) complex by the chlorate ion. However, in some investigations[130,155] a coordination mechanism has been proposed, according to which the complex $Mo(V)L.ClO_3$ formed is reduced at the electrode.

The organic ligands investigated can be arranged in the following sequence in terms of increasing catalytic activity (see Table): $H_2O \ll H_3Citr < HGl < H_2Tart < H_2Malic < H_2Tartron < H_2Trihydrox < H_2Glucar < Ph \ll HMandelic$. A detailed study[23,161] of the catalytic currents in the presence of mandelic acid (the most active and the most readily sorbed ligand on the surface of mercury) showed that the catalytic currents are described by a mechanism in which the slow oxidation of various molybdenum(V) complexes incorporating the chlorate ion takes place on the surface of the electrode and not in the layer near it, as follows from Koutecky's theory[10].

In a study of the W(VI)–ClO_3^- system, where two catalytic peaks, observed in the presence of pseudotungstate, are due to the oxidation of $HW_6O_{20}^{3-}$ and $H_2W_6O_{20}^{2-}$, Hodara and Glasner[167] also concluded that the reaction responsible for the catalytic chlorate current occurs on the surface of the electrode; metatungstate does not exhibit a catalytic activity.

The joint influence of molybdenum(VI) and tungsten(VI) salts on catalytic ClO_3^- currents is of interest. The first catalytic ClO_3^- peak, due to the involvement of molybdenum(V), appreciably increases after the introduction of tungstate(VI) into the solution, which can be explained by the appreciable contribution of tungsten(V) to the catalytic activity of the heteropolyacid formed, which comprises tungsten(VI) and molybdenum(VI).[162]

On passing from titanium to molybdenum, the catalytic activity increases appreciably (see Table). The electrochemical reduction of BrO_3^- is catalysed by molybdenum(VI) in acetate buffer solution at pH 5.0. In the presence of resacetophenone isoniazid hydrazone the catalytic wave shifts towards more positive potentials and has the form of a peak with $E_p = -0.7$ V.[165] The authors[165] do not explain the generation of the catalytic BrO_3^- current.

The catalytic BrO_3^- current for selenium (a non-transition element) in solution at pH 2.5–4.0 is observed at the potentials of the second wave of selenium. It corresponds to the oxidation of H_2Se to zerovalent selenium[168,169] and obeys the Koutecky theory.

The catalytic chlorate currents have been used to determine ClO_3^- ions[114,129] and admixtures of titanium in trichlorosilane[121], in metallic aluminium of type Al 74[a], in steels[127,131,160], in natural waters and soil solutions[133,163], in rocks[158], in soils[159], in pure solutions[147,148,153], in technical sulphuric acid[164], and in tungsten[162]. Furthermore, the catalytic ClO_3^- currents are widely used in the determination of the polarographically inactive pyrogallol, salicylic and sulphosalicylic acids and catechol[123,125,149], and citric[124], glucaric[147], glycolic[148], tartronic[153], and mandelic[156] acids. Isopentyl alcohol, agar-agar[148], Tween 80,[153] and phenol[157] can be determined from the decrease of the catalytic current. Mandelic acid has come to be most widely used as the ligand for analytical purposes[158–160,163,164].

The catalytic bromate currents are used for highly sensitive determinations of titanium[133,134,135], vanadium[136], and molybdenum[165] (in solutions, and biological objects[166]) and of selenium[168,169].

4. Catalytic Currents of the Perchlorate Ion

In an acid medium perchlorates have a lower standard oxidation-reduction potential than chlorates, which is one of the causes of their low reactivity at room temperature. The catalytic perchlorate currents are therefore observed only for highly active catalysts such as molybdenum and tungsten. The catalytic ClO_4^- currents are not observed in the presence of titanium(IV) in view of the low rate of oxidation of titanium(III) by ClO_4^- ions; $k = 8.9 \times 10^{-2}$ litre mole^{-1} s^{-1} at 40 °C.[170]

The catalytic current in the Mo(VI)–ClO_4^- system has been observed by many investigators[139,171–180]. This phenomenon was first noted[171] in the polarography of Mo(VI) in $HClO_4$ solutions.

The formation of molybdenum(VI) and tungsten(VI) complexes with chloride ions[176,181] and carboxylic acids (tartaric, citric, and oxalic)[180] decreases i_c. Numerous mechanisms have been proposed for the catalytic current, according to which the current is due to the oxidation of Mo(IV)[174,175] or the reduction at the electrode of the complex Mo(V).ClO_4;[176] these mechanisms have been inadequately justified. We believe that the mechanism according to which the current is due to the oxidation of Mo(III) by perchlorate ions, proposed by Kolthoff and Hodara[139], is most correct. The catalytic current in the W(VI)–ClO_4^- system corresponds to the oxidation by perchlorate of the W(V) formed on the electrode[181].

The Table shows that the activities of molybdenum and tungsten in the catalytic reduction of ClO_4^- ions are approximately the same. The catalytic perchlorate currents make it possible to determine Mo(VI) at concentrations down to 1×10^{-6} M;[172–175] to increase the sensitivity of the methods, the solutions are polarographed at 40 °C[177] or time–current polarography is used[182].

The catalytic perchlorate currents have been used for analytical purposes in the determination of admixtures of molybdenum in iron and steels[182], in $HClO_4$,[170] in plants[173], in rocks[174,175], in various industrial and biological objects[177], and in soils[183].

5. Catalytic Currents of Iodate and Periodate Ions

Catalytic currents of iodate and periodate ions are observed in systems with sulphur-containing organic substances such as cystine[184], dithiocarbamate, and xanthate[24]. The ClO_3^-, BrO_3^-, NO_2^-, and H_2O_2 species do not exhibit catalytic effects in these organic systems. In the cystine–IO_3^-(IO_4^-) system the catalytic wave is combined with the first cystine reduction wave and has the form of a peak whose height is a maximum at pH 8.6–9.2. The current i_c can be greatly increased by the preliminary concentration of cystine at a stationary mercury microelectrode or by introducing ammonium or magnesium ions, which behave as activators[37].

The electrode process is described by the Koutecky theory and includes the oxidation of cysteine to the initial depolariser as the rate-limiting stage[185]. The introduction of IO_3^- at pH 7–11 into diethyldithiocarbamate (DTC) and ethyl xanthate (EX) solutions, which give rise to anodic polarographic waves, results in the appearance of a cathodic catalytic wave at potentials in the range between −0.5 and −0.6 V, which is much larger than the anodic wave and has the properties of surface waves[24]. The catalytic IO_3^- and IO_4^- currents make it possible to determine very low concentrations of sulphur-containing compounds: when cystine is initially concentrated at a stationary mercury microelectrode, its concentrations down to 10^{-8}–10^{-6} M can be determined[184].

The catalytic halogenate and perhalogenate currents tend to increase with increase of the number of the *d* orbital of the transition element (see Table). In catalysis by non-transition elements and organic substances, the catalytic current is observed only for bromate, iodate, and periodate. The rates of reduction of the substrates are then high and comparable to the rates characteristic of the Ti(IV)–ClO_3^-.(BrO_3^-)–organic ligand systems.

