

THE KINETICS OF OXIDATION-REDUCTION POTENTIALS. VI*

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The author, together with I.I. Appenin and V.G. Tkachenko [1], has studied the kinetics of attainment of equilibrium oxidation-reduction potentials of the system $\text{Pt}/\text{Tl}_2(\text{SO}_4)_3$, Tl_2SO_4 ; $\text{H}_2\text{SO}_4/\text{KCl}_{\text{sat.}}$, $\text{Hg}_2\text{Cl}_2/\text{Hg}$ with hydrogen electrodes.

In this work, we obtained kinetic curves of two types: with an S-shaped part, and with a straight-line part replacing the S. The latter has already been the subject of preliminary consideration [2].

In the present work, both types of curve are considered quantitatively from a single point of view, on the basis of the general mechanism of the process.

Upon inserting a hydrogenated platinum electrode into an oxidation-reduction system, at the very first moment, a hydrogen electrode potential is produced on the platinum.

Then the oxidation-reduction system begins to impose its own potential upon the electrode. As the potential of the system $\text{Tl}^{+++}/\text{Tl}^+$ lies in the region of high oxidative significance, a loss of adsorbed hydrogen must take place from the electrode until its concentration on the surface corresponds to the equilibrium oxidation-reduction potential.

In the work of A.L. Rotinyan, I.I. Appenin, and V.G. Tkachenko [1], it was assumed that under the conditions of the experiment, the reaction:



would proceed from left to right, and that its kinetics would determine the attainment of equilibrium.

The velocity of the overall reaction (1) can be limited by the velocity of supply of trivalent thallium ions to the surface of the electrode, as well as by the velocity of the chemical reaction itself. In actual experiments, it is possible to encounter cases where the velocities of both these processes are of the same order.

The definite dependence of the speed of attainment of the potential upon the intensity of mixing of the solution testifies to the influence of the diffusion of Tl^{+++} ions toward the surface upon the kinetics of the reaction. On the other hand, the activity of the electrode itself has an influence upon the kinetics of the reaction.

These and other facts [2] testify that under experimental conditions, diffusion is of the same order as reaction velocity; therefore, in the general case, we divide the question concerning the kinetics of reaction into that concerning the commensurate velocities of diffusion and the chemical reaction proper.

In considering such cases, it is convenient to utilize the method suggested by Frank-Kamenetsky [3]; however, it is necessary to keep in mind that, by its very nature, it automatically postulates homogeneity of surface.

This method has lately been utilized successfully by a number of authors (A.B. Zdanovsky, [4], M. Tovbin [5], B.V. Drozdov [6]).

It has been most completely developed by B.V. Drozdov, who integrated the differential

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equation of the velocity which he had applied to the system he studied; this was the heterogeneous reaction involving the interchange on the surface of nickel particles.



In particular, B.V. Drozdov showed that on the basis of Frank-Kamenetsky's methods, it was possible to obtain an equation, entirely analogous to the empirical equation of Dintsen and Frost [7]:

$$k = \frac{1}{t} \ln \frac{1}{1-x} - \beta \frac{x}{t} \quad (3)$$

for the self-retarding homogeneous reaction. The coefficient β , which is less than unity, corresponds to the relative velocities of diffusion and reaction. $\beta = 1$ is the case where the kinetics are determined purely by diffusion. The other extreme case, $\beta = 0$, corresponds to purely chemical kinetics. Here x is the quantity of reacting material at time t , expressed as a fraction of unity.

It was experimentally shown that within the limits of the investigation, the velocity of reaction (1) is completely independent of the concentration of univalent thallium ions in the solution.

Consequently, in the general case of reaction (1) we may write the following expression for the velocity:

$$-\frac{dC_H}{dt} = k_1 C_H^2 C_{\text{Tl}^{+++}} - k_2 C_H^+ \quad (4)$$

where C_H is the surface concentration of atoms of hydrogen adsorbed on the electrode at time t ; $C_{\text{Tl}^{+++}}$ is the concentration of Tl^{+++} on the surface of the electrode at time t ; C_H^+ is the analogous concentration of hydrogen ions; k_1 and k_2 are the velocity constants of the direct and reverse reactions.

