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Kinetics of Concerted Processes Occurring in the Coordination Sphere of Polynuclear Complexes

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Abstract—The formal kinetics of concerted processes that occur in the coordination sphere of polynuclear complexes is considered. The kinetics of consumption of one-electron oxidants or reducing agents in many-electron oxidation (reduction) reactions catalyzed by clusters mimics the kinetics of a polymolecular reaction in specific cases. These reactions are analyzed for clusters with different numbers of nuclei, and a comparison with the experimental data is made.

Clusters play a key role in many processes, and their nature has always been of interest to researchers [1, 2]. One example is the catalytic dimerization of ethylene in the presence of the homogeneous tetrabutoxytitanium–triethylaluminum Ziegler catalyst. In this system, a binuclear active center of the catalyst $(L_zTi)_2$ is required for the simultaneous activation of two ethylene molecules that are converted into 1-butene [3]. Another example is the catalytic isomerization of 3,4-dichlorobutene to 1,4-dichlorobutene, which takes place in the coordination sphere of a tetranuclear Fe(III) cluster [4]. A number of analogous concerted reactions can also be cited [5]; however, much more examples can be found among many-electron redox reactions [6].

In many instances, a high catalytic activity of enzymes is associated with the fact that an active center containing several transition metal ions serves as a “switch” from one-electron to many-electron mechanisms [6]. This makes it possible to perform hindered (the Shaffer principle [7]) and noncomplementary [8] redox reactions of many-electron reduction of N_2, O_2, and CO_2 [6] or oxidation of H_2O [6, 9].

In this work, the kinetics of many-electron redox processes occurring in the coordination sphere of a cluster is analyzed.

Let us consider a many-electron process where several one-electron acceptors oxidize a substrate molecule (or several molecules) to a final product, for example, the four-electron oxidation of water to molecular oxygen with the one-electron oxidant A^+:

$$4A^+ + 2H_2O \longrightarrow 4A + O_2 + 4H^+.$$

This reaction has been studied earlier in the presence of the compounds of Co(III), Ag(II), Fe(III), Ce(IV), and other metals. In addition to cations, uncharged species, such as hydroxo complexes, or anions (for example, MnO_4^-) can serve as A^+. In terms of formal kinetics [10], the rate of this polymolecular reaction is expressed as $w = k[A^+]^4[H_2O]^2$. Even without considering water taken in a large excess, a collision of four A^+ species is required for the reaction. However, tetramolecular reactions do not exist because the probability of such a collision is extremely low [5]. Consequently, the processes of this kind should be explained in different way.

When two electron acceptors collide, a relatively long-lived dimer $(A^+)_2$ can be formed. It has corresponding counter-ions if it is charged. The sequence of several inelastic collisions results in a cluster (or a quasi-molecule) containing a required amount of reactants for a concerted process if other necessary conditions (energy and orientation) are met. Thus, we obtain a “frozen” collisional complex, which plays a key role in the reaction. The lifetime of this complex can be sufficiently long and it may wait for other conditions to be met. If such clusters are not formed spontaneously, the addition of specially synthesized polynuclear complexes makes it possible to catalyze uncomplementary reactions.

For the process of water oxidation by $(A^+)_2$ ions under discussion, the formation of a tetranuclear complex (T) is conceivable. This complex contains water and undergoes decomposition to release an O_2 molecule and four protons: $(A^+)_4 \cdot 2H_2O \longrightarrow A_4 + O_2 + 4H^+$. As a result of rapid exchange with the medium that contains both A^+ and the reduction product A, the inactive A_4 can be converted again into the active $(A^+)_4$ (nanoelectrode equilibrium [9]). To determine the rate of the process, $(A^+)_4$ should be calculated [9]. If the mononuclear species A^+ and A are statistically equiprobable constituents of T, the composition of a tetramer ensemble is described by the ordinary binomial distribution (the problem of black and white balls [12]) $C_4^m x^m(1 - x)^{4-m}$, where C_4^m is the binomial coefficient and m, a $x = [A^+]/([A^+] + [A])$, and the fraction of active T is equal to x^4 ($m = 4$). Thus, because the sum a of the oxidized and reduced forms of the oxidant is constant in