6. Catalytic Currents of Nitrate and Nitrite Ions

The catalytic currents of nitrate and nitrite ions are observed in the V(V)–NH_4Cl,[186] V(V)–EDTA,[187] Cr(III)–glycine[188], Cr(III)–EDTA,[189] molybdenum(VI),[139,177,180,190–195], and uranium(VI) [21,196–202] systems in various media. The catalytic currents for all the systems investigated are described by the Koutecky theory[10] and the reaction involving the oxidation of the depolariser reduction product by the nitrate or nitrite ion is rate-limiting. When the elements of the first transition series (vanadium and chromium) are used, V(II) or Cr(II) is oxidised to vanadium(IV) or chromium(III). The mechanism adopted is shown to be valid by the agreement between the rate constants for the Cr(II) oxidation reaction obtained by the chemical and polarographic methods[189].

The product of the reduction of NO_3^- by Cr(II) ions is NH_4^+.[189] The catalytic wave for the Mo(VI)–NO_3^- systems in acid sulphate[139,186,192], perchlorate[177], and chloride[192] solutions is located at the potentials of the Mo(V) → Mo(III) second wave and is due to the oxidation of Mo(III) to Mo(V). In contrast to nitrate ions, nitrite ions are involved in the oxidation of the Mo(V) formed to Mo(VI).[192]

The catalytic current in the U(VI)–NO_3^-(NO_2^-) systems is due to the oxidation of the U(III) formed to U(IV) [21,196–202] and the NO_3^- reduction product is hydroxylamine[203]. It has been established for the U(VI)–NO_3^- system[21] that the different signs of the charges of the reacting species exert an appreciable influence on the rates of the reactions responsible for the catalytic currents: the substrate has a negative charge and the catalyst has a positive charge. The rates of the NO_3^- or NO_2^- reduction reactions in the systems investigated (see Table) increase with increase of the number of the *d* or *f* orbital [sic], which is probably caused by the formation of labile systems capable of giving up electrons more readily on interaction with the oxidant.

The catalytic currents of nitrates are used for analytical purposes in order to determine the admixtures of molybdenum in technical and biological objects[177], in steels and reagents[193], in high-purity indium[194], in propene epoxidation products[195] and for the determination of uranium at very low concentrations, down to 1×10^{-8} M,[195–197,202] traces of uranium in rocks and untreated phosphates[201], NO_3^- and NO_2^-.[198]

7. Catalytic Currents of Persulphate Ions

The persulphate ion $S_2O_8^{2-}$ is reduced to SO_4^{2-} at positive potentials with participation of two electrons[39]. The specific adsorption of Br^- and I^- anions[204] or the formation of a sparingly soluble film of mercury iodide[205] have an inhibiting effect on its reduction. Chloride ions produce the same effect[206]. A catalytic wave, coinciding with the first copper(II) reduction wave, is observed in the Cu(II)–$S_2O_8^{2-}$–KCl system[206]. It is described by the Koutecky theory and is determined by the rate of oxidation of Cu(I) by persulphate ions with formation of Cu(II) and the SO_4^- radical-ion, which is consumed in the oxidation of Cu(I) or is reduced at the electrode. Interesting phenomena have been observed[207,208] in the study of the catalytic currents in the Cu(II)–$S_2O_8^{2-}$ system in 0.1 M $NaClO_4$ + 0.01 M $HClO_4$. A minimum arises on the polarogram in the presence of As(III) at $E = 0.1$ V, whose depth increases with increasing As(III), Cu(II), $S_2O_8^{2-}$, methanol, ethanol, and propanol concentrations and diminishes in the presence of acetonitrile, allylacetone, and Fe(III).[207] A minimum is also observed in the region of the reduction potential of the copper complex of EDTA (at $E \cong -0.5$ V) in $NaNO_3$ solutions containing 1 M ethylenediamine in the presence of As(III). To account for the results, a mechanism has been proposed in which the sulphate radical-anions formed are consumed in the oxidation of not only Cu(I) but also of As(III) and the other species investigated[207,208].

Catalytic Currents of Vanadium(IV)

In the generation of the catalytic oxygen currents described the oxidant-substrate is reduced at the electrode at much more negative potentials than the catalyst. However, there are systems in which part of the oxidant is reduced at the limiting current potentials of the catalyst wave and the oxidant reduction product is the catalyst itself, as, for example, in the V(IV)–V(III)–V(II)–H_2SO_4 system[209]. The polarogram of V(III) has a distinct diffusion wave with $E_{1/2} \cong -0.5$ V. When V(IV) is introduced, the V(III) reduction wave becomes indistinct and I_{lim} at the potentials corresponding to the V(III) diffusion current plateau exceeds the sum of i_d for V(III) and the V(IV) reduction current at this potential. The catalytic current is due to the oxidation of V(II) to V(III) by V(IV) ions. This process is accelerated by increase of pH in the range 0–1.3, which is due to the different oxidising capacities of the VO_2^{2+} and V(OH).HSO_4^{2-} cations, which predominate under the given conditions. The catalytic currents, complicated by the reduction of the oxidant itself, are observed also in the Mo(VI)–V(V)–EDTA system at pH 4–6.[210].

In the Mo(VI)–V(V) mixture in the presence of EDTA, the three-electron molybdenum(VI) wave increases and the second vanadium(V) reduction wave, corresponding to the process V(IV) → V(III), disappears, which can be explained by the involvement of V(V) ions in the catalytic Mo(III) oxidation reaction[210]. However, it is difficult to agree with this, since the potential corresponding to the reduction of the complex V(V).EDTA to V(IV).EDTA is more positive by ~0.7–0.8 V than the reduction potential of molybdenum(VI). The involvement of V(IV) complexes as the oxidants is most probable. The V(IV) catalytic currents, observed in the U(VI)–V(IV) system[211], are used to determine low uranium concentrations.

9. Catalytic Currents of Sulphuric and Certain Carboxylic Acids

The limiting reduction currents of sulphur dioxide, bromine, and iodine against the background of concentrated sulphuric acid are catalytic in nature[212] owing to the oxidation of the electrochemical reduction products of these depolarisers to their initial state by sulphuric acid.

Among carboxylic acids, oxalic and glyoxylic acids are known as oxidant-substrates[213]. Oxalic acid is reduced to glyoxylic acid at the mercury dropping electrode[214]. In the presence of uranium(VI) the reaction takes place at more positive potentials with formation of glycolic acid[213]. Under these conditions, the catalytic wave of oxalic acid coincides with the second uranium(VI) reduction wave: $UO_2^+ + 2e \rightarrow U(III)$. The same catalytic wave is observed also in the presence of glyoxylic acid. The catalytic reduction currents of the above acids are due to their reaction with U(III) to form glycolic acid and U(IV). The latter is reduced electrochemically to U(III) and the reactions described are then repeated[213].

The catalytic currents in the U(VI)–glyoxylic acid system can be used to determine U(VI) and glyoxylic acid[215].

III. THE FIXATION OF ATMOSPHERIC NITROGEN—A POSSIBLE APPLICATION OF THE CATALYTIC CURRENTS OF SUBSTRATES

The intensive development of agriculture requires the use of considerable amounts of inorganic fertilisers. Thus, from 1st July, 1938 to 30th June, 1939, 9.2×10^6 tonnes of nutrient elements were produced in the world in terms of N_2, P_2O_5, and K_2O,[216] while in the period 1977–1978 the corresponding figure was 106.1×10^6 tonnes, including 40.9×10^6 tonnes of N_2.[217] The present capacity of the world nitrogen industry meets less than 10% of the requirements of agriculture for nitrogen fertilisers[218].