As the experiments showed, the electrodes with which the measurements were made, could be divided into three types, according to their activity:

First type. Slightly active electrodes, on which the kinetics curve has an S-shaped twist.

For such electrodes, the velocity of reaction is so small that for the initial period C_H is of the same order as $C_{\text{Tl}^{+++}}$, and we cannot calculate the velocity of reaction independent of C_H .

On the other hand, no matter how little the activity of the electrode, it is natural to assume, as was done in the fifth paper [2], that the velocity of the reaction with regard to the atoms of hydrogen is not of the second, but of the first order. Then (4) can be rewritten:

$$-\frac{dC_H}{dt} = k_1 C_H C_{\text{Tl}^{+++}} - k_2 C_H^+ \quad (5)$$

Below it will be shown that (5) holds for experiments where (4) does not hold; therefore, we shall from now on utilize equation (5) instead of (4).

Second type. The electrodes are somewhat more active. For the first period of the reaction, the inequality $C_H \gg C_{\text{Tl}^{+++}}$ holds, but later, the velocity of this part depends only on the concentration of trivalent thallium ions on the surface of the electrode; in the final period, the inverse relation holds: $C_H \ll C_{\text{Tl}^{+++}}$ and the velocity varies as C_H to the first power.

Third type. Electrodes very active. In the first period, this case is distinguished from the preceding only by the greater value of the velocity constant, while in the final period the velocity of reaction depends only on C_H , being proportional to the concentration of adsorbed hydrogen atoms raised to the second power.

These characteristics of electrode behavior make their appearance upon reaching a

potential of +0.9 V, at which, according to Ershler's data [9], there begins the oxidation of the electrode with oxygen. Consequently, the difference in the activity of the electrodes is apparently related to the capacities of the different electrodes to be oxidized in different ways.

The kinetics curves for the electrodes of the second and third types are quantitatively included in the indicated scheme [2], and we shall therefore limit ourselves here to a review of the first case.

As after a very short interval of time the velocity of reaction must become equal to the velocity of diffusion of the trivalent thallium ions to the surface, we may write:

$$K_1 C_H C_{Tl^{+++}} - K_2 C_{H^+}^2 = \frac{D}{\lambda} (C_0 - C_{Tl^{+++}}); \quad (6)$$

where C_0 is the concentration of Tl^{+++} on the outer surface of the motionless layer of liquid adjoining the electrode, whose thickness is λ ; D is the coefficient of diffusion of the trivalent thallium ions.

As the diffusion of Tl^{+++} proceeds with a finite velocity, C_0 must be somewhat less than the volume concentration of trivalent thallium ions C_{ox} [5].

Determining $C_{Tl^{+++}}$ by (6), we obtain:

$$C_{Tl^{+++}} = \frac{\frac{D}{\lambda} C_0 + K_2 C_{H^+}^2}{K_1 C_H + \frac{D}{\lambda}} \quad (7)$$

Substituting (7) into (5), we obtain:

$$-\frac{dC_H}{dt} = \frac{\frac{K_1 D C_0}{\lambda} C_H + K_1 K_2 C_{H^+}^2 + C_H}{K_1 C_H + \frac{D}{\lambda}} - K_2 C_{H^+}^2 \quad (8)$$

For the transition from the surface concentration of hydrogen ions to the easily measured electrode potential, we shall to the first approximation consider the capacity of the double layer (ϵ) as independent of the potential.

Then from the equation:

$$-\frac{dC_H}{dt} = \frac{\epsilon}{nF} \cdot \frac{dE}{dt} \quad (9a)$$

it is easy to obtain the approximate relation [2]:

$$C_H = \frac{\epsilon}{nF} (E_p - E) = \frac{\epsilon}{nF} \Delta E \quad (9)$$

which satisfactorily expresses the difference of the potentials from their equilibrium value.

