

$$\frac{\partial \bar{p}_1}{\partial x'} = (1-x') \frac{\partial^2 \bar{p}_1}{\partial x'^2} \quad (23)$$

Hence, again it can be seen that it is only with $\partial \bar{p}_1 / \partial x' = 0$ that Raoult's law is obtained as a special case. Since in the general case $\partial \bar{p}_1 / \partial x' = f(x')$, then $\partial^2 \bar{p}_1 / \partial x'^2 \neq 0$, and as a result the validity of Eqn. (23) is not restricted to Raoult's law. Therefore the statement of Varshavskii et al.⁵ that "Reshetnikov's point of view leads to an absurd conclusion" is lacking in substance.

It follows from the above that:

1) The fundamental error made by Varshavskii et al. in deducing the "new form of the van der Waals equation" (4*) is to neglect the volume of the liquid phase. 2) It can be shown that the statement of Lewis, that the activity coefficients f_i in Eqn. (5*) are subject to the Gibbs-Duhem relationship (6*) ($p, T = \text{const.}$) is incorrect and leads to $x'' = x'$. The quantities f_i obey the approximate Duhem-Margules Eqn. (9). 3) It can be shown that the attempt of Varshavskii et al.^{4,5} to prove that the validity of the relationships (1*) and (18) is restricted to the region of ideal systems is futile.

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MECHANISM OF THE CATHODIC REDUCTION OF OXALIC ACID ON MERCURY

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The results obtained by Listopadov and Antropov¹ for the electrochemical reduction of oxalic acid at a mercury electrode are explained on the hypothesis that molecules and

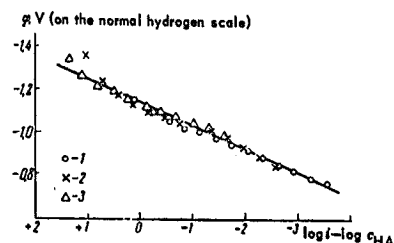


Fig. 1. Check of applicability of Eqn. (1) to explain data obtained by Listopadov and Antropov¹. The values of i include corrections for the discharge of H^+ ions. The data refer to the following pH values: 1) 1.72; 2) 2.86; 3) 3.84.

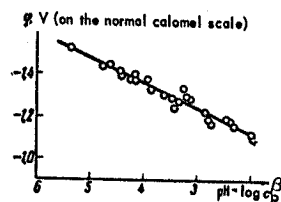


Fig. 2. Check of applicability of Eqn. (2) to explain data obtained by the present author^{2,3}. Eqn (2) is employed in a form which takes no account of the fraction of the current due to hydrogen evolution (see Eqns. 4 and 5 below).

anions of oxalic acid take part in the reaction, it being assumed also that their reduction occurs as a result of the primary addition of hydrogen ions activated in the double layer in the course of discharge.

Such a conclusion disagrees with our previous work^{2,3} according to which the primary process is the addition of the first electron to an undissociated $H_2C_2O_4$ molecule. On comparing the results in these papers^{1,2}, Listopadov and Antropov conclude that the equation used in our work² to explain the experimental regularities is a special case of the equation which they used¹, and therefore that it is valid only under certain conditions. Here, both in the treatment of our results and in the concepts which these authors develop¹, there are a number of inaccuracies, which we should like to point out.

Let us examine the equations based upon theories in these papers¹⁻³. The concept of the slow addition of the first electron to the $H_2C_2O_4$ molecule gives the following equation for the potential of the mercury electrode^{2,3}:

$$\varphi = \text{const.} - \frac{RT}{\alpha F} \ln i + \frac{RT}{\alpha F} \ln c_{HA} \quad (1)$$

where i is the current density and c_{HA} the concentration of undissociated $H_2C_2O_4$ molecules.

The slow addition of protons, which can take place with molecules and anions of oxalic acid, leads in the opinion of Antropov and Listopadov¹ to the equation

$$\varphi = \frac{RT}{\alpha F} \ln(1 + g c_R) - \frac{RT}{\alpha F} \ln i - \frac{RT}{\alpha F} \text{pH} \quad (2)$$

where c_R is the total analytical concentration of oxalic acid in the solution, and g and β are constants, having the values

of 0.01 and 0.53 respectively for the mercury electrode.

Without for the present examining in detail the derivation of Eqns. (1) and (2), we shall restrict ourselves to the question — how far do these equations represent the experimental results obtained^{1,3}?

A check of Eqn. (1) showed that it satisfactorily describes all the experimental results for the pH range 1.5 to 4, as has already been reported³. It is true that, in the opinion of Listopadov and Antropov¹, their data do not satisfy Eqn. (1). In fact, however, examination of their results shows that only data obtained at pH 0.07, 0.67, and 1.03 do not obey Eqn. (1), so that the conclusion that Eqn. (1) is correct at pH values between 1.5 and 4 remains valid*. The above is supported by our calculations shown in Fig. 1.