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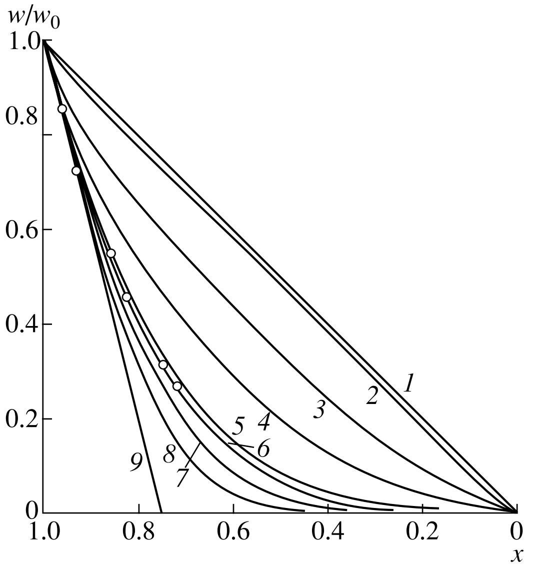

Fig. 1. Phase trajectories of consumption of a one-electron reactant in the four-electron process performed in the coordination sphere of a tetranuclear cluster. The curves were calculated for $K_{i,j}$ equal to (*1*) 0, (*2*) 0.1, (*3*) 0.5, (*4*) 1, (*5*) 2, (*7*) 4, (*8*) 10, or (*9*) 10 000, and (*6*) for a binomial distribution. Experimental points correspond to the oxidation of water by $(Mn^{4+})_4$ clusters to O_2 [9].

the course of the overall process, the reaction rate is proportional to the fourth power of $[A^+]$; that is, in this case, the unimolecular dissociation of tetramers T simulates a tetramolecular reaction $-dx/dt = kx^4$ [10]. The tetranuclear cluster $(A^+)_4$ is a "frozen" collisional complex of four A^+ one-electron oxidants.

The binomial distribution in tetramers, imposed by a "potentiostat" of A^+ ions and A (external equilibrium), can be noticeably distorted by disproportionation reactions between different T species (internal equilibrium). The entire scheme of the equilibria can be represented as follows (for simplicity, ligands are everywhere omitted):

$$\begin{tikzcd}
A^{+} + \overset{+}{A}_{i}A_{4-i} \arrow[r, shift left] \arrow[d, shift left, "\overset{+}{A}_{j}A_{4-j}"] & \overset{+}{A}_{i+1}A_{3-i} + A \arrow[l, shift left] \arrow[d, shift left, "\overset{+}{A}_{j}A_{4-j}"] \\
\overset{+}{A}_{i-1}A_{5-i} + \overset{+}{A}_{j+1}A_{3-j} \arrow[u, shift left, "-\overset{+}{A}_{j}A_{4-j}"] & \overset{+}{A}_{i}A_{4-i} + \overset{+}{A}_{j+1}A_{3-j} \arrow[u, shift left, "-\overset{+}{A}_{j}A_{4-j}"]
\end{tikzcd}$$

Here, only the equilibria of T species with each other and monomers from the medium are considered without regard for equilibria between different *n*-mers (for example, between T and dimers or trimers). The first line corresponds to a nanoelectrode [9] (external) equilibrium of tetramers with the "potentiostat" of components of the A^+/A redox pair. The vertical equilibria are associated with redox reactions between the tetramers.

To describe the kinetics of the process, the concentration of the active tetramers $(A^+)_4$ should be known. In the subsequent discussion, it will be more convenient to deal with phase trajectories rather than integral curves that describe the changes in $[A^+]$ with time. Recall that a phase trajectory is a mapping of the kinematic behavior of an autonomous dynamic system in the $\{m\mathrm{d}x/\mathrm{d}t, x\}$ coordinates [13]. In the case under consideration, the relative rate w/w_0 of chemical reaction and the molar fraction x were chosen as coordinates.