Here E_p is the equilibrium potential of the oxidation-reduction electrode, and E the potential at any moment which corresponds to the given concentration of hydrogen atoms adsorbed on the electrode.

Substituting (9) in (8), we obtain:

$$W = \frac{dE}{dt} = \frac{\frac{K_1 D C_0}{\lambda} \Delta E + K_1 K_2 C_{H^+}^2 \Delta E}{\frac{K_1 \epsilon}{nF} \Delta E + \frac{D}{\lambda}} - \frac{K_2 C_{H^+}^2}{\epsilon} \quad (10)$$

Equations (8) and (10) may be subjected to integration; however, in connection with the indefiniteness of the value of the potential at time $t = 0$, it is more convenient to carry out

the experimental verification of (10) in the following manner; let us write (10) thus:

$$\frac{W}{\Delta E} + \frac{K_2 \varepsilon \lambda}{DnF} W + \frac{K_2 C_{H^+}^2 nF}{\varepsilon \Delta E} - K_1 C_0 = 0. \quad (11)$$

At the moment of inserting the electrode in the solution, that is, at $t = 0$, $W = 0$. Consequently, from formula (11):

$$\frac{K_2 C_{H^+}^2 nF}{\varepsilon \Delta E_{t=0}} - K_1 C_0 = 0, \quad (12)$$

that is, the curve must pass through the origin.

From (12) we obtain

$$C_0 = \frac{K_2}{K_1} \frac{C_{H^+}^2 nF}{\varepsilon \Delta E_{t=0}}. \quad (13)$$

In equation (11), the term

$$\frac{K_2 C_{H^+}^2 nF}{\varepsilon \Delta E}$$

expresses the influence of the reverse reaction.

If $K_2 \ll K_1$, then (11) is converted into the approximate equation:

$$\frac{W}{\Delta E} + \frac{K_1 \lambda \varepsilon}{DnF} W - K_1 C_0 = 0, \quad (14)$$

where at $t = 0$, $K_1 C_0$ can only tend toward zero, without being equal to zero, as, strictly speaking, would be expected.

Consequently, if we grant the justification of the above equation, then the experimental data plotting $\frac{W}{\Delta E}$ against W must lie on straight lines; in this way, there are obtained three sections of straight lines with different slopes, and not a single straight line for all periods of the reaction.

In Figs. 1 and 2 are given those results from the work of Rotinyan, Appenin, and Tkachenko [1] which have served for testing equation (14). On the basis of the experimental data, large scale curves of the kinetics were drawn, by means of which the value of the derivative dE/dt was graphically determined. In this way, there were obtained values for the velocity of establishment of the potential as a function of time as depicted in Figs. 3 and 4.

In Figs. 5, 6, 7, 8, and 9 are presented the results of verification of formula (14) according to the data of Figs. 1 and 2.

The straight lines of the different parts are constructed so that there is no break between them, that is, the first part includes the data up to the minimum of velocity, the second from the minimum to the maximum, and the third from the maximum of velocity to the end of the reaction. As can be seen from Fig. 5 for the first part, the data of all the curves of Fig. 1 lie along a single straight line. The angular coefficient

$$\frac{K_1 \lambda \varepsilon}{DnF} \quad (15)$$

for the given part, is independent of the dilution, or more properly, of the concentration of trivalent thallium ions in the solution.

The independence of the angular coefficient of the curve from the concentration of Tl^{+++} ions follows directly from (15), if we consider that the capacity of the double layer in the given part is not a function of the concentration. The latter may correspond to the actual case if we assume that in the first second after the introduction of the electrode into the