The industrial methods of producing bound nitrogen are energy consuming and are carried out at high temperatures and pressures, while the enzymic fixation of nitrogen† takes place in nature under very mild conditions. Consequently, the fixation of atmospheric nitrogen under mild conditions is possible in principle and the development of industrial fixation methods is an urgent problem in modern chemical science.

The fixation of atmospheric nitrogen under mild conditions is a reaction catalysed by electron-transfer reagents[219]. It is therefore interesting to consider them under the conditions of the electrochemical regeneration of mediators, together with the catalytic currents of molecular nitrogen as the substrate. The non-enzymatic fixation of nitrogen under mild conditions was first described by Vol'pin and Shur[220]. Numerous studies (surveyed in reviews[221–224]) on this question were published over a short period.

Thermodynamically feasible nitrogen fixation reduction processes are difficult because in the dissociation of the triple bond in the N_2 molecule most of the energy (131 kcal [225] out of 225 kcal [226]) is consumed in the rupture of the first bond. In the direct reduction one must therefore use particularly powerful reductants. The formation of complexes of nitrogen molecules with transition elements[227,228] makes it possible to distribute more uniformly the dissociation energy of the π-bonds in the N_2 molecule among separate stages.

Nitrogen can be reduced stepwise with participation of two, four, and six electrons, leading to the formation of N_2H_2, N_2H_4, and NH_3. The four-electron process, involving the reduction of nitrogen to hydrazine, is energetically most favourable[222]. The N_2–reductant (transition element and others) system under the conditions of the electrochemical generation of the reductant resembles the systems already considered, in which the catalytic currents of oxidant substrates are observed. One cannot therefore rule out the possibility that the study of the oxidant catalytic currents, including the molecular nitrogen current, may lead to the refinement of the mechanism of the nitrogen fixation process or may lead to the discovery of new principles for the selection of nitrogen-fixing systems "working" under mild conditions.

Vol'pin and Shur[220], who observed the fixation of nitrogen at room temperature also in aprotic (etheral and hydrocarbon) media, used powerful reductants such as $LiAlH_4$, C_2H_5MgBr, and (iso-C_4H_9)Al. Nitrogen fixation was observed in the presence of transition metal salts ($CrCl_3$, $MoCl_5$, WCl_5, $FeCl_3$, and $TiCl_4$). Ammonia was evolved in the hydrolysis of the products formed. Many investigators whose studies have been surveyed[221–224] used transition elements (V, Mn, Co, Zr, Ru, Os, and Nb), apart from the elements in the above salts, as catalysts and the reductants were alkali, alkaline earth (Mg) and lanthanide (La and Ce) metals, alkali metal naphthalides and hydrides[219,222–224], and sodium amalgam[229]; electrochemical reduction has also been employed[230–234]. As expected, hydrazine and ammonia were obtained in the hydrolysis of the products of the nitrogen-fixing systems. In the systems investigated the transition elements played the role of catalysts or, in rare instances, the role of both catalysts and reductants [for example, in the V(II)–Mg(II)–N_2 system[235,236]]. The catalytic effect of the transition element is manifested under a rigorously specific combination of conditions: the standard potential of the reductant must be greater or equal to the potential of the catalyst and greater than the potential of hydrazine; the reductant must exhibit a specific activity in relation to nitrogen[222].

Under the conditions investigated, the nitrogen activation stage consists of the formation of the dinuclear complex MN_2M,[237] in which the transition element M is in the d^1 or d^3 state. In subsequent steps electrons are transferred from the reductant to the activated nitrogen. This mechanism is identical with that of the catalytic reduction of nitrogen in biological processes catalysed by nitrogenase[219,222] and other enzymes[238,239]. In electrochemical systems the cathode is a universal reductant, at which one can establish any potentials for the reduction of substances, including molecular nitrogen. It is not therefore fortuitous that investigators have resorted to electrochemical methods[230–234], including polarography, to study the fixation of nitrogen.

The fixation of molecular nitrogen has also been studied by the molecular orbital (MO) method in relation to reactions in the $[N_2 + H]^{\cdot}$, $[N_2 + H^{\cdot}]^+$, and $[N_2^- + H^{\cdot}]^-$ model systems[240].

The nitrogen fixation mechanism presented above can ensure the appearance of the catalytic polarographic current of nitrogen. The behaviour of the nitrogen-fixing systems V(II)–catechol[241] and Mo(III)–Mg(II)–Na(Hg) [242] has been studied. The lack of literature data for the catalytic polarographic currents of molecular nitrogen as the oxidant-substrate in nitrogen-fixing systems is probably associated with the fact that the rate of oxidation of the intermediate transition metal complex by molecular nitrogen is not high enough to be appreciable under polarographic conditions. However, in principle, it will be possible to observe the catalytic polarographic current of molecular nitrogen under certain conditions and to use it as an indicator for the selection of nitrogen fixation conditions.

Thus transition and certain non-transition elements are used as catalysts of the reactions responsible for the catalytic polarographic currents of substrates. The catalytic activity of an inorganic catalyst increases with the number of its *d* orbital. Complex formation in most cases leads to an increase in activity of the catalyst, but sometimes the opposite phenomenon takes place.

The maximum activities of many catalysts are observed at pH values close to the p*K* for their hydrolysis, which can be used to estimate the activities and the degrees of involvement of various hydrolysed forms of catalysts in the catalytic process.

The properties of oxidant-substrates are shown by H_2O_2, ClO_3^-, BrO_3^-, IO_3^-, ClO_4^-, IO_4^-, NO_2^-, NO_3^-, NH_2OH, V(V), V(IV), $S_2O_8^{2-}$, H_2SO_4, $H_2C_2O_4$, COHCOOH, and saturated compounds, organic halogeno-compounds, sulphur-containing compounds, and amino-compounds. The strongest oxidants can be arranged in the following sequence in order of increase of their reactivity. $ClO_4^- < NH_2OH < NO_2^- < NO_3^- < H_2O_2 < S_2O_8^{2-} < IO_4^- < IO_3^- < BrO_3^- < ClO_3^-$ (see Table).

The generation of catalytic currents is in most of the cases examined due to the oxidation of the reduced form of the catalyst by the substrate in the layer near the electrode or

†By the fixation of nitrogen, we understand a process involving the complete or partial rupture of the N≡N bond.

on the electrode surface. In systems with hydrogen peroxide one cannot rule out the possibility of the reduction at the electrode of the substrate bound in a complex with one of the forms of the catalyst.

The catalytic currents have found extensive applications in analytical practice for the analysis of admixtures of the catalyst, substrates, and polarographically inactive substances forming complexes with the catalyst, and also in the study of complex formation. One cannot rule out the possibility of using the catalytic currents also in the study of the molecular nitrogen fixation processes under mild conditions.

