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Abstract

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STATIONARY POTENTIALS OF ZINC AND AMALGAMATED ZINC IN SULFATE SOLUTIONS CONTAINING VARIABLE AMOUNTS OF ZINC AND HYDROGEN IONS

(Presented by Academician A. N. Frumkin on 20/II 1960)

The magnitude of the electrode potential established at the metal—solution interface in the absence of an external polarizing-current field is determined by the electrode processes occurring at the electrode under consideration (^{1,2}). A. N. Frumkin (^{1}) showed that during the self-dissolution (with hydrogen evolution) of metals in acid electrolytes, depending on the ratio of the rates of the electrode processes occurring on the dissolving metal, both practically equilibrium and substantially nonequilibrium potentials may be realized. Typical representatives of metals dissolving in acid solutions at nonequilibrium potentials are iron (^{3}) and nickel (^{4}). Their stationary potentials depend linearly on the logarithm of the concentration of hydrogen ions in the solution and do not depend on the concentration of like ions. In contrast to iron and nickel, metals such as lead (^{5}) and cadmium (^{6}) dissolve in acid electrolytes at practically equilibrium potentials. The difference in the behavior of the metals listed is determined by the fact that, in the case of self-dissolution of metals of the first group, the cathodic process proceeds mainly through the discharge of hydrogen ions, whereas in the case of metals of the second group it proceeds chiefly through the discharge of like metal ions (^{1,2,7}).

In the present work, using zinc and amalgamated zinc electrodes as an example, a case was studied in which comparable amounts of hydrogen and metal ions participate in the cathodic process. According to data available in the literature (^{8,9}), the dissolution of zinc in solutions of H_2SO_4 and HCl occurs at a substantially nonequilibrium potential. It could be assumed that decreasing the acid concentration and increasing the concentration of zinc ions in the solution would make it possible to bring about a transition from nonequilibrium to practically equilibrium zinc potentials. In this connection, sodium sulfate containing variable amounts of H_2SO_4 and $ZnSO_4$ was used as the electrolyte. The total concentration of $H_2SO_4 + Na_2SO_4$ was kept constant (1 N). Polycrystalline zinc containing $1 \cdot 10^{-4}\%$ impurities was used as the electrode material.* The salts were twice recrystallized and calcined; the acid and water were twice distilled.

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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

The measurements were carried out in an atmosphere of purified hydrogen at 25°. The electrode potentials reported in the article are referred to the zero of the hydrogen scale.

Figure 1 gives the curves $\varphi_0' - \lg[\mathrm{Zn}^{++}]$, characterizing the dependence of the stationary potential of the zinc electrode on the concentration of zinc ions in the solution at different concentrations of H_2SO_4. The concentration $[\mathrm{Zn}^{++}]$ is expressed in normalities. The curves in Fig. 1 were constructed on the basis of the mean values of the potentials observed in solutions stirred with hydrogen. The errors in determining the zinc potentials were 0.5-1 mV in the case of $[H_2SO_4] \lesssim 10^{-3}\ N$, and 3-5 mV in the case of $[H_2SO_4] \simeq 10^{-2}$—$10^{-1}\ N$. From Fig. 1 it is seen that, at $[H_2SO_4] = 10^{-4}\ N$, in the concentration interval $[\mathrm{Zn}^{++}]$ from $3 \cdot 10^{-3}$ to $1 \cdot 10^{-1}\ N$, a linear dependence is observed between φ_0' and $\lg[\mathrm{Zn}^{++}]$, corresponding to the Nernst equation (curve 1). The slope coefficient of the rectilinear portion of curve 1 in Fig. 1 is equal to 29 mV, i.e., within the limits of error, it coincides with the theoretical value. With increasing acidity of the solution the curves φ_0'—$\lg[\mathrm{Zn}^{++}]$ deviate ever more sharply from a rectilinear dependence. In a solution of $0.1\ N\ H_2SO_4 + 0.9\ N\ Na_2SO_4$, the potential of zinc is practically independent of the concentration of zinc ions in the solution.

Fig. 1. Stationary potentials of zinc at various concentrations of H_2SO_4:
$1 - 10^{-4}\ N$; $2 - 5 \cdot 10^{-4}\ N$; $3 - 10^{-3}\ N$; $4 - 10^{-2}\ N$; $5 - 10^{-1}\ N$

Fig. 2. Stationary potentials of amalgamated zinc at various concentrations of H_2SO_4:
$1 - 10^{-3}\ N$; $2 - 10^{-2}\ N$; $3 - 10^{-1}\ N$; $4 - 2 \cdot 10^{-2}\ N$; $5 - 5 \cdot 10^{-1}\ N$; $6 - 1\ N$

From Fig. 2 it is seen that, in the case of amalgamated zinc, the rectilinear dependence φ_0'—$\lg[\mathrm{Zn}^{++}]$, corresponding to the Nernst equation, is preserved at much higher concentrations of H_2SO_4 than in the case of zinc.

