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Catalysis of noncomplementary reactions by transition metals clusters. Kinetic description

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The formal kinetics of noncomplementary redox reactions in the coordination sphere of polynuclear complexes is considered. The kinetic descriptions of these processes and noncluster reactions differ substantially. The conditions were revealed under which the intracluster multielectron transformations of the substrate imitate the polymolecular reaction of consumption of one-electron reactants. The number of one-electron reactants in the coordination sphere of the reactive cluster is equal to the first derivative of the phase trajectory of the process with respect to the conversion at the very beginning of the reaction.

Key words: kinetics, noncomplementary processes, clusters, catalysis, polymolecular reaction, phase trajectory.

Many important natural processes are noncomplementary[1] biochemical reactions. For example, the largest-tonnage process of all processes known on the Earth, photosynthesis, includes the reduction of CO_2 with water. About 100 billions of tons of organic matter is annually synthesized due to photosynthesis, and somewhat greater amount of O_2 is released to the atmosphere.[2] Each O_2 molecule is formed by the four-electron oxidation of two H_2O molecules by four rather weak one-electron oxidants $P680^{+\bullet}$ in the oxygen-releasing active center of the enzyme, which contains the cluster of four Mn ions. Another significant natural process is a less scaled reaction of nitrogen reduction in the coordination sphere of the so-called FeMo-coenzyme of nitrogenases containing one Mo ion and seven Fe ions.[3] In this case, 6 electrons (and 6 protons) should be brought to the N_2 molecule to form two NH_3 molecules along with additional two electrons for the conjugated evolution of H_2. As a result, we have the eight-electron reduction of the substrate and 2 H^+ are reduced by eight one-electron reducing agents.[3] Laccase, catalase, and many other redox enzymes can be mentioned, whose necessary part is also the polynuclear metallic cofactor. Biomimetic[4] studies of simpler (compared with enzymes) chemical model systems, which perform main functions of enzymes, are also often carried out using transition metal clusters. For example, the complex containing eight molybdenum ions is used for the catalytic reduction of N_2 with sodium amalgam.[5]

All complicated reactions considered above are noncomplementary because they do not satisfy the principle of equivalent electron exchange (Shaffer's principle[6]). A significant consequence follows from this principle: noncomplementary reactions can be acceler-

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ated by compounds that are capable of simultaneous acting as one- and multielectron oxidants or reducing agents.[7]

The high catalytic activity of enzyme is related, in many cases, to the fact that the active site containing several transition metal atoms serves as a unique switch from the one-electron mechanism to the multielectron mechanism.[8] Noncomplementary processes of multielectron reduction of N_2, O_2, and CO_2 and oxidation of H_2O and many other substrates occur in such a way.[8]

Since polynuclear complexes play such an important role in biochemical and chemical processes, it seems necessary to study their kinetic behavior in homogeneous systems.

In this work, we revealed the main kinetic regularities in multielectron noncomplementary reactions that occur in coordination spheres of binuclear and tetranuclear cluster complexes.

Results and Discussion

The kinetics of consumption of one-electron reactants during multielectron processes can be described by simple equilibria between a polynuclear complex and a medium.[9] From the one side, the transition[9] to the cluster catalyst from the bulky metallic catalyst of noncomplementary processes (macroelectrode[10]) can be performed through a colloidal metallic particle or micelle (microelectrode[11]) by a successive decrease in the size of the catalyst particle, *viz*., a switch for the individual action of several one-electron reactants involved in the same collective multielectron act without escaping intermediate products into the volume.[8]

Now let us attempt to approach the cluster catalyst from another side beginning from the mononuclear complex and gradually increasing its size. Consider the hypothetical redox bimolecular reaction in which two one-electron oxidants A^+ oxidize substrate S by two electrons being reduced to particles A