Figure 1 demonstrates the phase trajectories of the consumption of A^+ in the decomposition of T. The curves were calculated using two balance equations

$$ax = 4[(A^+)_4] + 3[(A^+)_3A] + 2[(A^+)_2A_2] + [A^+A_3]$$

and

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

and three equilibria (with the equilibrium constants $K_{i,j}$): $(A^+)_4 + (A^+)_2A_2 \rightleftarrows 2(A^+)_3A(K_{4,2})$, $(A^+)_3A + A_3A^+ \rightleftarrows 2(A^+)_2A_2(K_{3,1})$, and $A_4 + (A^+)_2A_2 \rightleftarrows 2A_3A^+(K_{2,0})$; in the balance equations, $x = [A^+]/([A^+] + [A])$ is the fraction of the oxidant in the mixture and $a = [A^+] + [A]$. For simplicity, the oxidant and its reduced form are considered to belong almost completely to T. Otherwise, the solution is analogous; however, an ensemble of tetramers is considered with due regard to correction factors, and the parameter a is only a fraction of the initial $[A^+]$. In the calculation of curves shown in Fig. 1, all of the three equilibrium constants $K_{i,j}$ were taken equal, except for curve *6*, which corresponds to the binomial distribution of A^+ and A over T (in this case, $K_{4,2} = K_{2,0} = 8/3$ and $K_{3,1} = 9/4$ [12]). It is difficult to distinguish between the dissociation of tetramers at very low $K_{i,j}$ from an ordinary unimolecular reaction of A^+ (in Fig. 1, curve *2* with $K_{i,j} = 0.1$ and straight line *1* with $K_{i,j} = 0$, respectively). This is clear because tetramers behave as independent species whose properties are unaffected by the reaction products. Phrased simpler, the insertion of the reaction products A into $(A^+)_4$ does not damage these reactive species in this particular case. At very high $K_{i,j}$, the dissociation of $(A^+)_4$ is also described by a unimolecular reaction rate law (straight line *9*); however, the process was stopped after the conversion of a quarter of the oxidant. The reaction did not proceed to a deeper degree, because 25% of the A species formed poison the remainder 75% oxidant by uniformly distributing over tetramers. It is clear that a quarter of the reactant will be converted only if it completely enters into the composition of tetramers. However, if the fraction of T in the reaction mixture is small, a small amount of the reduced acceptor suffices to deactivate them. Under these conditions, the conversion will be much lower than 25% (self-poisoning by a reaction product). The displaying point will move from the point (1, 1) of the phase plane to a small distance along the phase trajectory during the whole reaction time.

For all phase trajectories, $\mathrm{d}w/\mathrm{d}x = 4$ at $x = 1$, i.e., at the zero conversion; this is indicative of the number of oxidants in an active cluster $(A^+)_4$ equal to 4. The experimental data on water oxidation by the tetramers

$(Mn^{IV+})_4$ (circles in curve *6*) mimics a tetramolecular reaction although quaternary collisions do not occur. The fact that the binomial distribution of Mn^{IV+} and Mn^{III+} ions is retained in manganese tetramers is associated with the circumstance that external equilibria are attained in this system much more rapidly than internal equilibria. This is favored in part by the fact that the oxidant is far from being completely present in tetramers; a considerable amount of manganese is also incorporated into dimers [9].

The reactions of dimers (D) can be described similarly. In this case, the two balance equations for ions $(A^+)_2$ and $ax = 2[(A^+)_2] + [AA^+]$ and the sole internal equilibrium $a(1 - x) = 2[A_2] + [AA^+]$ are used to determine the concentration of the active complex $(A^+)_2 + A_2 \rightleftarrows 2AA^+(K)$. Once again, for simplicity, we assume that almost all A^+ ions and A occur in dimers. Curve *5* in Fig. 2 corresponds to a binomial distribution of A^+ and A in dimers ($K = 4$). In this case, the kinetic curve of consumption of the oxidant A^+ is described by the ordinary bimolecular reaction rate law $[A^+]^{-1} = (k/a)t + \text{const}$ up to completion of the reaction. The only difference is that the observed reaction rate constant is equal to the rate constant of unimolecular dissociation of the dimer divided by the initial concentration of the one-electron oxidant. Only this fact makes it possible to distinguish a classical bimolecular reaction from cluster catalysis in the case when the concentration of dimers is extremely low and is described by the quadratic function $[(A^+)_2] = K_d[A^+]^2$, which follows from the equilibrium $A^+ + A^+ \rightleftarrows (A^+)_2$. In this case, not only the kinetic curve of consumption of A^+, but also the initial rates are described by a bimolecular reaction rate law. However, if [D] is high, the initial rates of the reactions under consideration are linear rather than quadratic functions of $[A^+]_0$.