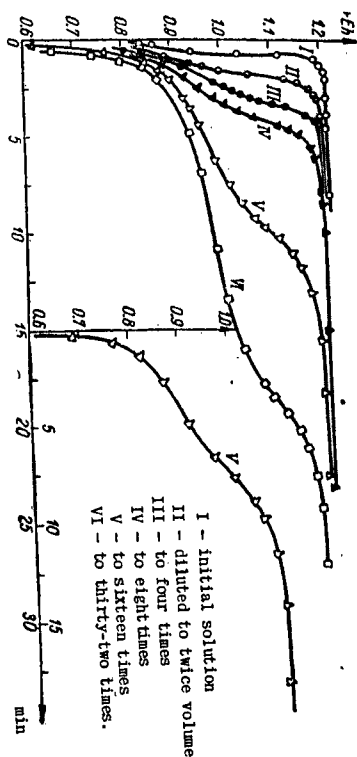


Fig. 1. Influence of the dilution on the speed of attainment of equilibrium potentials. Starting with a solution containing in moles per liter: $\text{Ti}_2(\text{SO}_4)_3 \cdot 10^{-3}$; $\text{Ti}_2\text{SO}_4 \cdot 0.625 \cdot 10^{-4}$, $\text{H}_2\text{SO}_4 \cdot 0.174$. Electrode No. 3, dimensions 25.6×0.1 mm. Temp. 25° . In the Riechardt corner is drawn the curve obtained with electrode No. 14, measuring in the Riechardt corner is drawn the curve obtained with electrode No. 14, measuring 25.6×0.1 mm, in a solution containing in moles per l. $\text{Ti}_2(\text{SO}_4)_3 \cdot 0.625 \cdot 10^{-4}$, $\text{Ti}_2\text{SO}_4 \cdot 0.312 \cdot 10^{-4}$, $\text{H}_2\text{SO}_4 \cdot 0.174$ (curve from first series of experiments). Along the axis of ordinates lie the positive values of the electrode potential, in volts, on the hydrogen scale. Along the axis of abscissas the time, in minutes, from the moment of inserting the electrode into the solution.

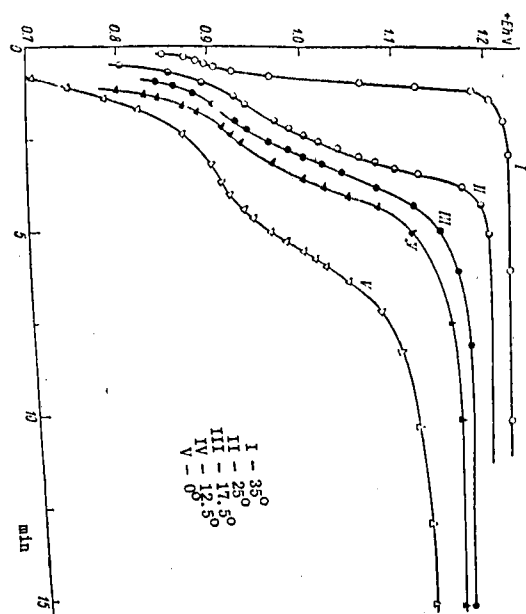


Fig. 2. Influence of the temperature on the velocity of attainment of equilibrium potentials. The solution contained in moles per liter $\text{Ti}_2(\text{SO}_4)_3 \cdot 2.50 \cdot 10^{-4}$, $\text{Ti}_2\text{SO}_4 \cdot 0.625 \cdot 10^{-4}$, $\text{H}_2\text{SO}_4 \cdot 0.174$. Electrode No. 3, 25.6×0.1 mm. Along the ordinate axis are the positive values of the electrode potential, in volts, hydrogen scale; along axis of abscissas, the time, in minutes, from moment of inserting electrode into solution.