REFERENCES

1. J.Heyrovsky and J.Kuta, "Principles of Polarography" (Translated into Russian), Izd.Mir, Moscow, 1965, p.560.
2. R.J.P.Williams, "Metals of Life" (Translated into Russian), Izd.Mir, Moscow, 1975, p.236.
3. K.B.Yatsimirskii, "Vvedenie v Bioneorganicheskuyu Khimiyu" (Introduction to Bioinorganic Chemistry), Izd.Naukova Dumka, Kiev, 1976, p.115.
4. G.K.Budnikov, T.V.Troepol'skaya, and N.A.Ukhanovich, "Elektrokhimiya Khelatov Metallov v Nevodnykh Sredakh" (The Electrochemistry of Metal Chelates in Non-Aqueous Media), Izd.Nauka, Moscow, 1980, p.192.
5. Ya.I.Tur'yan, Uspekhi Khim., 1973, **42**, 969 [Russ. Chem.Rev., 1973(6)].
6. Ya.I.Tur'yan, "Khimicheskie Reaktsii v Polyarografii" (Chemical Reactions in Polarography), Izd. Khimiya, Moscow, 1980, p.336.
7. S.G.Mairanovskii, "Kataliticheskie i Kineticheskie Volny v Polyarografii" (Catalytic and Kinetic Waves in Polarography), Izd.Nauka, Moscow, 1966, p.288.
8. R.Brdička and K.Wiesner, Naturwiss., 1943, **31**, 277.
9. K.Wiesner, Z.Elektrochem., 1943, **49**, 164.
10. J.Koutecky, Coll.Czech.Chem.Comm., 1953, **18**, 311.
11. R.Brdicka and J.Koutecky, J.Amer.Chem.Soc., 1954, **76**, 907.
12. R.Brdička, "Advances in Polarography", Pergamon Press, London, 1960, Vol.2, p.655.
13. J.Koutecky and J.Koryta, Electrochim.Acta, 1961, **3**, 318.
14. R.Brdička, V.Hanus, and J.Koutecky, "Progress in Polarography", Intersci.Publ., New York, 1962, Vol.1, p.145.
15. S.I.Sinyakova, "Sovremennye Metody Analiza. Metody Issledovaniya Khimicheskogo Sostava i Stroeniya Veshchestva" (Modern Analytical Methods. Methods for the Investigation of the Chemical Composition and Structure of Matter), Izd.Nauka, Moscow, 1965, p.192.
16. S.I.Sinyakova and Yu.S.Milyavskii, Zavod.Lab., 1971, **37**, 1153.
17. S.I.Sinyakova, V.F.Toropova, Yu.S.Milyavskii, and L.A.Anisimova, "Uspekhi i Perspektivy Razvitiya Polyarograficheskogo Metoda (Pienarnye Doklady na V Vsesoyuznom Soveshchanii po Polyarografii)" [Advances in and Prospects for the Development of the Polarographic Method (Plenary Reports at the Vth All-Union Conference on Polarography)], Izd. Shtiintsa, Kishinev, 1972, p.117.
18. E.G.Chikryzova, Symposium, "Novye Napravleniya v Polyarograficheskom Metode" (New Trends in the Polarographic Method), Izd.Shtiintsa, Kishinev, 1975, p.46.
19. Yu.S.Milyavskii, Elektrokhimiya, 1979, **15**, 644.
20. C.P.Andrieux, J.M.Dumas-Bouchiat, and I.M.Saveant, J.Electroanalyt.Chem., 1978, **87**, 39, 55; **88**, 43.
21. T.D.Nikolaeva, S.I.Zhdanov, and P.M.Zaitsev, Elektrokhimiya, 1979, **15**, 1642.
22. I.Hodara and A.Glasner, Electrochim.Acta, 1970, **15**, 923, 931.
23. P.M.Zaitsev, Z.V.Zaitseva, S.I.Zhdanov, and T.D.Nikolaeva, Zhur.Anal.Khim., 1980, **35**, 1951.
24. V.F.Toropova, Yu.N.Polyakova, and N.I.Movchan, Izv.Vys.Ucheb.Zaved., Khim. i Khim.Tekhnol., 1979, **22**, 302.
25. M.Brezina, W.Khalib, I.Koryta, and M.Musilova, J.Electroanalyt.Chem., 1977, **77**, 237.
26. Yu.P.Skobochkina and Z.N.Timofeeva, Elektrokhimiya, 1980, **16**, 1206.
27. Yu.S.Milyavskii, Elektrokhimiya, 1974, **10**, 449.
28. R.A.Shein and Yu.S.Milyavskii, Elektrokhimiya, 1975, **11**, 770.
29. Yu.S.Milyavskii, Elektrokhimiya, 1976, **12**, 1499.
30. Yu.S.Milyavskii and Ya.I.Tur'yan, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI)(No.1219-78).
31. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry: A Comprehensive Text" (Translated into Russian), Izd.Mir, Moscow, 1969, Part 3, Chapters 29 and 30.
32. K.B.Yatsimirskii and I.I.Alekseeva, Izv.Vys.Ucheb. Zaved., Khim. i Khim.Tekhnol, 1958, 1, 53.
33. V.A.Nazarenko, V.P.Antonovich, and E.M.Nevskaya, "Gidroliz Ionov Metallov v Razbavlennykh Rastvorakh" (Hydrolysis of Metal Ions in Dilute Solutions), Atomizdat, Moscow, 1979, p.192.
34. A.A.Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Izd.Khimiya, Moscow–Leningrad, 1966, p.623.
35. S.Basolo and R.G.Pearson, "The Mechanisms of Inorganic Reactions" (Translated into Russian), Izd. Mir, Moscow, 1971, p.592.
36. H.B.Mark, G.A.Rechnitz, and R.A.Greinke, "Kinetics in Analytic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972.
37. P.Bonchev, "Complexing and Catalytic Activity. Activation of Homogeneous-Catalytic Reactions in Solutions" (Translated into Russian), Izd.Mir, Moscow, 1975, p.272.
38. K.B.Yatsimirskii, "Kineticheskie Metody Analiza" (Kinetic Analytical Methods), Izd.Khimiya, Moscow, 1967, p.200.
39. I.M.Kolthoff and J.J.Lingane, "Polarography", Intersci.Publ., New York–London, 1952, Vol.1, p.420.
40. V.F.Toropova and R.S.Zabbarova, Izv.Vys.Ucheb. Zaved., Khim. i Khim.Tekhnol., 1969, **12**, 1487.
41. V.F.Toropova, V.A.Vekslina, and N.G.Chovnykh, Zhur.Anal.Khim., 1971, **26**, 2132.
42. I.M.Kolthoff and E.P.Parry, J.Amer.Chem.Soc., 1951, **73**, 5315.
43. R.Brdička and C.Tropp, Biochem.Z., 1957, 289, 301.
44. R.Brdička and K.Wiesner, Coll.Czech.Chem.Comm., 1947, **12**, 39.
45. I.M.Kolthoff and E.P.Parry, J.Amer.Chem.Soc., 1951, **73**, 3718.
46. Z.Pospišil, Coll.Czech.Chem.Comm., 1953, **18**, 337.