At very low values of K, the dissociation of D is adequately described by a rate law of unimolecular reaction (Fig. 2, straight line *1*, when $K = 0$, and the mixed dimer AA^+ is not formed). At very high values of K (Fig. 2, straight line *8*), the kinetics also corresponds to a unimolecular reaction; however, in this case, the process is terminated after the consumption of a half of the oxidant. As in the case of tetramers, under these conditions, the unimolecular reaction of dimers will terminate well before, if the oxidant is far from being completely incorporated into the dimers.

For the entire bundle of phase trajectories, the derivative of the relative rate with respect to the conversion at the beginning of the process ($x = 1$) is equal to two, i.e., the number of oxidizing equivalents in the active D species.

In some cases, the distribution of the acceptor over dimers is described by the equilibrium constant $K = 1$, which results from the equality of the redox potentials of the pairs $(A^+)_2/AA^+$ and AA^+/A_2. Indeed, the equilibrium $(A^+)_2 + A_2 \rightleftarrows 2AA^+$ is a redox process, the free Gibbs energy of which is related to the oxidative potentials of the above pairs by the following simple expression: $\Delta G = RT\ln K = n_e F(E'_2 - E'_1) = 0$ and $K = 1$. In this expression, n_e is the number of transferred electrons, and F is the Faraday constant. To obtain the kinetic curve of acceptor consumption, the concentration of active dimers should be expressed as a function of $[A^+]$; next, the rate equation should be integrated in t. As a result, a kinetic curve is obtained, which is inconsistent with either a bimolecular or a unimolecular reaction. For example, at $K = 1$, the kinetic curves of consumption of a one-electron or two-electron oxidant in the dissociation of D are described by the linear anamorphosis $\varphi = 8k_0t + \text{const}$, where $\varphi(x) = x^{-1}\{1 + 4(\alpha - \beta)^{-1}[(\alpha - x)(x - \beta)]^{1/2}\} + 8(\alpha - \beta)^{-1}\arctan[(x - \beta)/(\alpha - x)]^{1/2} + 6\ln\{(x - \beta)^{1/2} + [\beta(\alpha - x)/\alpha]^{1/2}\} - 6\ln x\{(x - \beta)^{1/2} - [\beta(\alpha - x)/\alpha]^{1/2}\}$, $\alpha = 1.07735$, and $\beta = -0.07735$ (see Appendix). Experiments on the decomposition of $(Mn^{4+})_2$ are consistent with this relationship [9]. In this reaction, two two-electron oxidants (Mn^{4+}/Mn^{2+}) in an active dimer perform the four-electron oxidation of water.

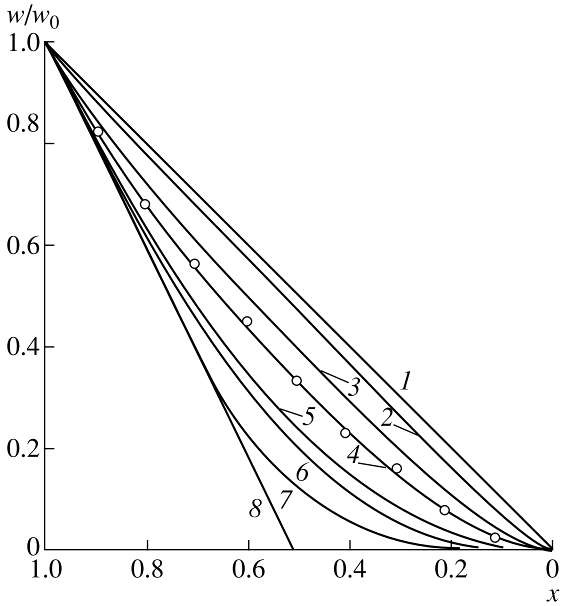

Fig. 2. Phase trajectories of consumption of the reactant in the process performed in the coordination sphere of a dimer complex. The curves were calculated for K equal to (*1*) 0, (*2*) 0.01, (*3*) 0.25, (*4*) 1, (*5*) 4, (*6*) 8, (*7*) 40, and (*8*) 10 000. Experimental points correspond to the oxidation of water by Co^{3+} ions [14].