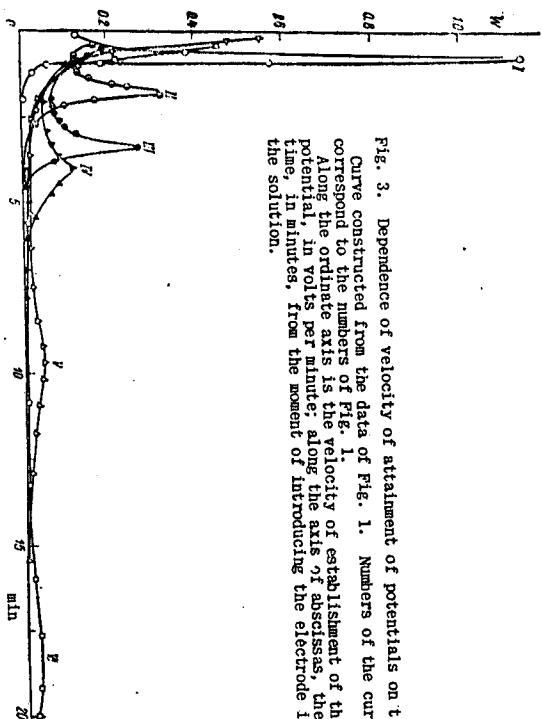


Fig. 3. Dependence of velocity of attainment of potentials on time. Curve constructed from the data of Fig. 1. Numbers of the curves correspond to the numbers of Fig. 1. Along the ordinate axis is the velocity of establishment of the potential, in volts per minute; along the axis of abscissas, the time, in minutes, from the moment of introducing the electrode into the solution.

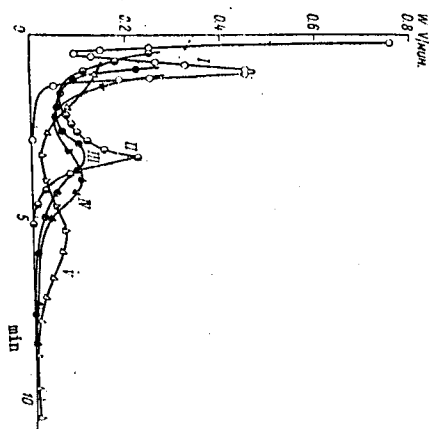


Fig. 4. Dependence of the velocity of establishment of the potentials on time. The curves are constructed from the data of Fig. 2. The numbers of the curves correspond to the numbers of Fig. 2. Along the ordinate axis is the velocity of establishment of the potential, in volts per minute; along the axis of abscissas, the time in minutes, from the moment of introducing the electrode into the solution.

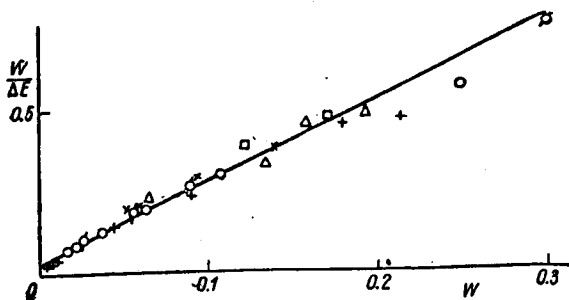


Fig. 5. Verification of equation (14) by the data of Fig. 1 (first part)

The data for curve I of Fig. 1 are not included.
 $\square$ - corresponds to curve II, Fig. 1. $\triangle$ - curve III;
 $\times$ - curve IV; $\circ$ - curve V; $+$ - curve VI.
 The symbol $\odot$ denotes the results for the curve drawn in the right-hand corner of Fig. 1.

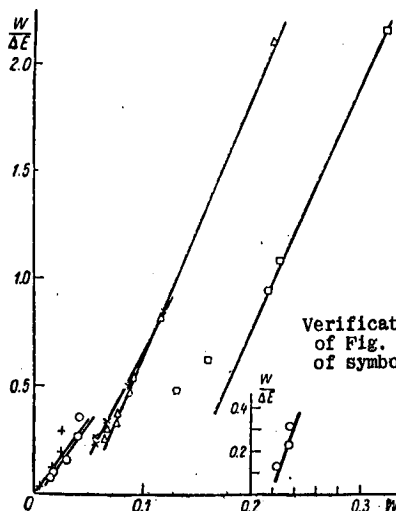


Fig. 6.

Verification of equation (14) by data of Fig. 1 (second part). For meaning of symbols, see Fig. 5.