$$SA^+ + A^+ \xrightarrow{k_2} 2\,A + S_{ox}.$$

As an example, imagine a possible (in principle) oxidation reaction of H_2O_2 to O_2 by two mononuclear Co^{III} complexes. Accept for simplicity that the substrate is localized in the coordination sphere of one of the A^+ complexes. The decay rate of the one-electron oxidant A^+ is described by the law of the bimolecular reaction with the rate constant k_2 (L mol^{-1} s^{-1}). The kinetic curve of the A^+ decay can be linearized in the ($[A^+]^{-1}$, t) coordinates, and the initial reaction rates are proportional to $[A^+]_0{}^2$. Now imagine that all A^+ particles (as well as A) exist in a solution only in the form of dimers $A^+{}_2$ and A_2. Assume that the unification of two A^+ to form the dimer does not result in the complete loss of reactivity of the one-electron oxidants. In this case, in the absence of the feedback (*i.e.*, completely indifferent character of the reaction product A_2), the process is the monomolecular transformation of the S substrate into S_{ox}, and the $(A^+)_2$ dimer is transformed into the A_2 product, which is incapable of further oxidation reactions. Now the kinetic curve of the A^+ decay is rectified in the semilogarithmic coordinates ($\ln[A^+]$, t), and the initial rates of the process w_0 are proportional to $[A^+]_0$. Thus, we see that the kinetic description of substrate oxidation occurring in the coordination sphere of the cluster differs from the kinetics of the standard bimolecular reaction between two kinetically independent A^+ particles.

The kinetics of the cluster noncomplementary reaction stops to be described by the equation of the first order in the presence of the feedback, *i.e.*, the A_2 reaction product is not removed from the game. For the positive feedback, in the general case, autocatalysis should be observed. We do not consider this variant. Different variants are probable for the negative feedback. In fact, A_2 can participate in the redox equilibrium resulting in the deactivation of the active binuclear clusters $(A^+)_2$ by the reaction products

$$(A^+)_2 + A_2 \rightleftharpoons 2\,A^+A \qquad (1)$$

with the equilibrium constant K, which depends on the difference between the redox potentials of the $A^+{}_2/A^+A$ and A^+A/A_2 pairs. The kinetics of the A^+ decay at the fast establishment of equilibrium (1) depends on the K value. At $K = 0$ we have the considered above case of the monomolecular intracluster transformation of the substrate in the absence of the feedback. When $K = 4$, the kinetics of the A^+ decay during one experiment imitates the bimolecular reactions and can be linearized in the ($[A^+]^{-1}$, t) coordinates with the observed reaction rate constant k_1/a, where k_1 is the rate constant (s^{-1}) of monomolecular intracluster transformation in the $(A^+)_2$ dimer, and a is the initial analytical concentration $[A^+]_0$, *i.e.*, the double initial concentration of the $(A^+)_2$ dimers. The initial rates of the process w_0 increase linearly with $[A^+]_0$. Thus, at $K = 4$ the monomolecular transformation in the coordination sphere of the binuclear cluster can mistakenly be taken as the bimolecular reaction of two mononuclear A^+ particles when judging from the kinetic curve of the A^+ decay only. Moreover, if far from all reactant A^+ (as well as product A) is contained in dimers D but only minor its fraction according to the equilibrium $A^+ + A^+ \rightleftharpoons (A^+)_2$ with the low equilibrium constant $K_d = [A^+{}_2]/[A^+]^2$, when $[A^+{}_2]_0$ is approximately proportional to the square of $[A^+]_0$, then the intracluster transformations imitates the simple bimolecular reaction of the A^+ decay by the initial rates as well because $w_0 = k_1[A^+{}_2]_0 = k_1K_d[A^+]_0{}^2 = k_{eff}[A^+]_0{}^2$. In the general case, the rate of substrate transformation is $w = k[(A^+)_2]$. Thus, depending on the K in equilibrium (1), different kinetic curves are observed. The phase trajectory of the process can be calculated for each K value.[12]

Such phase trajectories[12] of the A^+ consumption during the decomposition of the active binuclear com-

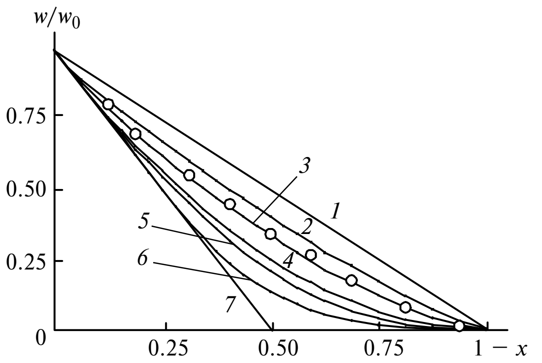

Fig. 1. Phase trajectories of the reactant decay during the process in the coordination sphere of the dimeric complex. The curves were calculated for *K*: 0 (*1*), 0.25 (*2*), 1 (*3*), 4 (*4*), 8 (*5*), 40 (*6*), and 10000 (*7*). Experimental points correspond to water oxidation with the Co^{3+} ions and were taken from Ref. 14; $1 - x$ is the conversion, w/w_0 is the relative rate, and w_0 is the initial reaction rate.