47. I.Riha and L.Serak, Coll.Czech.Chem.Comm., 1955, **20**, 640.
48. S.I.Sinyakova and Yu.S.Milyavskii, Zhur.Neorg. Khim., 1967, **12**, 663 [Russ.J.Inorg.Chem., 1967(3)].
49. Yu.S.Milyavskii and S.I.Sinyakova, Izv.Akad. Nauk SSSR, Ser.Khim., 1967, 2384.
50. Yu.S.Milyavskii and S.I.Sinyakova, Zhur.Anal. Khim., 1968, **23**, 1188.
51. H.Koneko, K.Nozaki, and T.Ozawa, Rev.Polarogr. (Japan), 1977, **23**, 17.
52. H.Koneko, Rev.Polarogr.(Japan), 1978, **24**, 73.
53. Yu.S.Milyavskii and S.I.Sinyakova, Izv.Akad. Nauk SSSR, Ser.Khim., 1968, 988.
54. I.M.Kolthoff and R.Woods, J.Electroanalyt.Chem., 1966, **12**, 385.
55. Yu.S.Milyavskii and Ya.B.Khusid, Zhur.Anal.Khim., 1974, **29**, 2359.
56. R.K.Sharipov and O.A.Songina, Zhur.Anal.Khim., 1964, **19**, 1322.
57. I.H.Kennedy, J.Phys.Chem., 1960, **64**, 1590.
58. R.K.Sharipov and O.A.Songina, Zhur.Anal.Khim., 1965, **20**, 683.
59. S.G.Samokhvalov, Agrokhimiya, 1965(5), 118.
60. N.S.Sharipova and N.Zh.Ibraeva, "Sbornik Rabot po Khimii" (Collected Reports on Chemistry), Izd. Kazakhsk.Univ., Alma-Ata, 1973, No.3, p.211.
61. R.K.Sharipov and O.A.Songina, Zhur.Anal.Khim., 1966, **21**, 800.
62. L.I.Budarin, T.I.Rumyantseva, and G.G.Sherina, Zhur.Anal.Khim., 1964, **19**, 470.
63. L.I.Budarin, T.I.Rumyantseva, and G.G.Sherina, Izv.Vys.Ucheb.Zaved., Khim. i Khim.Tekhnol., 1964, p.715.
64. K.B.Yatsimirskii and L.I.Budarin, Zhur.Neorg. Khim., 1962, 7, 1824 [Russ.J.Inorg.Chem., 1962(8)].
65. I.M.Kolthoff and E.P.Parry, Analyt.Chem., 1953, **25**, 188.
66. M.T.Henne and J.W.Collat, J.Electroanalyt.Chem., 1964, **7**, 359.
67. Yu.S.Milyavskii, Elektrokhimiya, 1979, **25**, 644.
68. F.Haber and I.Weiss, Naturwiss., 1932, **20**, 948.
69. I.A.Kulikov, V.S.Koltunov, V.I.Marchenko, A.S.Milovanova, and L.N.Nikishova, Zhur.Fiz. Khim., 1979, **53**, 647 [Russ.J.Phys.Chem., 1979(3)].
70. B.Matyška and D.Duškova, Coll.Czech.Chem.Comm., 1957, **22**, 1747.
71. B.Matyška, Coll.Czech.Chem.Comm., 1957, **22**, 1758.
72. B.Matyška and F.P.Dousek, Coll.Czech.Chem. Comm., 1958, **23**, 1044.
73. S.V.Elinson and K.I.Petrov, "Analiticheskaya Khimiya Tsirkoniya i Gafniya" (Analytical Chemistry of Zirconium and Hafnium), Izd.Nauka, Moscow, 1965, p.240.
74. N.M.Gibalo, "Analiticheskaya Khimiya Niobiya i Tantala" (Analytical Chemistry of Niobium and Tantalum), Izd.Nauka, Moscow, 1964, p.352.
75 O.W.Kowarth and J.R.Hunt, J.Chem.Soc.Dalton Trans., 1979, 1388.
76. A.I.Busev, "Analiticheskaya Khimiya Molibdena" (Analytical Chemistry of Molybdenum), Izd.Akad. Nauk SSSR, Moscow, 1962, p.302.
77. N.S.Sharipova, "Sbornik Rabot po Khimii" (Collected Reports on Chemistry), Min.Vys i Sredn. Spets.Obrazovaniya Kazakh SSR, Alma-Ata, 1973, No.3, p.217.
78. A.I.Busev, V.M.Ivanov, and T.A.Sokolova, "Analiticheskaya Khimiya Vol'frama" (Analytical Chemistry of Tungsten), Izd.Akad.Nauk SSSR, Moscow, 1976, p.240.
79. L.G.Sillén and A.Martel, "Stability Constants of Metal-Ion Complexes", The Chem.Soc., London, Spec.Publ.No.17, 1964.
80. V.I.Spitsyn, A.F.Kuzina, S.I.Zhdanov, and I.V.Kaimin, Zhur.Neorg.Khim., 1970, **15**, 1290 [Russ. J.Inorg.Chem., 1970(5)].
81. T.D.Avtokratova, "Analiticheskaya Khimiya Rutenia" (Analytical Chemistry of Ruthenium), Izd. Akad.Nauk SSSR, Moscow, 1962, p.264.
82. S.I.Ginzburg, K.A.Gladyshevskaya, N.A.Ezerskaya, I.V.Prokof'eva, A.N.Fedorova, O.M.Ivonina, and N.V.Fedorenko, "Rukovodstvo po Analizu Platinovykh Metallov i Zolota" (Manual of the Analysis of Platinum Metals and Gold), Izd.Nauka, Moscow, 1965, p.314.
83. F.E.Beamish, "Analytical Chemistry of the Noble Metals" (Translated into Russian), Izd.Mir, Moscow, 1969, Vol.1, p.297; Vol.2, p.400.
84. S.I.Ginzburg, N.A.Ezerskaya, I.V.Prokof'eva, N.V.Fedorenko, V.I.Shlenskaya, and N.K.Belen'kii, "Analiticheskaya Khimiya Platinovykh Metallov" (Analytical Chemistry of Platinum Metals), Izd. Nauka, Moscow, 1972, p.614.
85. V.M.Vdovenko, L.N.Lazarev, and Ya.S.Khvorostin, Radiokhimiya, 1965, **7**, 232; 1965, **8**, 637.
86. D.L.Furman, Atomic.Abs.Newsletter, 1969, **8**, 105.
87. S.I.Sinyakova, I.V.Markova, and N.G.Galeroyan Trudy Kom. po Anal.Khim.Akad.Nauk SSSR, 1965, **15**, 164.
88. F.Strud, Coll.Czech.Chem.Comm., 1939, **11**, 391.
89. S.I.Sinyakova and Yü-Ch'ih Shên, Dokl.Akad.Nauk SSSR, 1960, **131**, 101.
90. I.M.Kolthoff and I.Jordan, J.Amer.Chem.Soc., 1952, **74**, 570, 4801.
91. I.M.Kolthoff and I.Jordan, Analyt.Chem., 1952, **24**, 1071.
92. V.F.Voropova, N.G.Chovnykh, V.A.Vekslina, and V.V.Vashchenko, Zhur.Anal.Khim., 1970, **25**, 464.
93. A.Kurtenacker and I.Werner, Z.anorg.Chem., 1896, **11**, 111.
94. A.Stachler, Ber., 1904, **37**, 4732.
95. A.Blažek and J.Koryta, Coll.Czech.Chem.Comm., 1953, **18**, 326.
96. A.Călusaru, Isotopenpraxis, 1968, **4**, 401.
97. A.Călusaru, Uspekhi Khim., 1979, **48**, 221 [Russ. Chem.Rev., 1979(2)].
98. A.A.Popel', R.S.Zabbarova, and Z.N.Khazieva, Izv. Vys.Ucheb.Zaved., Khim. i Khim.Tekhnol., 1978, **31**, 855.
99. J.Koryta, Coll.Czech.Chem.Comm., 1954, **19**, 666.
100. V.F.Toropova and A.A.Averko-Antonovich, Zhur. Anal.Khim., 1972, **27**, 116.
101. S.I.Sinyakova and N.K.Stepanova, Zhur.Anal. Khim., 1968, **23**, 1405.
102. P.Szücs and I.Lovasi, Kohašz.lapok, 1965, **8**, 369.
103. Erch-Kang Wang and Wei-Chin Sung, Hua Hsueh Hsueh Pao, 1965, **31**, 384; Chem.Abs., 1966, **64**, 7360.
104. R.U.Vakhobova, E.V.Nikitina, and G.F.Rachinskaya, Dokl.Akad.Nauk Tadzh.SSR, 1975, **18**, 40.
105. G.F.Rachinskaya, R.U.Vakhobova, and Yu.S.Milyavskii, Zhur.Anal.Khim., 1976, **29**, 1482.
106. G.F.Rachinskaya, R.U.Vakhobova, and Yu.S.Milyavskii, Zhur.Anal.Khim., 1976, **29**, 1712.
107. R.U.Vakhobova, G.F.Rachinskaya, F.P.Lykova, and Yu.S.Milyavskii, "VII Vsesoyuznoe Soveshchanie po Polyarografii. Tezisy Dokladov" (The VIIth All-Union Conference on Polarography. Abstracts of Reports), Tbilisi, 1978, p.255.