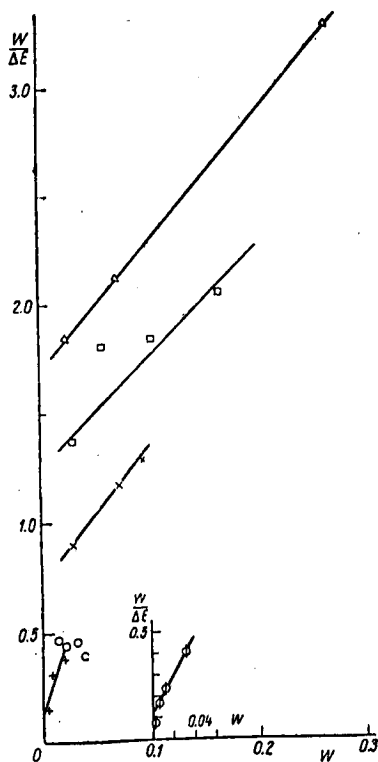


Fig. 7. Verification of equation (14) by data of Fig. 1 (third part). For meaning of symbols see Fig. 5.

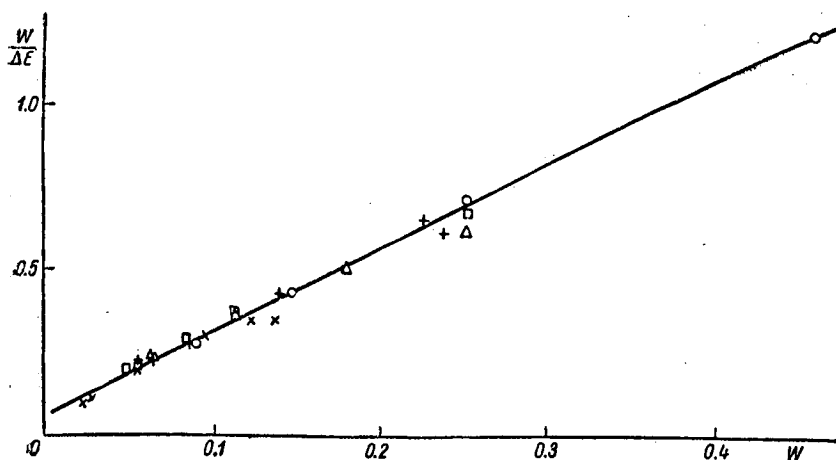


Fig. 8. Verification of equation (14) by data of Fig. 2 (first part)

$\circ$ - corresponds to Curve for temperature of 35° ; $\triangle$ - 25° ;
 $+$ - 17.5° ; $\square$ - 12.5° ; $\times$ - 0° .

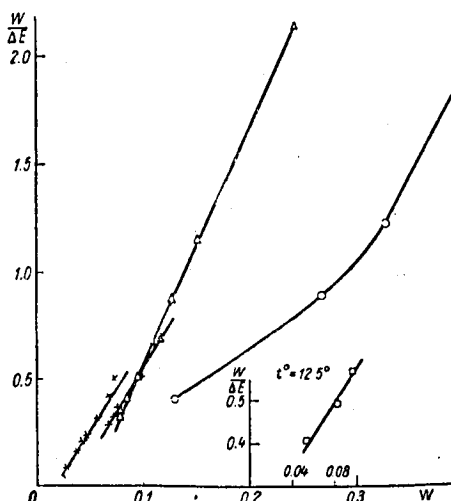


Fig. 9.

Verification of equation (14) by data of Fig. 2 (second part). For meaning of symbols, see Fig. 8.

solution, the double layer already possesses the structure of a plane condenser, while the diffused part takes time to form.

For the second part, (equation (14) is also confirmed fairly satisfactorily (Fig. 6).

Here the angular coefficient of the curve is a function of the concentration of Tl^{+++} ions. Its value increases along with the increase in concentration of trivalent thallium ions, a fact which is related to the decrease in the diffusion of the double layer and the resulting increase of its capacity. In this part, as is obvious, the diffusion structure of the double layer is manifested.

