

POTENTIALS CORRESPONDING TO THE ONSET OF PASSIVATION AND THEIR RELATION TO THE ZERO POINTS OF METALS*

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As noted earlier by Ya. M. Kolotyrkin [1], the concept of the zero points of metals may prove useful when studying passivation phenomena. This proposition is supported by the experimental relationship of [2] between the current at the onset of passivation and the electro-capillary activity of additives, as analyzed on the basis of the reduced or φ scale of potentials introduced by L. I. Antropov.

It is well known that the potentiostatic anode-dissolution curve of passivating metals has a characteristic point, namely, the potential of the onset of passivation, ε_{op} . It is interesting to compare the values of ε_{op} for various metals under identical conditions of passivation. The most reliable values of ε_{op} satisfying this requirement are given for a number of metals in Table 1.

The number of items considered may be somewhat increased by including data relating to the ε_{op} of alloys studied under analogous conditions (Table 2).

The values of the zero points of pure metals are taken from the latest publications, in which they were determined either by calculation (Ti, Mo, Ni, Fe) or experiment (Cr, Fe).

* This article is published by way of stimulating discussion—Ed. note.

TABLE 1. Zero Points $\varepsilon_q = 0$ of Some Metals and Potentials Corresponding to the Onset of Passivation in 1 N H_2SO_4 at 25°, Expressed on the Normal Hydrogen Scale (ε_{op} , V)

No.	Metal	ε_{op} , V	References	$\varepsilon_q = 0$, V	References
1	Iron	+0.38; +0.46	[3-4]	0.00; -0.37	[9-11]
2	Titanium	-0.31	[5-6]	-0.70	[9, 12]
3	Molybdenum	-0.20	[7]	-0.38	[12]
4	Nickel	+0.15	[8]	-0.18	[9, 12]
5	Chromium	-0.35	[8]	-0.45	[13]

TABLE 2. Potentials at the Onset of Passivation for Certain Alloys in 1 N H_2SO_4 at 25°

Composition of alloy	ε_{op} , V	References	Composition of alloy	ε_{op} , V	References
Fe-14% Cr	-0.09	[14]	Fe-25% Cr -3.0% Ni	-0.11	[15-16]
Fe-25% Cr	-0.18	[15]	Fe-25% Cr -0.5% Mo	-0.22	[15-16]
Fe-31% Cr	-0.19	[14]	Fe-25% Cr -1.0% Mo	-0.22	[15-16]
Fe-25% Cr -0.5% Ni	-0.18	[15-16]	Fe-25% Cr -2.0% Mo	-0.19	[15-16]
Fe-25% Cr -1.0% Ni	-0.18	[15-16]	Fe-25% Cr -3.0% Mo	-0.19	[15-16]
Fe-25% Cr -2.0% Ni	-0.14	[15-16]	1Kh18N9T	-0.15	[8]

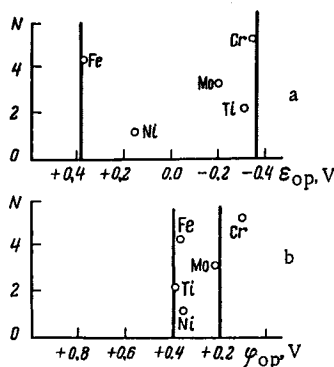


Fig. 1

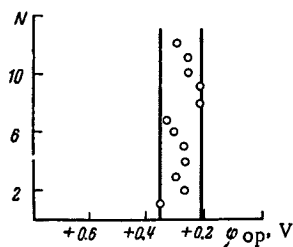


Fig. 2

Fig. 1. Potentials for the onset of passivation on pure metals in 1 N H_2SO_4 at 25°. a) According to the hydrogen scale; b) according to the zero-point scale. The y axis gives the serial number of the metal in Table 1.

Fig. 2. Potentials for the onset of passivation on alloys in 1 N H_2SO_4 at 25° on the zero-point scale. The y axis gives the serial number of the alloy in Table 2.

There are no published data on the zero points of the alloys listed. The values of these may be estimated on the following basis. All the alloys indicated in Table 2 are solid solutions. The zero points of the latter ordinarily coincide with the zero point of the most negative component even if there is only a little of this in the alloy [17]. For the alloys of Table 2 the component in question is chromium, so that we may put $\text{all } \varepsilon_q = 0 = \text{Cr } \varepsilon_q = 0$.†

Analysis of Tables 1 and 2 leads to the following conclusions. The potentials corresponding to the onset of passivation, reckoned relatively to the same comparison electrode, depend greatly on the nature of the metal. In the group of pure metals presented the values of ε_{op} embrace a range between -0.35 V (Cr) and $+0.38$ V (Fe), the accuracy of the potentiostatic measurements being about ± 0.01 V [18-19]. The composition of the alloys has a considerable influence on the critical passivation current and the velocity of self-dissolution [16], but has little effect on the value of ε_{op} .

Figures 1 and 2 give the potentials at the onset of passivation for the metals and alloys in Tables 1 and 2, expressed in the zero-point scale [9]‡:

$$\varphi_{op} = \varepsilon_{op} - \varepsilon_q = 0.$$

It follows from Fig. 1 that the potentials corresponding to the onset of passivation for the pure metals considered (on condition that $\text{Fe } \varepsilon_q = 0 = 0.00$ V) are equal to

$$\varphi_{op} = +0.3 \pm 0.1 \text{ V.}$$

The observed fluctuations in the value of φ_{op} (± 0.1 V) may be largely ascribed to errors in the theoretical calculation of the values of $\varepsilon_q = 0$ [9, 12].

The values of φ_{op} for the alloys (see Fig. 2) are also approximately equal to $+0.3$ V.

Thus we find that the potential corresponding to the onset of passivation as expressed in the zero-point scale, is independent of the nature of the particular member of the series of metals. This fact is analogous to that observed by L. I. Antropov, namely, that electro-reduction on a number of metals was sharply retarded at the same value of potential φ in each case, when this was reckoned on the zero-point scale [9].

† The effect of Ti on the $\varepsilon_q = 0$ of alloy 1Kh18N9T may be neglected since its content is under 0.7% [20].

‡ In calculating $\text{Fe } \varphi_{op}$ we took the value of $\text{Fe } \varepsilon_{op} = +0.38$ V recently found [4] by a better method than that used in [3].

In conclusion, the author takes pleasure in thanking L. I. Antropov for his interest in this paper.

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