108. J.M.Saveant and E.Vianello, Electrochim.Acta, 1965, **10**, 905.
109. J.H.Christie and J.Lauer, Analyt.Chem., 1964, **36**, 2037.
110. J.J.Lingane and J.H.Christie, J.Electroanalyt. Chem., 1967, **13**, 227.
111. G.Farnia, G.Sandona, and E.Vianello, J.Electro-analyt.Chem., 1978, **88**, 147.
112. G.M.Panchenkov and V.P.Lebedev, "Khimicheskaya Kinetika i Kataliz" (Chemical Kinetics and Catalysis), Izd.Khimiya, Moscow, 1974, p.592.
113. I.M.Kolthoff, R.Belcher, V.A.Stenger, and G.Matsuyana, "Volumetric Analysis", Vol.III, "Titration Methods: Oxidation-Reduction Reactions" (Translated into Russian), Goskhimizdat, Moscow, 1961, p.840.
114. J.Koryta and I.Tenygl, Coll.Czech.Chem.Comm., 1954, **19**, 839.
115. J.Koryta, Coll.Czech.Chem.Comm., 1955, **20**, 1125.
116. K.Micka, Coll.Czech.Chem.Comm., 1963, **28**, 1978.
117. D.E.Smith, Analyt.Chem., 1963, **35**, 602, 610.
118. Kao Hung, Chang Tsow-shien, and Chang Wen-bin, Scientia Sinica, 1964, **13**, 1411.
119. Chang Tsow-shien, Chen Huog-yan, and Zhow Ziag-dzon, Acta scient.natur.univ.Nankin, 1965, **9**, 80.
120. Kao Hung, Chang Tsow-shien, and Huang Wen-yn, Scientia Sinica, 1965, **14**, 193.
121. G.S.Supin, "Metody Analiza Khimicheskikh Reaktivov i Preparatov" (Methods of Analysis of Chemical Reagents and Preparations), Izd.IREA, Moscow, 1966, No.12, p.132.
122. K.Tanako, K.Mopuhara, and K.Nakaho, J.Chem. Soc.Japan, Pure Chem.Sec., 1965, **90**, 478.
123. K.Nakano, K.Tanako, and X.Myron, Japan.Anal., 1970, **19**, 1680.
124. Ya.I.Tur'yan and E.V.Saksin, Zhur.Anal.Khim., 1970, **25**, 998.
125. E.V.Saksin and Ya.I.Tur'yan, Zhur.Anal.Khim., 1970, **25**, 2362.
126. Ya.I.Tur'yan and E.V.Saksin, Elektrokhimiya, 1971, **7**, 86.
127. E.G.Chikryzova and S.Ya.Mashinskaya, Zhur.Anal. Khim., 1971, **26**, 1105.
128. E.G.Chikryzova and S.Ya.Mashinskaya, Zhur.Anal. Khim., 1972, **27**, 1960.
129. E.G.Chikryzova and S.Ya.Mashinskaya, Zhur.Anal. Khim., 1981, **36**, 1301.
130. E.G.Chikryzova, L.G.Kiriyak, S.Ya.Mashinskaya, and S.M.Bardina, Symposium, "Voprosy Kinetiki i Kataliza" (Problems of Kinetics and Catalysis), Izd. Ivanovsk Politekh.Inst., Ivanovo, 1976, p.42.
131. E.G.Chikryzova and S.Ya.Mashinskaya, Zavod.Lab., 1974, **40**, 1442.
132. E.G.Chikryzova and S.Ya.Mashinskaya, Symposium, "O Povyshenii Chuvstvitel'nosti Polyarograficheskikh Metodov" (The Improvement of the Sensitivity of Polarographic Methods), Izd.Shtiintsa, Kishinev, 1976, p.13.
133. V.F.Toropova and R.S.Zabbarova, Zhur.Anal.Khim., 1970, **25**, 1059.
134. V.F.Toropova, V.A.Vekslina, and N.G.Chovrykh, Zhur.Anal.Khim., 1972, **27**, 346.
135. A.Kh.Miftakhova, R.S.Zabbarova, Z.A.Sabitova, and V.F.Toropova, Izv.Vys.Ucheb.Zaved., Khim. i Khim.Tekhnol., 1976, **19**, 1364.
136. V.S.N.Rao and S.B.Rao, Talanta, 1979, **26**, 502.
137. S.Himeno, Bull.Chem.Soc.Japan, 1976, **49**, 2451.
138. V.S.N.Rao and S.V.Rao, J.Electroanalyt.Chem., 1977, **78**, 379.
139. I.M.Kolthoff and I.Hodara, J.Electroanalyt.Chem., 1963, **5**, 2.
140. I.M.Kolthoff and I.Hodara, J.Electroanalyt.Chem., 1962, **4**, 369.
141. P.Delahey and J.L.Stiehl, J.Amer.Chem.Soc., 1952, **74**, 3500.
142. D.Kyriacon, Analyt.Chem., 1969, **41**, 844.
143. E.G.Chikryzova and L.G.Kiriyak, Zhur.Anal.Khim., 1972, **27**, 1747.
144. L.G.Kiriyak and E.G.Chikryzova, Izv.Akad.Nauk Mold.SSR, Ser.Biol.i Khim.Nauk, 1973, No.2, p.59.
145. E.G.Chikryzova and S.M.Bardina, in "Teoriya i Praktika Polyarograficheskogo Metoda Analiza" (Theory and Practice of the Polarographic Analytical Method), Izd.Shtiintsa, Kishinev, 1973, p.3.
146. S.M.Bardina, E.G.Chikryzova, and I.P.Bersuker, "Tezisy Dokladov XII Vsesoyuznogo Chugaevskogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the XIIth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Novosibirsk, 1973, p.199.
147. E.G.Chikryzova and L.G.Kiriyak, Zhur.Anal.Khim., 1974, **29**, 899.
148. E.G.Chikryzova and S.M.Bardina, Zhur.Anal.Khim., 1974, **29**, 2414.
149. E.G.Chikryzova and L.G.Kiriyak, Zhur.Anal.Khim., 1974, **29**, 2420.
150. E.G.Chikryzova and Nguyan vyon Nam, Zhur. Obshch.Khim., 1974, **46**, 1331.
151. E.G.Chikryzova, L.G.Kiriyak, S.Ya.Mashinskaya, and S.M.Bardina, in "Novosti Polyarografii. Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Polyarografii" (New Developments in Polarography. Abstracts of Reports at the VIth All-Union Conference on Polarography), Izd.Zinatne, Riga, 1975, p.199.
152. S.M.Bardina and E.G.Chikryzova, in "Novosti Polyarografii. Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Polyarografii" (New Developments in Polarography. Abstracts of Reports at the VIth All-Union Conference on Polarography), Izd. Zinatne, Riga, 1975, p.248.
153. E.G.Chikryzova, S.M.Bardina, and G.A.Popovich, Zhur.Obshch.Khim., 1976, **46**, 2317.
154. K.S.Pakhomova and L.P.Volkova, Zhur.Anal.Khim., 1976, **31**, 958.
155. L.G.Kiriyak and E.G.Chikryzova, in "Kinetika i Mekhanizm Geterogennykh i Gomogennykh Khimicheskikh Protsessov" (Kinetics and Mechanisms of Heterogeneous and Homogeneous Chemical Processes), Izd.Shtiintsa, Kishinev, 1977, p.24.
156. S.M.Bardina and E.G.Chikryzova, Zhur.Anal.Khim., 1978, **33**, 358.
157. E.G.Chikryzova and L.G.Kiriyak, "VII Vsesoyuznoe Soveshchanie po Polyarografii. Tezisy Dokladov" (The VIIth All-Union Conference on Polarography. Abstracts of Reports), Tbilisi, 1978, p.255.
158. T.Ya.Belova, L.P.Volkova, and K.S.Pakhomova, Zavod.Lab., 1978, **44**, 1176.
159. R.F.Davletchina, L.A.Vorob'eva, T.Ya.Belova, L.P.Volkova, and R.G.Pats, Symposium, "Nauchnye Doklady Vysshei Shkoly. Biologicheskie Nauki" (Scientific Reports from Higher Educational Establishments. Biological Sciences), 1978, No.11, p.136.