plex $(A^+)_2$ at different numerical values of the *K* equilibrium constant (equation (1)) are presented in Fig. 1. The phase plane[12] is presented in the coordinates: conversion $(1 - x)$—relative rate of the process w/w_0. In order to determine the concentration of the $(A^+)_2$ active complex, use two balance equations for the oxidant and its reduced form during the whole process: $ax = 2(A^+)_2 + AA^+$ and $a(1 - x) = 2A_2 + AA^+$ and equilibrium (1) with different *K*. These three equations determine completely three concentrations of dimers with different compositions at any conversion. To simplify calculations, we accept that almost all reactant is contained in the D dimers. If not, the solution does not qualitatively change, and only quantitative changes appear, which can be reflected by the replacement of *K* by the "effective" constant K_{eff}. The phase trajectory for the standard bimolecular reaction coincides with curve *4* (Fig. 1). Curve *4* (Fig. 1) corresponds to the statistically equiprobable binomial distribution of A^+ and A in the dimers (in this case, $K = 4$). For this particular case, the kinetic curve of consumption of the one-electron oxidant A^+ is described to the end of the reaction by the law of a bimolecular process $[A^+]^{-1} = (k/a)t + \text{const}$. In all other cases, the phase trajectories and kinetic curves of the A^+ decay during intracluster substrate transformation differ from the standard bimolecular process. At very low *K* values (for example, at $K = 0.01$), the consumption of $[A^+]$ during the decomposition of active D dimers is described quite satisfactorily by the law of a first order, except for the short initial region of the phase trajectory (and of the kinetic curve). Straight line *1* (Fig. 1) corresponds to the standard monomolecular reaction. The same straight line corresponds to the cluster transformation of D with $K = 0$ when the mixed-valence D complex is not formed at all. At very high *K* (line *7*), the kinetics of the A^+ decay is monomolecular again. However, in this case, the process stops after only a half of the oxidant is transformed because the reaction rate tends to zero as the *x* conversion approaches 0.5. Thus, the phase trajectories for the intracluster two-electron process can cover the region between lines *1* and *7* on the phase plane (depending on the *K* value), whereas the bimolecular reaction is described by the single curve *4*. It is seen that the kinetic behavior of the cluster process is much more diverse. For the whole beam of phase trajectories, the derivative of the relative rate with respect to conversion $(1 - x)$ at the beginning of the process ($x = 1$) equals two, *i.e.*, the number of oxidative equivalents in the binuclear D cluster. The phase trajectories allows one to establish the composition of the decayed cluster but cannot provide an information on the reaction rate constant, which can be obtained only by the integral (*i.e.*, kinetic) curve.

For the description of the kinetics of the acceptor decay, the dependence of the concentration of active dimers on $[A^+]$ should be expressed in the analytical form and then the equation of the reaction rate should be integrated. As a result, we obtain the kinetic curve, which is not consistent with either the bimolecular or monomolecular reaction in common meaning. For example, at $K = 1$ the kinetic curves of the oxidant consumption during the monomolecular D decay should be described by a linear anamorphosis in the following form[13]: $\varphi = 8k_0t + \text{const}$, where $\varphi(x) = x^{-1}\{1 + 4(\alpha - \beta)^{-1}[(\alpha - x)(x - \beta)]^{1/2}\} + 8(\alpha - \beta)^{-1}\text{arctg}[(x - \beta)/(\alpha - x)]^{1/2} + 6\ln\{(x - \beta)^{1/2} + [\beta(\alpha - x)/\alpha]^{1/2}\} - 6\ln x\{(x - \beta)^{1/2} - [\beta(\alpha - x)/\alpha]^{1/2}\}$, $\alpha = 1.07735$, and $\beta = -0.07735$. At other *K* values, the different analytical expressions are obtained for the linear anamorphoses and kinetic curves $[A^+] = f(t)$. Experimental data on the reduction of $(Mn^{4+})_2$ accompanied by O_2 evolution in very dilute (<0.003 *M*) solutions of Mn^{IV} agree well with the linear anamorphosis presented above. Using the tangent slope of $\varphi(x)$, one can easily determine the k_0 rate constant of the monomolecular decay of the bimolecular cluster, whose pre-exponent turned out to be close to a standard value of 10^{13} s^{-1}.

