# CRITERIA FOR DISPROPORTIONATION IN MULTISTAGE PROCESSES

V. V. Losev and A. I. Molodov

UDC 541.13

Particles of intermediate valence are formed during multistage electrode processes, further oxidation occurring both at the electrode and by disproportionation (DPP). Let us use a divalent-metal amalgam to consider the criteria that permit establishment of intermediate-particle DPP and determination of the electrode-process mechanism. The overall reaction $M \rightleftarrows M^{2+} + 2e^-$ occurs at such an electrode, resulting from a combination of three stages:

$$M \underset{k_{c_1}}{\overset{k_{a_1}}{\rightleftarrows}} M^+ + e^-, \tag{1}$$

$$M^+ \underset{k_{c_2}}{\overset{k_{a_2}}{\rightleftarrows}} M^{2+} + e^-, \tag{2}$$

$$2M^+ \underset{k''_d}{\overset{k'_d}{\rightleftarrows}} M + M^{2+} \tag{3}$$

with the exchange currents $i_{01}$, $i_{02}$, and $i_{0d}$. Let us consider the possible variants of the stage-rate relationships.

A. $i_{02} \ll i_{01} < i_{0d}$. The equations for the rates of the anodic and cathodic processes have the form:

$$i_a = k_{a1}[M] \exp(\beta_1 nF\varphi / \nu RT), \tag{4}$$

$$i_c = k_{c1}[M^+] \exp(-\alpha_1 nF\varphi / \nu RT), \tag{5}$$

where $\nu$ is the stoichiometric number [1], n = 2, and $\alpha_1$ and $\beta_1$ are the true transfer coefficients of Eq. (1). The process goes through Eqs. (1) and (3), with $\nu = 2$; using the equilibrium condition for Eq. (3), we obtain

$$i_a = k_{a1}[M] \exp(\beta_1 F\varphi / RT), \tag{6}$$

$$i_c = k_{c1} K^{-1/2} [M]^{1/2} [M^{2+}]^{1/2} \exp(-\alpha_1 F\varphi / RT), \tag{7}$$

where K is the equilibrium constant of Eq. (3). The rate of the cathodic process thus depends on the metal concentration in both the solution and the amalgam; the exponents for the metal are fractional [2]. At the equilibrium potential ($\varphi = \varphi_e$), we have $i_a = i_c = i_0$. Using this condition, Eqs. (6) and (7) yield:

$$\varphi_e = \text{const} + [RT / 2(\alpha_1 + \beta_1)F] \cdot \ln([M^{2+}] / [M]). \tag{8}$$

Comparing Eq. (8) with the Nernst equation, we find $\alpha_1 + \beta_1 = 1$. It can be seen from Eqs. (6) and (7) that the true transfer coefficients coincide with the apparent coefficients [3], i.e., we have $\alpha + \beta = 1$, in contrast to a reaction without DPP (variant F). Using this equation at $\varphi_e$, Eqs. (6) and (7) yield an expression for the exchange current $i_{0F} = \text{const}\,[M]^{(1+\alpha)/2}[M^{2+}]^{\beta/2}$. The exchange currents therefore depend to a greater extent on the metal concentration in the amalgam than on that in the solution. An important criterion of this mechanism is the nonelectrochemical-exchange effect, i.e., the discrepancy in the exchange currents found by the electrochemical ($i_0$) and radiochemical ($i_{0r}$) methods, with $i_{0r} > i_0$ [4]. Thus, isotopic exchange for a radioactive amalgam can take place through Eqs. (1) and (3) at a rate $i_0$ or by the mechanism $\overset{*}{M} + M^{2+} \rightarrow M^+ + \overset{*}{M}{}^+$ and $M^+ + \overset{*}{M}{}^+ \rightarrow M + \overset{*}{M}{}^{2+}$ at a rate equal to $\frac{1}{2}\, i_{0d}$ (since the DPP reaction occurs twice); $i_{0r} = \frac{1}{2}\, i_{0d} + i_0$. The latter relationship permits experimental determination of the exchange rate in Eq. (3).

B. $i_{01} \ll i_{02} > i_{0d}$. This variant is symmetric with variant A. For example, we have

$$i_0 = \text{const}\,[M]^{\alpha/2}[M^{2+}]^{(1+\beta)/2},$$

L. Ya. Karpov Physicochemical Institute, Moscow. Translated from Élektrokhimiya, Vol. 4, No. 11, pp. 1366-1370, November, 1968. Original article submitted March 1, 1968.

where $\alpha = \alpha_2$, $\beta = \beta_2$, and $\alpha + \beta = 1$. This variant and variant D, which is discussed below, are interesting because, when the solution contains no $M^{2+}$ ions, anodic dissolution of the metal should initially proceed through Eqs. (1) and (2); only after some $M^{2+}$ has accumulated does the process go through Eqs. (3) and (2). This peculiarity can be utilized to determine the mechanism involved, with the aid of non-steady-state measurements.