160. S.M.Bardina, E.G.Chikryzova, and V.A.Kovrigin, Zavod.Lab., 1979, **46**, 201.
161. P.M.Zaitsev, S.I.Zhdanov, Z.V.Zaitseva, and T.D.Nikolaeva, Zhur.Anal.Khim., 1980, **25**, 1763.
162. I.M.Kolthoff and J.Hodara, J.Electroanalyt.Chem., 1963, **5**, 165.
163. E.Kh.Gol'dberg and R.F.Davletchina, Symposium, "Metody Analiticheskogo Kontrolya Okruzhayushchei Sredy. Materialy Seminara" (Methods for the Analytical Monitoring of the Environment. Seminar Proceedings), Moskovsk.Dom Nauchno-Tekhn. Propagandy, Moscow, 1980, p.108.
164. P.M.Zaitsev and E.N.Dergacheva, "Metody Analiza i Kontrolya Kachestva Produktsii v Khimicheskoi Promyshlennosti" (Methods of Analysis and Control of the Quality of Production in Chemical Industry), Izd.NIITEKhIM, Moscow, 1980, No.4, p.38.
165. M.K.Murali and S.B.Rao, Z.anal.Chem., 1980, **303**, 121.
166. V.F.Toropova, V.A.Vekslina, S.A.Vashchenko, and L.N.Kitaeva, Symposium, "Novosti Polyarografii. Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Polyarografii" (New Developments in Polarography. Abstracts of Reports at the VIth All-Union Conference on Polarography), Izd.Zinatne, Riga, 1975, p.183.
167. J.Hodara and A.Glasner, Electrochim.Acta, 1970, **15**, 923, 931.
168. V.F.Toropova and O.V.Kopylova, Zhur.Anal.Khim., 1977, **32**, 1159.
169. V.F.Toropova, Yu.N.Polyakova, O.V.Kopylova, and N.I.Filippova, Symposium, "VII Vsesoyuznoe Soveshchanie po Polyarografii. Tezisy Dokladov" (The VIIth All-Union Conference on Polarography. Abstracts of Reports), Tbilisi, 1978, p.247.
170. F.R.Duke and P.R.Qinney, J.Amer.Chem.Soc., 1954, **76**, 3800.
171. V.Holtja and R.Geyer, Z.anorg.Chem., 1941, **246**, 258.
172. G.P.Haight, Jnr., Analyt.Chem., 1951, **23**, 1505.
173. J.B.Jones, Anal.Chim.Acta, 1954, **10**, 584.
174. S.I.Sinyakova and M.I.Glinkina, Zhur.Anal.Khim., 1956, **11**, 544.
175. S.I.Sinyakova and M.I.Glinkina, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the IVth Conference on Electrochemistry), Izd.Akad. Nauk SSSR, Moscow, 1959, p.201.
176. G.P.Haight, Jnr., Acta Chem.Scand., 1961, **15**, 2012.
177. B.Stach and K.Schöne, Microchim.Acta, 1977, 11, 565.
178. G.P.Haight, Jnr. and W.F.Sager, J.Amer.Chem.Soc., 1952, **74**, 6056.
179. G.P.Haight, Jnr., Anal.Chem., 1953, **25**, 642.
180. E.W.Zahow and R.I.Robinson, J.Electroanalyt. Chem., 1962, **3**, 263.
181. H.A.Laitinen and W.A.Ziegler, J.Amer.Chem.Soc., 1953, **75**, 3045.
182. S.Tokio, M.Takahiko, and I.Hitoshi [tentative spelling (Ed. of Translation)], Iron and Steel Inst., Japan, 1964, **50**, 2119; Ref.Zhur.Khim., 1966, 3G118.
183. V.A.Bol'shakov and G.P.Stoilov, Pochvovedenie, 1964(5), 95.
184. V.F.Toropova, Yu.N.Polyakova, O.V.Kopylova, and I.P.Munina, Zhur.Anal.Khim., 1978, **33**, 1370.
185. B.Benesch and R.Benesch, J.Amer.Chem.Soc., 1955, **77**, 5877.
186. M.J.Johnson and R.I.Robinson, Analyt.Chem., 1952, **24**, 366.
187. F.Bauman, J.Electroanalyt.Chem., 1963, **6**, 245.
188. R.E.Hamm and C.D.Witrow, Analyt.Chem., 1955, **27**, 1913.
189. N.Tanaka and T.Ho, Bull.Chem.Soc.Japan, 1966, **39**, 1043.
190. Ya.P.Gokhshtein, "Trudy Komissii po Analiticheskoi Khimii" (Transactions of the Commission on Analytical Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1949, Vol.11(V), p.54.
191. M.L.Nichols and L.H.Rogers, Ind.Eng.Chem.Anal. Ed., 1944, **16**, 137.
192. D.T.Chow and R.I.Robinson, Analyt.Chem., 1953, **25**, 1493.
193. A.T.Violanda and W.D.Cooke, Analyt.Chem., 1964, **36**, 3287.
194. R,U.Bikbulatova and S.I.Sinyakova, Zhur.Anal. Khim., 1964, **19**, 1434.
195. A.V.Sokolov, G.Ya.Suchkova, and L.S.Glazkova, Trudy NII Sintetich.Spirtov i Organich.Produktov., 1974, No.6, 211; Ref.Zhur.Khim., 1975, 15G70.
196. I.M.Kolthoff, W.E.Harris, and G.Matsujama, J.Amer.Chem.Soc., 1944, **66**, 1782.
197. W.E.Harris and I.M.Kolthoff, J.Amer.Chem.Soc., 1945, **67**, 1484.
198. K.Keilin and I.W.Otvos, J.Amer.Chem.Soc., 1946, **68**, 2665.
199. I.W.Collat and J.J.Lingane, J.Amer.Chem.Soc., 1954, **76**, 4214.
200. J.Koryta, Coll.Czech.Chem.Comm., 1955, **20**, 667.
201. G.Jang, W.Ochsenfeld, and F.Habashi, Z.anal. Chem., 1959, **171**, 27.
202. T.Murota, J.Chem.Soc.Japan, Pure Chem.Sec., 1960, **81**, 1240.
203. A.I.Alekperov and S.I.Zhdanov, Zhur.Neorg.Khim., 1960, **5**, 1543 [Russ.J.Inorg.Chem., 1960(7)].
204. T.V.Kalish and A.I.Frumkin, Zhur.Fiz.Khim.,1954, **28**, 473.
205. I.M.Kolthoff and Y.Okinaka, J.Amer.Chem.Soc., 1961, **83**, 47.
206. I.M.Kolthoff and R.Woods, J.Amer.Chem.Soc., 1966, **88**, 1371.
207. R.Woods and I.M.Kolthoff, Analyt.Chem., 1966, **38**, 1297.
208. R.Woods, I.M.Kolthoff, and E.I.Meehan, Inorg. Chem., 1965, **4**, 697.
209. J.Olver and I.Russ, J.Phys.Chem., 1962, **66**, 1699.
210. J.H.Kennedy and K.Iensen, Analyt.Chem., 1965, **37**, 310.
211. S.I.Sinyakova, in "Analiticheskaya Urana" (Analytical Chemistry of Uranium), Izd.Akad.Nauk SSSR, Moscow, 1963, p.165.
212. A.A.Vlček, Coll.Czech.Chem.Comm., 1951, **16**, 465.
213. T.D.Nikolaeva and S.I.Zhdanov, Elektrokhimiya, 1978, **14**, 1127.
214. S.G.Mairanovskii, J.Stradyns, and V.V.Bezuglyi, "Polyarografiya v Organicheskoi Khimii" (Polarography in Organic Chemistry), Izd.Khimiya, Leningrad, 1975, p.352.
215. T.D.Nikolaeva and S.I.Zhdanov, Zhur.Anal.Khim., 1979, **34**, 326.
216. V.P.Smirnov and A.V.Peterburgskii (Editors), "Agrokhimiya" (Agrochemistry), Izd.Kolos., Moscow, 1975, p.512.
217. Annual Fertilizer Review, 1978, FAO, Rome, 1979.
218. I.I.Broomhead,"Recent Chemistry of Nitrogen Fixation", Search, 1975, Vol.6, p.238; Ref.Zhur.Khim., 1976, 1L29.