The circles in curve *3* (Fig. 1) were put according to experimental data.[14] The experimental points for H_2O oxidation with the binuclear $(Mn^{4+})_2$ complexes obey well the same curve. The authors[14] explained the kinetics of the Co^{3+} acceptor consumption during water oxidation by the collective action of the $(Co^{3+})_2$ dimeric particle and Co^{3+} on water. The good agreement of the experimental data with curve *3* (Fig. 1) shows that the two-electron oxidation of water to H_2O_2 occurs in fact (the derivative of the phase trajectory equal to 2 at the beginning of the reaction indicates the combined action of two acceptors).

If the dimers cannot react directly with each other and, hence, the *K* equilibrium constant is not rigidly specified by the difference of redox potentials of the $A^+{}_2/A^+A$ and A^+A/A_2 pairs, we can expect the binomial distribution of A^+ and A over D, that is, the formal kinetics of the A^+ decay according to the law of a bimolecular reaction. An example is the reduction of superoxide dismutase in an excess of H_2O_2,[15] which is well described to 90% conversion by the law of a bimolecular reaction. Although it has been found that all binuclear clusters of the manganese ions contained in the cofactor of this enzyme have the same redox potentials,[16] which should finally result[13] in $K = 1$ at the fast establishment of internal redox equilibria (1), the kinetics of the process agrees with $K = 4$. It is most likely that the protein globules prevent mutual contacts of the binuclear prosthetic groups of Mn_2, which does not allow internal equilibria to be established. In this case, the composition of the cluster (the oxidant distribution over dimers) depends on the composition of the medium, and $K = 4$ can be obtained.

Now let us consider the hypothetical multielectron process due to which several one-electron acceptors oxidize a molecule (several molecules) of the substrate to the final product, *e.g.*, four-electron oxidation of H_2O. We accept again that the substrates are coordinated by the cluster ions

$$4\,Fe^{3+} + 2\,H_2O \longrightarrow 4\,Fe^{2+} + O_2 + 4\,H^+.$$

The iron ions indicated in the equation can enter the composition of any compounds (hydroxo complexes, complexes with different ligands), so that the superscript figures correspond to the oxidation state of iron in the cluster rather than its charge. Even ignoring water taken in a great excess, to perform the reaction according to the formal kinetics,[17] four Fe^{3+} ions must collide. However, the probability of this collision is very low.[18] The reaction can proceed *via* the different path, namely, by the decomposition of the tetranuclear complex (T) to the O_2 molecule, four protons, and the reduced inactive cluster

$$(Fe^{3+})_4 \cdot 2\,H_2O \longrightarrow (Fe^{2+})_4 + O_2 + 4\,H^+.$$

In this process, the catalyst-switch $(Fe^{3+})_4$ should surmount Shaffer′s prohibition and also Wigner—Witmer prohibition because this reaction is spin-forbidden (the oxygen molecule with spin 1 is formed of two water molecules with the zero spin).

As a result of the fast exchange with the medium containing the Fe^{3+} and Fe^{2+} species, inactive $(Fe^{2+})_4$ can be transformed again (with some probability) into active $(Fe^{3+})_4$ (external equilibrium[9]). The decomposition of active T with O_2 evolution is repeated, *etc.* Of the full set of T: $(Fe^{3+})_4$, $(Fe^{3+})_3Fe^{2+}$, $(Fe^{3+})_2(Fe^{2+})_2$, $Fe^{3+}(Fe^{2+})_3$, and $(Fe^{2+})_4$, only the first one is active because it contains the number of Fe^{3+} necessary for the four-electron process to occur. Therefore, to determine the process rate, we have to calculate $[(Fe^{3+})_4]$. When the Fe^{3+} and Fe^{2+} ions enter T statistically equiprobably, the composition of the ensemble of tetramers is determined by the binomial distribution (the problem about black and white balls[19]) $C_4{}^m x^m (1 - x)^{4-m}$, where $x = [Fe^{3+}]/([Fe^{3+}] + [Fe^{2+}])$, and the fraction of active T is equal to x^4 ($m = 4$). Thus, the reaction rate is proportional to the fourth power of $[Fe^{3+}]$, *i.e.*, in this case, the decomposition of T imitates the tetramolecular reaction according to Van′t Hoff[17] of the consumption of the one-electron oxidant $-dx/dt = kx^4$.