Points in curve *4* (Fig. 2) are plotted in accordance with the experimental data published in [14]. Baxendale and Wells [14] explained the consumption of the acceptor Co^{3+} in water oxidation by the collective interaction between the dimeric $(Co^{3+})_2$ species and the Co^{3+} ion (three-electron oxidation of water to the $HO_2^{\bullet}$ radi-

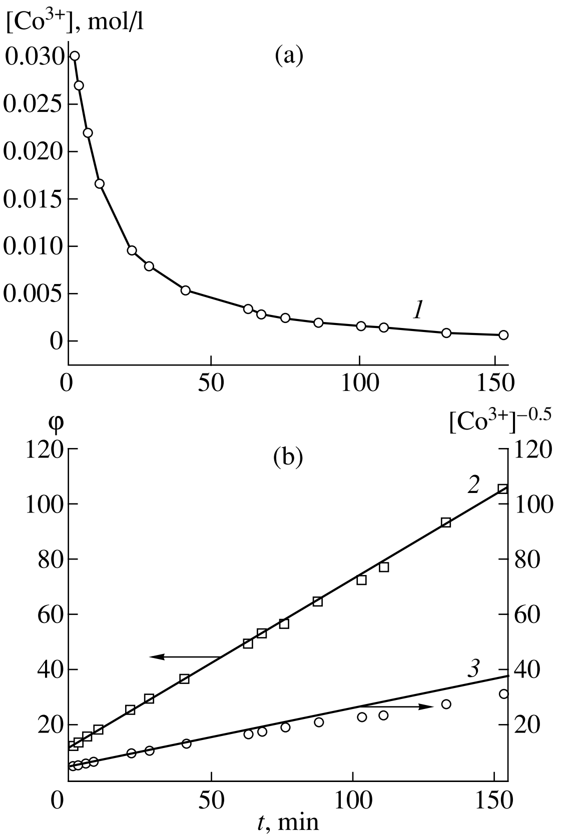

Fig. 3. (a) (*1*) Kinetic curve of consumption of Co^{3+} ions and (b) its linear anamorphoses in the (*2*) $\{\varphi(x), t\}$ and (*3*) $\{[Co^{3+}]^{-1/2}, t\}$ coordinates. Experimental data were taken from [14].

cal). Many researchers agreed on this explanation, even with some uncertainties. However, a good agreement between the experimental data [14] and curve *4* in Fig. 2 demonstrates that the two-electron oxidation of water to H_2O_2 really occurs (at $K = 1$) at the rate-limiting step of the process (the derivative of the phase trajectory at $x = 1$ is indicative of the combined effect of two acceptors). Thus, the derivative of the phase trajectory at $x = 1$ corresponds to the number of oxidant atoms in an active cluster rather than to the number of transferred electrons.

Figure 3 (straight line *2*) shows a linear anamorphosis of the kinetic curve of consumption of Co^{3+} ions in the $\{\varphi, t\}$ coordinates, which was plotted using the experimental data from [14] (curve *1*). It can be seen that the curve is adequately linearized. For comparison, the same data were plotted in the $\{[Co^{3+}]^{-1/2}, t\}$ coordinates (straight line *3*) in accordance with the reaction mechanism suggested by Baxendale and Wells [14]. In this case, the agreement is not so good, and the deviations of the experimental points from the straight line indicate that the reaction order is underestimated. In addition to that, the mechanism proposed by the authors of [14] is not self-consistent. It is clear from their data that the initial rates of Co^{3+} ion reduction (w_0) linearly increase with an increase in $[Co^{3+}]_0$. This contradicts the mechanism proposed in [14] but agrees with the two-electron oxidation of water in the cluster. According to the scheme considered above, a linear growth of w_0 with an increase in $[Co^{3+}]_0$ should be observed under conditions when the solution contains dimers $(Co^{3+})_2$ in substantial amounts as stated by the authors of [14].

If dimers cannot directly interact with each other, the reactant distribution over D can be considered ordinary binomial. Consequently, we believe that the formal kinetics of oxidant consumption obeys a bimolecular rate law. The reduction of superoxide dismutase in an excess of H_2O_2 [15] is an example. This process is adequately described by a rate law for bimolecular reaction up to 90% conversion. The linear dependence of the initial rate of reduction on $[Mn^{3+}]$ indicates that this is not a classical bimolecular reaction. In addition, the redox potentials of a number of model dimers were found to be identical [16]; that is, in the case of the direct interaction of two D with each other, it should be expected that $K = 1$. It is likely that the complex protein globules of the enzyme interfere with mutual contacts between manganese-containing prosthetic groups giving no way of internal equilibria in the ensemble of dimers.