Table 1

Stationary potentials φ_0' of zinc and amalgamated zinc in solutions containing no additions of $ZnSO_4$

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* Before the experiments the surface of the electrodes was treated with HNO_3 and then washed with water.

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Fig. 3. Curves 1—3—zinc, curves 1′—3′—amalgamated zinc at different concentrations of $ZnSO_4$: 1, 1′—10^{-3} N; 2, 2′—10^{-2} N; 3, 3′—10^{-1} N

Figure 2: Fig. 3. Curves 1—3—zinc, curves 1′—3′—amalgamated zinc at different concentrations of $ZnSO_4$: 1, 1′—10^{-3} N; 2, 2′—10^{-2} N; 3, 3′—10^{-1} N

$[H_2SO_4]$, N pH	10^{-4} 4.85	10^{-3} 3.84	10^{-2} 2.81	10^{-1} 1.74	$2 \cdot 10^{-1}$ 1.44	$5 \cdot 10^{-1}$ 0.67	1.0 0.36
φ_0' (volt) Zn	0.897	−0.864	−0.832	−0.805	–	–	−0.774
φ_0' (volt) Zn(Hg)	–	−0.915	−0.903	−0.870	−0.858	−0.829	−0.814

Table 1 gives the mean values of the stationary potentials of zinc and amalgamated zinc, φ_0', observed in solutions with various pH in the absence of additions of zinc sulfate (the electrolytes were stirred with hydrogen).

The curve φ_0'—pH, constructed for the zinc electrode on the basis of the data of Table 1, has a rectilinear section with a slope coefficient

28 mV, which agrees with the data of A. L. Rotinyan, N. P. Fedot' ev, and Li Un Sok (^{9}), who obtained for zinc in 0.01—5 N H_2SO_4 solutions $d\varphi_0'/d\text{pH} = -25$—30 mV. In the case of amalgamated zinc, the linear portion of the φ_0'—pH curve was less sharply expressed.

The increase in the degree of deviation of the φ_0'—lg$[Zn^{++}]$ curves from the Nernst equation, observed with increasing acidity of the solution (Figs. 1 and 2), is evidently connected with an increase in the share of participation of hydrogen ions in the cathodic process. At the stationary potential φ_0', the rate of the cathodic process of discharge of hydrogen ions will be compensated by the difference between the rates of the anodic and cathodic processes occurring with the participation of zinc atoms and ions*:

$$k_1[H^+]_s e^{-\alpha F\varphi_0'/RT} = k_2' e^{\beta_1 F\varphi_0'/RT} - k_2[Zn^{++}]_s e^{-\alpha_1 F\varphi_0'/RT}. \qquad (1)$$

In equation (1), $[H^+]_s$ and $[Zn^{++}]_s$ are the concentrations of hydrogen and zinc ions at the electrode surface, which under self-dissolution will, generally speaking, differ from those ($[H^+]_0$ and $[Zn^{++}]_0$) in the bulk of the solution. For the sake of simplification we shall assume that $[H^+]_s = [H^+]_0$ and $[Zn^{++}]_s = [Zn^{++}]_0$. This condition will be fulfilled the better, the lower the rate of self-dissolution of the electrode and the more intensive the stirring of the electrolyte.

Fig. 3. Curves 1—3—zinc, curves 1′—3′—amalgamated zinc at different concentrations of $ZnSO_4$: $1, 1'$—10^{-3} N; $2, 2'$—10^{-2} N; $3, 3'$—10^{-1} N.