The binomial distribution can be violated strongly by disproportionation reactions between various T in the ensemble of tetramers. The complete scheme of the equilibria of tetramers can be presented in the following form (A^+ is the one-electron oxidant as in the case of dimers):

$$\begin{tikzcd}
A^+ + A_i{}^+A_{4-i} \arrow[r, rightleftharpoons] \arrow[d, rightleftharpoons, "-A_j{}^+A_{4-j}"', "A_j{}^+A_{4-j}"] & A^+{}_{i+1}A_{3-i} + A \arrow[d, rightleftharpoons, "-A_j{}^+A_{4-j}"', "A_j{}^+A_{4-j}"] \\
A^+{}_{i-1}A_{5-i} + A^+{}_{j+1}A_{3-j} & A_i{}^+A_{4-i} + A^+{}_{j+1}A_{3-j}
\end{tikzcd}$$

The first raw corresponds to the external[9] equilibria of the $A_i{}^+A_{4-i}$ tetramers with a "potentiostat" of the components of the A^+/A redox pairs and/or other polynuclear complexes (except T). The vertical equilibria are related to the redox reactions between the $A_j{}^+A_{4-j}$ tetramers themselves (internal equilibria in the T ensemble). In this case, to calculate phase trajectories, we used two equations of balance:

$$ax = 4(A^+)_4 + 3(A^+)_3 + 2(A^+)_2A_2 + A^+A_3,$$

$$a(1 - x) = 4A_4 + 3A_3A^+ + 2(A^+)_2A_2 + A(A^+)_3$$

and three internal equilibria:

$$(A^+)_4 + (A^+)_2A_2 \rightleftharpoons 2(A^+)_3A\ (K_{42}),$$

$$(A^+)_4 + A_4 \rightleftharpoons 2(A^+)_2A_2\ (K_{40}),$$

$$(A^+)_4 + A^+A_3 \rightleftharpoons (A^+)_3A + (A^+)_2A_2\ (K_{41}).$$

Here $x = [A^+]/([A^+] + [A])$ is the fraction of the oxidant in the mixture, and $a = [A^+] + [A]$. The combined solution of these 5 equations at the $(1 - x)$ conversion allows us to determine the concentrations of all tetramers and relative rates. The whole phase trajectory at a fixed set of the K_{ij} equilibrium constants is thus calculated. Six intracluster equilibria are possible in the T ensemble; however, 3 of them are the products of three others. Therefore, any 3 equilibria can be chosen from the K_{ij} set. To simplify the calculation, we accepted that almost all reactant enters the composition of T, *i.e.*, only the internal equilibria are taken into account without the influence of the external equilibria (the first raw of the general scheme). In calculation all K_{ij} equilibrium constants were taken as equal (also for simplification), except for curve *5* (Fig. 2) corresponding to the binomial distribution of A^+ and A over T. In this case, the equilibrium constant have the values $K_{42} = 8/3$, $K_{41} = 6$, and $K_{40} = 16$. It is difficult to distinguish the decay of T at very low K_{ij} from the standard monomolecular reaction of A^+ (curve *2* and straight line *1* in Fig. 2, respectively). At very high K_{ij}

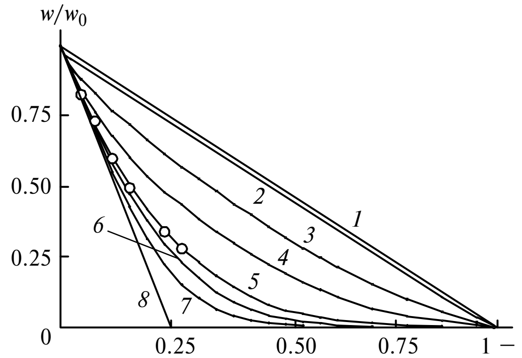

Fig. 2. Phase trajectories of the one-electron reactant decay during the four-electron process in the coordination sphere of the tetranuclear cluster. The curves were calculated for K_{ij}: 0 (*1*), 0.1 (*2*), 0.5 (*3*), 1 (*4*), binomial distribution (*5*), 4 (*6*), 10 (*7*), and 10000 (*8*). Experimental points correspond to water oxidation to O_2 with the $(Mn^{4+})_4$ clusters and were taken from Ref. 9.