C. $i_{02} \ll i_{0d} < i_{01}$.* This case is formally analogous to hydrogen evolution with a retarded recombination stage [4].

$$i_a = k_d'[M^+]^2 = k_d' K_1 [M]^2 \exp(2F\varphi/RT), \quad (9)$$

$$i_c = i_0 = i_{0r} = k_d''[M][M^{2+}], \quad (10)$$

with $\nu = 1$, $\alpha = 0$, and $\beta = 2$. As can be seen, the rate of the anodic process is proportional to the square of the amalgam concentration, while that of the cathodic process is independent of the potential but depends on the amalgam concentration and coincides with the exchange current. These features readily establish the occurrence of mechanism C.

D. $i_{01} \ll i_{0d} < i_{02}$. This variant is symmetric to variant C. For example, we have $i_c = k_d' K_2 [M^{2+}]^2 \exp(-2 \cdot F\varphi/RT)$, $\alpha = 2$, and $\beta = 0$.

E. $i_{01} \approx i_{02} \ll i_{0d}$. In this special case, mechanisms A and B occur simultaneously at the electrode. The limiting factor is Eq. (1) in the anodic region and Eq. (2) in the cathodic region. Since the dependence of $i_a$ and $i_c$ on the metal concentrations in the two phases differs for mechanisms A and B, one can, by varying the metal concentration in one phase, readily switch to the region in which mechanism A or B predominates and thus distinguish this case from the others.

Table 1 compares the principal criteria for the various mechanisms and for the case $i_{0d} \ll i_{01}, i_{02}$ (variant F) [2, 8]. As can be seen from this table, determination of the exponents for the reacting particles makes it possible to establish whether a DPP reaction occurs and to differentiate mechanisms A-D; however, determination of an additional parameter ($\nu$ or $i_{0r}$) is necessary in order to distinguish case E from, for example, case F. Similar kinetic equations and criteria are obtained for a trivalent metal when a DPP reaction occurs.

Our previous investigations with dilute Cu, Zn, In, and Bi amalgams showed that the anodic process rate was proportional to the first power of the amalgam concentration and independent of the metal concentration in the solution, while the cathodic-process rate increased linearly with the metal concentration in the solution [2, 3, 8, 9], i.e., there were no delayed DPP reactions at these electrodes (mechanisms of types C and D). In Zn and In amalgams, $i_0 = i_{0r}$ [3, 9]. In the case of Bi, the comparable rates of the successive electrochemical stages caused $i_{0r}$ to be less than $i_0$ and there was no nonelectrochemical exchange [8, 9]. Mechanisms of types A, B, and E, which include a rapid-DPP stage, therefore did not occur at these electrodes.

Use of the criteria discussed above thus permits unequivocal detection of intermediate-particle DPP during multistage processes.

It must be noted that the literature has, until recently, contained no adequately grounded conclusions regarding mechanisms with DPP stages [10-12]. Thus, Markovac and Lovrecek [11] used the slope of the polarization curve as their sole basis for hypothesizing that anodic dissolution of an indium amalgam (0.3% by weight) proceeds by a mechanism of type A. However, the anomalously high value of $\beta$ ($\approx 1$) observed by these authors is improbable for a mechanism of type A (see Table 1), and their assumption that the intermediate-particle concentration rises with $\varphi$ contradicts their premise that the limiting stage is $In \rightarrow In^+ + e^-$. Actually, the limiting-particle concentration with this limiting stage cannot noticeably exceed the equilibrium level. In investigating the process $Tl^+ \rightleftarrows Tl^{3+} + 2e^-$, Jordan and Catharino quite justifiably concluded that the anodic and cathodic regions of the process are limited by the stages $Tl^+ \xrightarrow{k_a} Tl^{2+} + e^-$ and $Tl^{3+} + e^- \xrightarrow{k_c} Tl^{2+}$, where $k_a$ is almost three orders of magnitude greater than $k_c$, but their conclusion that the subsequent rapid reaction is DPP was not confirmed experimentally [12]. However, the cathodic process would go through a DPP stage independent of $\varphi$ if the latter were almost an equilibrium stage and it would be followed by a subsequent delayed stage $Tl^{2+} + e^- \rightarrow Tl^+$, i.e., a mechanism of type A ought to occur. Neither the order of the reactions nor the stoichiometric number was determined in either of the articles mentioned above.

* This mechanism, proposed by Heyrovsky [5], has been criticized [6]; in his most recent monograph [7], Heyrovsky has essentially agreed with the criticism and not attempted to defend the mechanism.