The kinetic method for determining the number of required donors in an active cluster was applied to the reaction of nitrogen reduction to ammonia in the homogeneous V(II)–di-*tert*-butylpyrocatechol model mixture [17]. The kinetics of ammonia formation is consistent with the kinetics of an octamolecular reaction, which is impossible, according to van't Hoff, $-dx/dt = kx^8$ [10]. In the calculation of reaction rates, a parallel reaction of water reduction was taken into account, and the initial rate of the process was estimated by extrapolation because of the absence of relevant data. Despite all these rough approximations, the observed reaction may be considered to be an eight-electron rather than six-electron process as would be expected from the stoichiometry of the reaction $N_2 + 6e^- + 6H^+ = 2NH_3$. The reaction kinetics may be considered supporting the viewpoint of Bazhenova and Shilov [18], according to which the six-electron reduction of nitrogen to ammonia is accompanied by the formation of a hydrogen molecule. Detailed discussion of nitrogen reduction can be found in [19].

The following conclusions can be drawn from a theoretical analysis of the kinetics of consumption of one-electron (or two-electron) oxidants (reducing agents) in many-electron processes:

(1) In many-electron redox reactions that proceed in the coordination sphere of a polynuclear complex, the number of oxidants (reducing agents) is equal to the first derivative of the phase trajectory on the (w, x) coordinates at the very beginning of the process ($x = 1$).

(2) If a statistically equiprobable binomial distribution occurs in an ensemble of *n*-mer clusters, the unimolecular dissociation of an *n*-mer in the cluster catalysis of an uncomplementary process simulates the for-

mal kinetics of an n-molecular reaction of oxidant (reducing agent) dissociation.

In conclusion, a paradoxical fact should be mentioned. Van't Hoff failed to experimentally support his well-known equation that describes the rate of a polymolecular reaction at $n \geq 4$, even though repeated attempts were made [10]. Although the equation was obtained on the assumption of elastic collisions of the reactants, it can be supported experimentally for $n \geq 4$ only in the case of concerted reactions that occur in the coordination sphere of polynuclear complexes. It can be seen that the molecularity according to van't Hoff can be at most three, whereas the quasi-molecularity in the decomposition of a cluster can be eight or even higher.

Thus, the kinetic description of concerted reactions that proceed in the coordination spheres of clusters considerably extends the area of application of the formal kinetics.

APPENDIX

Let us denote the molar fraction of A^+ by $x = [A^+]/([A^+] + [A]) = [A^+]/a$. Then, the molar fraction of A is equal to $(1 - x) = [A]/a$. Let us assume that all A^+ and the reduced form A enter the composition of dimers, which are in the following rapidly attained redox equilibrium (I) with the equilibrium constant K:

$$(A^+)_2 + A_2 \rightleftarrows 2AA^+. \qquad \text{(I)}$$

To determine the concentration of the reactive species $(A^+)_2$, let us write the material balance equations for A^+ ions and A:

$$ax = 2[(A^+)_2] + [AA^+], \qquad (1)$$

$$a(1 - x) = 2[A] + [AA^+]. \qquad (2)$$

The solution to equations (1) and (2) makes it possible to express $[A^+]$ in terms of the molar fraction x:

$$[(A^+)_2] = (a/4)\{K + 2x(4 - K) - [K^2 + 4Kx(1 - x)(4 - K)]^{1/2}\}/(4 - K).$$

For the rate of consumption of A^+ expressed in terms of the molar fraction, we obtain the equation $-dx/dt = k_0[1 + 6x - (1 + 12x - 12x^2)^{1/2}]/6$, where k_0 is the rate constant of the dissociation of $(A^+)_2$.