The stationary potential φ_0' will lie positive of the equilibrium potential φ_0 by an amount $\Delta\varphi = \varphi_0' - \varphi_0$. If the rate of the cathodic process of hydrogen-ion discharge at the equilibrium potential φ_0 and concentration $[\mathrm{H}^+]_0 = 1$ is denoted by I_0', then, after substituting the value $\varphi_0' = \varphi_0 + \Delta\varphi$ into equation (1), we obtain

$$I_0'[\mathrm{H}^+]_0 e^{-\alpha F \Delta\varphi/RT} = i_0 \left(e^{\beta_1 F \Delta\varphi/RT} - e^{-\alpha_1 F \Delta\varphi/RT}\right), \tag{2}$$

where i_0 is the exchange current corresponding to the given concentration of zinc ions $[\mathrm{Zn}^{++}]_0$ in the solution. Solving equation (2) with respect to $\Delta\varphi$, we obtain:

$$\Delta\varphi = a + k\left[\lg\left(1 - e^{-2F\Delta\varphi/RT}\right) + \mathrm{pH}\right], \tag{3}$$

where

$$a = -\frac{2.3RT}{F(\alpha+\beta_1)} \lg \frac{i_0 f_{\mathrm{H}^+}}{I_0'}, \qquad k = \frac{2.3RT}{F(\alpha+\beta_1)}. \tag{4}$$

It follows from equation (4) that the quantity a will be constant when $[\mathrm{Zn}^{++}] =$ const and $f_{\mathrm{H}^+} =$ const.

The degree of validity of the assumption, adopted in deriving equation (3), concerning the absence of concentration changes in the near-electrode layer of the solution can be judged on the basis of the influence of stirring of the solution on the value of the electrode potential. Experiments carried out with amalgamated zinc showed that the transition from stirring the solution with hydrogen to stirring with a magnetic stirrer practically does not change the values potential of the electrode*, which confirms the stated assumption. Similar measurements with a zinc electrode showed that the transition to more intensive stirring shifts the potential of the zinc electrode in the positive direction by amounts reaching 10 mV (see Table 2). A similar effect of stirring of the electrolyte in the $\mathrm{Zn/ZnSO_4}$ system was also observed by other authors (^{11}), who explained it by concentration polarization with respect to hydrogen ions. In view of the above, the experimental verification of equation (3) was carried out taking into account the shifts of the potential $\Delta\varphi_\mathrm{p}$.

Table 2

Shifts of the zinc-electrode potential $\Delta\varphi_\mathrm{p}$ (mV) observed under the influence of stirring*

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* In equation (1), in accordance with the works (^{10}), the normalization $\alpha_1 + \beta_1 = 2$ has been adopted. Constancy of the activity coefficients of ions and of the ψ_1-potential is assumed.

$[ZnSO_4]$, N	$[H_2SO_4]$, N	$[H_2SO_4]$, N	$[H_2SO_4]$, N	$[H_2SO_4]$, N	$[H_2SO_4]$, N	$[H_2SO_4]$, N
	10^{-4}	10^{-3}	$4 \cdot 10^{-3}$	10^{-2}	$2 \cdot 10^{-2}$	10^{-1}
10^{-3}	2.0	4.5	8.0	9.5	9.0	0.5
10^{-2}	1.0	4.0	6.5	10.0	8.5	0.5
10^{-1}	0	1.5	8.0	9.5	5.0	0.5

* A further increase in the intensity of stirring of the solution did not change the magnitude of $\Delta\varphi_p$.

It is seen from Fig. 3 that the experimental data, on the whole, obey well equation (3), derived on the basis of the theory of slow discharge. Significant deviations from the rectilinear dependence are observed only in the case of self-dissolution of the zinc electrode in the most acidic of the electrolytes studied (0.1 N H_2SO_4 + 0.9 N Na_2SO_4). A possible cause of the indicated deviations was activation of the surface of the solid zinc electrode at a considerable rate of its self-dissolution. This explanation is supported by the absence of a similar effect in the case of amalgamated zinc.

The rectilinear portions of curves 1-3 in Fig. 3, in accordance with equation (3), have practically identical slopes $k = 40$ mV**. On the basis of equation (4), for the zinc electrode we obtain $\alpha + \beta = 1.47$. Using the value $\alpha = 0.5$ obtained for the zinc cathode in work (^{9}), we obtain $\beta_1 = 0.97$, which is consistent with the value $\beta_1 = 0.92$ obtained in work (^{12}) from anodic oscillograms ($b_A = 64$ mV). Lines 1′—3′ in Fig. 3 have a slope $k = 37$ mV.

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* Small shifts of the potential of amalgamated zinc in the negative direction, not exceeding 1–2 mV, were apparently due to a slight increase in the concentration of zinc ions in the near-electrode layer.

** In solutions containing no zinc ions, with stirring by a magnetic stirrer, for metallic zinc there was obtained $\partial\varphi_0/\partial\mathrm{pH} = 41$ mV.

Note: Figure translations are in progress. See original paper for figures.

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