In carrying out calculations based on Eqn. (1) they¹ introduce a correction for the fraction of the current i_{H^+} employed in hydrogen evolution, and point out that Eqn. (1) is not applicable without such a correction. It is in fact necessary to take into account the fraction of the current i_{H^+} due to reduction of H^+ ions. However, the method adopted for this purpose in their paper¹ is not the only one. In our papers^{2,3}, and also in the calculation of the data for Fig. 1, the appropriate correction was introduced by subtracting from the experimental values of i the values of i_{H^+} calculated from the equation

$$\log i_{H^+} = \frac{-1675 - \varphi}{116} - \text{pH},$$

which represents the discharge of H^+ ions on mercury (φ being measured with reference to the normal calomel electrode). Our Eqn. (1)^{2,3} is, of course, applicable only after the introduction of such corrections.

A check of Eqn. (2) showed that it could explain both Listopadov and Antropov's experimental results¹ and ours^{2,3} over the pH range 1–3.8. In the examination of the data in our papers^{2,3}, account was taken of the fact that they already include corrections for the current i_{H^+} . The corresponding curve is shown in Fig. 2.

It follows from the above that, formally, both equations can be used to explain the behaviour observed experimentally in the electrochemical reduction of oxalic acid. However, Eqn. (1) has the advantage of containing only one constant, whereas Eqn. (2) contains two constants. The chief evidence in favour of Eqn. (1), however, would be an analysis of the concepts underlying the deduction of the two equations.

The derivation of Eqn. (1)^{2,3} is based on proportionality between the rate of the cathode reaction and the concentration of undissociated oxalic acid molecules. In the deduction of Eqn. (2) the total current is regarded by Listopadov and Antropov¹ as consisting of two components:

$$i_{H^+} = k_1 c_{H^+} e^{-\alpha_1 \varphi F/RT}, \quad (3)$$

and

$$i_{HA} = k_2 c'_R c_{H^+} e^{-\alpha_2 \varphi F/RT}, \quad (4)$$

where i_{HA} is the current due to reduction of oxalic acid, c_{H^+} the concentration of hydrogen ions, and c'_R the total surface concentration of oxalic acid. It is further supposed that the

relationship between c'_R and the volume concentration of oxalic acid c_R obeys the Freundlich equation:

$$c'_R = k c_R^g, \quad (5)$$

and it is also assumed that $k k_2/k_1 = g$ and $\alpha_1 = \alpha_2$.

Eqn. (2) is obtained by adding together Eqns. (3) and (4), taking into account Eqn. (5). The mistake in such a deduction lies in the fact that if, as has been assumed¹, all forms of oxalic acid, both ions and molecules, take part in the reduction of $H_2C_2O_4$, and the overall rate of reaction is governed by the rate of addition of H^+ ions to them, then the current should consist of at least two components:

$$i'_{HA} = k_3 c_{HA} c_{H^+} e^{-\alpha_3 \varphi F/RT}, \quad (6)$$

and

$$i''_{HA} = k_4 c_A c_{H^+} e^{-\alpha_4 \varphi F/RT}, \quad (7)$$

where c_A is the concentration of oxalate anions. The sum of Eqns. (6) and (7) could be equivalent to Eqn. (4) only on condition that $\alpha_3 = \alpha_4$ and $k_3 = k_4 = k_2$. The latter condition, however, can hardly be satisfied, as is demonstrated especially clearly in numerous papers by Czech workers.

It has been suggested¹ that Eqn. (1) reduces to Eqn. (2) under certain conditions (when the ratio of the dissociation constant of oxalic acid to the concentration of H^+ ions is greater than unity); this would be in fact possible if $c_A = c_R$, but only if Eqn. (2) did not involve the assumption that c'_R is related to c_R by the Freundlich equation. The latter, however, leads to the appearance in Eqn. (2) of the expression c_R^g , which with $\beta \neq 1$ eliminates the possibility of Eqn. (1) passing into Eqn. (2) under any conditions. Further, there are no grounds for applying the Freundlich equation to the adsorption of organic substances on a smooth surface, especially to such feebly adsorbed compounds as oxalic acid.

From the above considerations it may be postulated that the slow stage in the electrochemical reduction of oxalic acid on a mercury electrode is the single-electron discharge of undissociated $H_2C_2O_4$ molecules. Such a conclusion is supported also by Kuta's results⁴. Possible reasons for the occurrence of the process by different mechanisms at $\text{pH} < 1.5$ and $\text{pH} > 4$ and also the unsuitability of a number of other explanations for this process at $1.5 < \text{pH} < 4$ were shown previously³.

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THE OVERVOLTAGE OF THE DEPOSITION OF METALS OF THE IRON GROUP

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The electrodeposition of metals of the iron group is accompanied by high polarisation¹. Thus at a current density

* Only values of φ for certain pH values at very low i ($< 3 \times 10^{-6}$ A/cm²) diverge from this relationship.