the decomposition of $(A^+)_4$ is also described by the law of a monomolecular reaction (line *8*) but the process stops after 25% conversion of the oxidant is achieved. These limiting values are similar to those for the binuclear complexes (see above). For all phase trajectories $dw/dx = 4$ at $x = 1$, which indicates the number of oxidant in the active cluster $(A^+)_4$, *i.e.*, 4. Experimental data on water oxidation with the $(Mn^{4+})_4$ tetramers (circles in curve *5*) imitate the tetramolecular reaction according to Van't Hoff. Recall that water was oxidized by the D clusters in a strongly dilute solution where T was absent (see above). Under those conditions, each Mn^{IV} complex acted as a two-electron oxidant, and each Mn^{IV} ion in the tetramers is the one-electron oxidant. Only the dw/dx derivatives allowed us to establish this fact because H_2O was oxidized with the clusters to O_2 by four electrons in both cases. In the dimers, only two two-electron acceptors were enough for this, whereas in the tetramers this reaction is performed by 4 one-electron oxidants (the same Mn^{IV} ions). The experimental data on dihydrogen evolution in the chemical model of nitrogenase, V^{II}—di-*tert*-butylpyrocatechol,[20] in the absence of N_2 obey well curve *5*.

The anamorphosis of the kinetic curve can be calculated for T as for the dimers to determine the rate constant of the decay of the one-electron reactant. This calculation was performed at $K_{ij} = 1$. However, the expression of the linear anamorphosis for T is too cumbersome to be presented here. We see that the phase trajectories can answer, under some conditions, the question about the composition of the reactive cluster, which cannot be understood using kinetic curves and their linear anamorphoses. Thus, in the case of cluster catalysis of noncomplementary reactions, analysis of the phase trajectories in the w/w_0—$(1 - x)$ coordinates can provide an additional information about the process compared to analysis of kinetic curves only.

Note that when nitrogen is reduced in the vanadium(II)—di-*tert*-butylpyrocatechol system, the kinetics of ammonia formation imitates the octamolecular reaction,[20] whereas in the vanadium(II)—pyrocatechol system this kinetics is not observed. In the latter case, the phase trajectory shows that the octanuclear clusters have the same redox potentials and $K_{ij} = 1$. Evidently, the di-*tert*-butylpyrocatechol complexes should also have equal redox potentials and, hence, all constant should be equal to 1. However, due to the much slower process in this system, the sufficiently weak interaction of the active clusters with the medium results in the transition of priority from internal equilibria between the octamers themselves to external equilibria. The first derivatives of the phase trajectories are equal to eight in both cases. This indicates that in both systems the formation of ammonia molecules occurs in the coordination sphere of the octanuclear clusters. The most exciting in this process is the fact that in such a simple model of nitrogenase, as in the enzyme itself, the formation of the hydrogen molecule is conjugated with that of ammonia.

Evidently, the simplest model of reactants as elastic balls cannot be accepted for the explanation of intracluster transformations. By contrast, the collision of particles should be accompanied by a more or less long coexistence. The corresponding steric and other changes should occur within some average lifetime in the cluster of the necessary number of molecules of the reactants and substrate (naturally, when the energy storage is sufficient for surmounting the potential barrier in the way to the final state of the system). These changes will finally result in the formation of the product from the substrate. Thus, the reactive cluster of several one-electron reactants can be considered as the "frozen" encounter complex (FEC), *i.e.*, the stark analog of the encounter complex in the habitual formal kinetics. When the lifetime of FEC is very short, we can expect only bimolecular reactions, and the finite lifetime of FEC is needed for trimolecular processes to occur. Even bimolecular processes often require a sufficient time interval for changes necessary for the reaction. These are enzymatic processes in which the substrate should exist in a complex with the enzyme during the time of an order of milliseconds.[21] Unlike enzymatic catalysis where the lifetime of the enzyme-substrate complex is important, we analyzed the cases where the substrate exists for a rather long time in the coordination sphere of the cluster. The composition of the cluster itself, unlike the enzyme, changes during the process, which we had to take into account. The kinetic description of the process will be much more complicated if the substrate-cluster lability is supplemented to changes in the reactivity of the active sites.

Analysis of the kinetics of the consumption of one-electron (or two-electron) oxidants (reducing agents) in cooperative processes allows us to formulate the following statements.

1. For multielectron redox reactions in the coordination sphere of the polynuclear complex, the number

of oxidants (reducing agents) is equal to the first derivative of the phase trajectory in the (w, $1 - x$) coordinates in the very beginning of the process ($x = 1$).

2. When the statistically binomial distribution is fulfilled in an ensemble of n-meric clusters, the monomolecular decomposition of the n-mer imitates the formal n-molecular kinetics of oxidant (reducing agent) decay.

It is quite clear that these assumption are realized only in the presence of the negative feedback, *i.e.*, the inhibition of the reaction by the products, and at promptly established equilibria (compared to the half-life).

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