Fig. 7 shows that equation (14) also represents the third part of the curves of Fig. 1. Only for curve V did the calculation fail to give a satisfactory result. The dependence of the slope upon the concentration of Tl^{+++} ions in this part is not manifested with sufficient clarity. We must observe that the verification of equation (14) is justified up to the value of potentials which depart from the equilibrium value by not more than 20 mV. Consequently, the influence of the reverse reaction upon the kinetics is insignificant.

The results obtained by utilizing the data in Fig. 2 are shown in Figs. 8 and 9.

From Fig. 8 it is clear that equation (14) includes the first part of the curves, for here, as before, the points of all the curves lie well on one and the same straight line. We must suppose that the lack of dependence of the slope upon the temperature in the first part is determined by the fact that the first portion of adsorbed hydrogen atoms to react are extremely active and demand less energy of activation. In connection with this, the increase in the velocity constant with temperature is compensated by the corresponding increase of the coefficient of diffusion, and the decrease of λ .

For the second part of the curves, equation (14) is justified up to a temperature of 25° (Fig. 9).

The curve obtained by plotting W/AE against W at 35° did not give a straight line, which, perhaps, is the result of a very sharp rise in the curve, and the consequent impossibility of obtaining definite values of the velocity.

The slope here increases with the rise of temperature. This, apparently, might be explained by the failure of the velocity constant to increase with the temperature to a corresponding extent. In actual fact, in this part the less active hydrogen atoms begin to react, and consequently, the increase of the constant with rising temperature is expressed more strongly.

The data on the influence of temperature for the third part are not given graphically; from these data, we can conclude that equation (14) is justified only for the curves at 17.5 and 25°. At a lower temperature, the kinetics curves for this part are apparently subordinated to laws of some other kind.

It is possible to base certain calculations on the dependence of the slope upon the concentration of trivalent thallium ions and the temperature. However, we have refrained from making such calculations because we consider the experimental data of Figs. 1 and 2 insufficiently precise for this purpose. The curves obtained represent averages for 2 to 5 parallel experiments, whose reproducibility in certain cases leaves something to be desired.

On the basis of what has been presented above, we may consider that equation (14) on the whole gives a picture of the phenomenon in the given case of attainment of equilibrium oxidation-reduction potentials.

CONCLUSIONS

We have carried out a kinetics analysis of the curves of attainment of equilibrium oxidation-reduction potentials of the system Tl^{+++}/Tl^+ on hydrogen electrodes; the experimental values were obtained by the author together with Appenin and Tkachenko. We have shown that the kinetics of attainment of equilibrium potentials are conditioned by the delayed reaction which involves removal of the surplus hydrogen atoms from the surface of the electrode by the trivalent

thallium ions: $Tl^{+++} + 2H_{ads.} \rightleftharpoons Tl^{+} + 2H^{+}$.

If we assume that the speed of the reaction is of the same order as the speed of diffusion of Tl^{+++} ions toward the surface of the electrode, then the curve of the kinetics with an S-shaped twist can be quantitatively accounted for by the velocity equation:

$$\frac{dC_H}{dt} = K_1 C_H C_{Tl^{+++}} = K_2 C_H^2$$

With the introduction of several additional limiting assumptions, this equation also corresponds to the curves with straight line sections, analyzed in previous papers.

LITERATURE CITED

- [1] A. L. Rotinyan, I. I. Appenin, and V. G. Tkachenko, J. Gen. Chem. (USSR), 16, 1599 (1946). - [2] A. L. Rotinyan, Proc. acad. sci. USSR 46, 64 (1945). - [3] D. A. Frank-Kamenetsky, J. Phys. Chem. (USSR), 13, 756 (1939). - [4] A. B. Zdanovsky, J. Phys. Chem. (USSR), 20, 869 (1946) - [5] M. Tovbin, J. Phys. Chem. (USSR) 20, 1435 (1946) - [6] B. V. Drozdov, Doctoral Dissertation, L. P. I. (1946). - [7] A. D. Stepukhovich, J. Gen. Chem. (USSR), 15, 341 (1945). - [8] B. V. Ershler, J. Phys. Chem. (USSR) 14, 357 (1940).

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