By simplifying and integrating the equation, we obtain the equality

$$-x^{-1} + 6\ln x + \int x^{-2}(1 + 12x - 12x^2)^{1/2}dx = 8k_0t. \qquad (3)$$

The remaining integral can be reduced to an integral of a rational fraction using the third Euler substitution: $(1 + 12x - 12x^2)^{1/2} = [-12(x - \alpha)(x - \beta)]^{1/2} = (x - \alpha)t$, where $\alpha = 1.07735$ and $\beta = -0.07735$ are the roots of the equation $1 + 12x - 12x^2 = 0$. The integral can easily be calculated by changing the variable $x = \alpha(t^2 + 12\beta/\alpha)/(t^2 + 12)$, $dx = 24\alpha(1 - \beta/\alpha)(t^2 + 12)^{-2}tdt$. The final expression for the linear anamorphosis of the kinetic curve at $K = 1$ has the form $\varphi(x) = 8k_0t$ + const, where the numerical value const = 11.932 and $\varphi(x) = \{1 + 3.464[(x + 0.07735)(1.07735 - x)]^{1/2}\}x^{-1} + 6.928 \arctan[(x + 0.07735)/(1.07735 - x)]^{1/2} + 6\ln\{(x + 0.07735)^{1/2} + [0.0718(1.07735 - x)]^{1/2}\}/x\{(x + 0.07735)^{1/2} + [0.0718(1.07735 - x]^{1/2}\}$.

This expression is identical to the corresponding expression in the text.

REFERENCES

1. Emanuel', N.M., Zaikov, G.E., and Kritsman, V.A., *Tsepnye reaktsii. Istoricheskii aspekt* (Chain Reactions: A Historical Aspect), Moscow: Nauka, 1989, p. 124.
2. Kachanova, Zh.P., Azizov, Yu.M., and Purmal', A.P., *Problemy kinetiki i kataliza. 13. Kompleksoobrazovanie v katalize* (Problems of Kinetics and Catalysis: 13. Complexation in Catalysis), Moscow: Nauka, 1968, p. 121.
3. Belov, G.P., Dzhabiev, T.S., and Kolesnikov, I.M., *J. Mol. Catal.*, 1982, vol. 14, no. 1, p. 105.
4. Golubeva, E.N., Smirnov, V.V., and Rostovshchikova, T.N., *Dokl. Akad. Nauk SSSR*, 1989, vol. 309, no. 2, p. 360.
5. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1984, p. 135.
6. Semenov, N.N., Shilov, A.E., and Likhtenshtein, G.I., *Dokl. Akad. Nauk SSSR*, 1975, vol. 221, no. 6, p. 1374.
7. Basolo, F. and Pearson, R.G., *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, New York: Wiley, 1967, p. 413.
8. Denisov, E.T., *Kinetika gomogennykh khimicheskikh reaktsii* (Kinetics of Homogeneous Chemical Reactions), Moscow: Vysshaya Shkola, 1978, p. 104.
9. Dzhabiev, T.S., *Kinet. Katal.*, 1998, vol. 39, no. 6, p. 900.
10. Van't Hoff, J., *Izbrannye trudy po khimii* (Selected Works in Chemistry), Moscow: Nauka, 1984, p. 25.
11. Gersten, S.W., Samuels, G.J., and Meyer, T.J., *J. Am. Chem. Soc.*, 1982, vol. 104, no. 14, p. 4029.
12. Venttsel', E.S. and Ovcharov, L.A., *Teoriya veroyatnostei i ee inzhenernye prilozheniya* (Probability Theory and Its Applications), Moscow: Nauka, 1988, p. 131.
13. Savel'ev, I.V., *Kurs obshchei fiziki* (General Physics), Moscow: Nauka, 1970, vol. 1, p. 231.
14. Baxendale, J.H. and Wells, C.F., *J. Chem. Soc., Faraday. Trans.*, 1957, vol. 53, p. 800.
15. Bull, C., Niederhoffer, E.C., Yoshida, T., and Fee, J.A., *J. Am. Chem. Soc.*, 1991, vol. 113, no. 11, p. 4069.
16. Brunold, T.C., Gamelin, D.R., Stemmler, T.L., *et al.*, *J. Am. Chem. Soc.*, 1998, vol. 120, no. 34, p. 8724.
17. Luneva, N.P., Mironova, S.A., Shilov, A.E., *et al.*, *Dokl. Ross. Akad. Nauk*, 1993, vol. 328, no. 5, p. 585.
18. Bazhenova, T.A. and Shilov, A.E., *Zh. Ross. Khim. Ob-va*, 1995, vol. 39, no. 1, p. 50.
19. Dzhabiev, T.S., Mironova, S.A., and Shilov, A.V., *Kinet. Katal.*, 1999, vol. 40, no. 6, p. 844.