219. A.E.Shilov, Symposium, "Problemy Khimicheskoi Kinetiki" (Problems of Chemical Kinetics), Izd.Nauka, Moscow, 1979, p.180.
220. M.E.Vol'pin and V.B.Shur, Dokl.Akad.Nauk SSSR, 1964, **156**, 1102.
221. J.Chatt and R.Z.Richard, "The Chemistry and Biochemistry of Nitrogen Fixation", Plenum Press, London, 1971, p.57.
222. A.E.Shilov, Uspekhi Khim., 1974, **43**, 863 [Russ. Chem.Rev., 1974(5)].
223. Hidoi Mesanobu, J.Japan Chem., 1978, **32**, 184; Ref.Zhur.Khim., 1978, 21B1070.
224. S.Kenkichi, Titaniumu Dzirokopiumu, 1978, **26**, 83; Ref.Zhur.Khim., 1978, 20B1172.
225. G.I.Likhtenshtein and A.E.Shilov, Zhur.Fiz.Khim., 1970, **44**, 849 [Russ.J.Phys.Chem., 1970(4)].
226. V.I.Vedeneev, L.V.Gurvich, V.N.Kondrat'ev, V.A.Medvedev, and E.L.Frankevich, Handbook, "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstva k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials and Electron Affinities), Izd.Akad.Nauk SSSR, Moscow, 1962, p.216.
227. Yu.G.Borod'ko and A.E.Shilov, Uspekhi Khim., 1969, **38**, 761.
228. A.D.Allen, R.O.Harris, B.R.Loescher, I.R.Stevans, and R.N.Whiteleg, Chem.Rev., 1973, **73**, 11.
229. L.P.Didenko, A.G.Ovcharenko, A.E.Shilov, and A.K.Shilova, Kinetika i Kataliz, 1977, **18**, 1078.
230. E.E.Van Tamehen and B.Akermarn, J.Amer.Chem. Soc., 1968, **90**, 4492.
231. A.F.Zueva, O.N.Efimov, A.D.Styrkas, and A.E.Shilov, Zhur.Fiz.Khim., 1972, **44**, 760 [Russ. J.Phys.Chem., 1972(3)].
232. S.I.Kulanovskaya, V.N.Tsarev, O.N.Efimov, and A.E.Shilov, "Elektrovosstanovlenie Azota v Gomogennoi Srede, Vklyuthayushchei Ti(III) i Mo(III)" [Electrochemical Reduction of Nitrogen in a Homogeneous Medium Incorporating Ti(III) and Mo(III)], Preprint from the Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka, 1977; Ref.Zhur.Khim., 1978, 3B1408.
233. S.I.Kulanovskaya, V.N.Tsarev, O.N.Efimov, and A.E.Shilov, Kinetika i Kataliz, 1977, **18**, 1045.
234. C.R.Dickson and A.J.Nozik, J.Amer.Chem.Soc., 1978, **100**, 8007.
235. A.E.Shilov, Kinetika i Kataliz, 1970, **11**, 305.
236. N.T.Denisov, N.I.Shuvalova, and A.E.Shilov, Kinetika i Kataliz, 1973, **14**, 1325.
237. N.T.Denisov, A.E.Shilov, N.I.Shuvalova, and T.P.Panova, React.Kinet.and Catal.Letters, 1975, **2**, 237.
238. A.E.Shilov, Symposium, "XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Referaty Dokladov i Soobshchenii" (The XIth Mendeleev Congress on General and Applied Chemistry. Abstracts of Reports and Communications), Izd.Nauka, Moscow, 1975, No.3, p.175.
239. G.I.Likhtenshtein, "XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Referaty Dokladov i Soobshchenii" (The XIth Mendeleev Congress on General and Applied Chemistry. Abstracts of Reports and Communications), Izd.Nauka, Moscow, 1975, No.3, p.182.
240. P.Pelikan, M.Haring, M.Ceppan, and M.Breza, J.Mol.Catal., 1979, **5**, 349.
241. V.V.Strelets, O.N.Efimov, L.A.Nikonova, and Ya.M.Zolotovitskii, "Elektrokhimicheskoe Issledovanie Sistemy V(II)–Pirokatekhin, Vosstanavlivayushchei Molekulyarnyi Azot" [Electrochemical Study of the Molecular Nitrogen Reducing System Vanadium(II)–Catechol], Preprint from the Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka, 1975; Ref.Zhur.Khim., 1976, 10B1511.
242. A.F.Zueva, O.N.Efimov, and V.V.Strelets, Elektrokhimiya, 1979, **15**, 232.

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