TABLE 1. Comparison of Main Criteria of Different Mechanisms

| Variant | Conditions | $\nu$ | Exponents: anodic process, $[M^{z+}]$ | Exponents: anodic process, $[M]$ | Exponents: cathodic process, $[M^{z+}]$ | Exponents: cathodic process, $[M]$ | Exchange current*: $x$ | Exchange current*: $y$ | Slopes of curves for $\varphi$ (ln i): cathodic process, $b_C$ | Slopes of curves for $\varphi$ (ln i): anodic process, $b_A$ | Apparent transfer coeffi.: $\alpha$ | Apparent transfer coeffi.: $\beta$ | Apparent transfer coeffi.: $\alpha+\beta$ | Isotopic exchange rate, $i_{0r}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | $i_{02} \ll i_{01} < i_{0d}$ | 2 | 0 | 1 | 1/2 | 1/2 | $\beta/2$ | $(1+\alpha)/2$ | $\infty > \lvert b_C \rvert > RT/F$; | $\infty > b_A > RT/F$ | $1 > \alpha > 0$ | $1 > \beta > 0$ | 1 | $\frac{1}{2} i_{0d} + i_0$ |
| B | $i_{01} \ll i_{02} < i_{0d}$ | 2 | 1/2 | 1/2 | 1 | 0 | $(1+\beta)/2$ | $\alpha/2$ | $\infty > \lvert b_C \rvert > RT/F$ | $\infty > b_A > RT/F$ | $1 > \alpha > 0$ | $1 > \beta > 0$ | 1 | $\frac{1}{2} i_{0d} + i_0$ |
| C | $i_{02} \ll i_{0d} < i_{01}$ | 1 | 0 | 2 | 1 | 1 | 1 | 1 | $\infty$ | $RT/2F$ | 0 | 2 | 2 | $i_0$ |
| D | $i_{01} \ll i_{0d} < i_{02}$ | 1 | 1 | 1 | 2 | 0 | 1 | 1 | $RT/2F$ | $\infty$ | 2 | 0 | 2 | $i_0$ |
| E | $i_{01} \approx i_{02} \ll i_{0d}$ | 2 | 0 | 1 | 1 | 0 | $\beta/2$ | $\alpha/2$ | $2RT/F > \lvert b_C \rvert > RT/F$ | $2RT/F > b_A > RT/F$ | $1 \geqslant \alpha \geqslant 1/2$ | $2 \geq \alpha+\beta \geq 1$ | 2 | $\frac{1}{2} i_{0d} + i_0$ |
| F | $i_{0d} \ll i_{01} < i_{02}$ | 1 | 0 | 1 | 1 | 0 | $\beta/2$ | $\alpha/2$ | $RT/F > \lvert b_C \rvert > RT/F2$ | $\infty > b_A > RT/F$ | $2 > \alpha > 1$ | $1 > \beta > 0$ | 2 | $i_0$ |
| | $i_{0d} \ll i_{02} < i_{01}$ | 1 | 0 | 1 | 1 | 0 | $\beta/2$ | $\alpha/2$ | $\infty > \lvert b_C \rvert > RT/F$ | $RT/F > b_A > RT/F2$ | $1 > \alpha > 0$ | $2 > \beta > 1$ | 2 | $i_0$ |

* The quantities x and y are the exponents in the equation $i_0 = \text{const}\,[M^{2+}]^x[M]^y$.

## LITERATURE CITED


1. P. Delahay, The Double Layer and Electrode-Process Kinetics [Russian translation], Moscow (1967).
2. V. V. Losev, L. E. Sribnyi, and A. I. Molodov, Élektrokhimiya, 2, 1431 (1966).
3. V. V. Losev and A. M. Khlopin, Transactions of the 4th Conference on Electrochemistry, 1956 [in Russian] (1959), p. 116; V. V. Losev and G. M. Budov, Zh. Fiz. Khim., 37, 578 (1963).
4. A. N. Frumkin, Dokl. Akad. Nauk SSSR, 119, 318 (1958).
5. J. Heyrovsky, Dis. Faraday Soc., 1, 212 (1947).
6. M. A. Loshkarev and A.A. Kryukova, Zh. Fiz. Khim., 26, 731 (1952); 30, 2336 (1956), A. N. Frumkin, Dokl. Akad. Nauk SSSR, 85, 373 (1952).
7. J. Heyrovsky and J. Kuta, Principles of Polarography [Russian translation], Moscow (1965).
8. V. V. Losev and V. V. Gorodetskii, Élektrokhimiya, 3, 1061, 1192 (1967).
9. G. M. Budov and V. V. Losev, Zh. Fiz. Khim., 37, 1230 (1963); A. I. Molodov and V. V. Losev, Élektrokhimiya, 1, 1253 (1965); V. V. Gorodetskii and V. V. Losev, Dokl. Akad. Nauk SSSR, 151, 361 (1963).
10. L. F. Kozin and N. N. Tananaeva, Tr. In-ta Khim. Nauk Akad. Nauk KazSSR, 9, 143 (1962); L. F. Kozin and E. E. Kobrand, Zh. Prikl. Khim., 38, 579 (1965).
11. V. Markovac and B. Lovrecek, J. Electrochem. Soc., 112, 520 (1965); 113, 838 (1966).
12. H. A. Catharino and J. Jordan, Talanta, 11, 59 (1964).