on the effect associated with the value of $\varphi_{Hg/M}$. According to available data, the arrangement of metals with respect to their overvoltages changes little on going from solid cathodes to mercury cathodes. This is consistent with the fact that the zero-charge points for even extremely dilute amalgams of most metals show a parallelism with the zero-charge points of the corresponding metals. This fact also demonstrates the lack of justification for attempts to relate the overvoltage of metals to such properties as, for example, the melting point.

Thus the criticisms of Vagramyan and coworkers are unfounded. They are based chiefly on an incorrect understanding of the physical significance of both the zero-charge point of metals, $\epsilon_{q=0}$, and the potential of an electrode on the φ scale.

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REPLY TO L.I.ANTROPOV'S PAPER "THE APPLICATION OF THE φ SCALE OF POTENTIALS TO METAL OVERVOLTAGE"

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Antropov considers that certain critical remarks in a paper by Popkov, Klimasenko, and Vagramyan on zero-charge points is "... based chiefly on the lack of a sufficiently clear understanding, by these authors, both of the physical significance of the zero-charge point of a metal, $\epsilon_{q=0}$, and the potential of an electrode on the φ scale". In this connection, let us briefly consider the essential features of these ideas.

It should first of all be noted that the idea of the part played by the charge on the metal surface in electrode processes was developed by Frumkin[1] long before this was done by Antropov. Antropov's ideas differ from those of Frumkin, however, in that the former attempts to explain all the varied complex electrode processes (metal corrosion, electrolytic reduction of organic compounds, electrodeposition of metals, etc.) on the basis of the charge on the electrode surface[2], whereas Frumkin considers that this charge is important only in some cases.

The idea of the zero-charge potential arose in connection with electrocapillary phenomena[3]. It is known that, with change in the electrode potential, the surface tension of mercury passes through a maximum. It is assumed that the maximum point of the electrocapillary curve corresponds to the uncharged metal surface (the so-called zero-charge point). To the left of the maximum, with the generally accepted convention, the surface is positively charged, and to the right negatively charged. Frumkin[1] has suggested that for other metals there also exist zero-charge points, whose position relative to the standard electrode potential depends on the nature of the metal. As early as 1934, Frumkin gave approximate values for the zero-charge points of seven metals (Ag, Pt, Cu, Hg, Ga, Cd, and Tl). To determine the charge on the surface of a metal in a solution of its ions, Antropov makes the following elementary calculation:

$$\varphi = \epsilon^0 - \epsilon_{q=0},$$

where ϵ^0 is the normal potential relative to the standard electrode and $\epsilon_{q=0}$ is the zero-charge potential relative to the same standard. Thus the data obtained for a series of metals give the so-called potentials on the φ scale. When $\varphi > 0$, the surface of the electrode is positively charged, and when $\varphi < 0$, it is negatively charged. The absolute value gives the magnitude of the charge on the electrode surface.

It should be noted that, in the determination of the charge on the electrode surface, Antropov makes use of the zero-charge potential derived not from data obtained in a medium containing ions of the metal concerned, but in a medium of foreign ions, whereas ϵ^0 corresponds to a potential jump determined in a solution of the ions of the metal concerned, with activity equal to unity. This determination of the charge on the surface is significant only if it is assumed that this charge does not depend on the nature of the foreign ions and the concentration of the ions of the metal concerned, otherwise erroneous results are obtained.

Antropov[4] considers that, when the surface of an electrode is positively charged, negatively charged ions are concentrated around it on the solution side, creating an "anionic grid" similar to that of ordinary radio triodes, and facilitating the discharge of metal ions. When the electrode surface is negatively charged, however, foreign positive cations will be attracted from the solution, hindering the discharge of the metal ions. These primitive ideas of Antropov are illustrated in Fig. 1. This concludes a very brief exposition of "the physical significance of the zero-charge points of metals, $\epsilon_{q=0}$, and the potential of an electrode on the φ scale".

Unfortunately, Antropov has not examined the physical significance of these phenomena very deeply, and does not

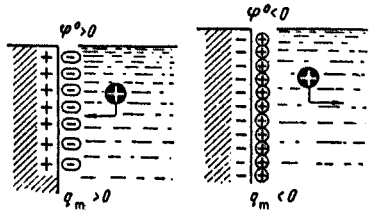

Fig. 1.

make allowance for the kinetic and hydrodynamic factors involved in the electrodeposition of metals. The above comparison with a triode is inappropriate, since an ion is not strictly localised. In the electrodeposition of a metal thermal movement of the species and convective currents near the electrode cause a continuous renewal of both discharging and non-discharging ions. Moreover, observation shows that the growth of crystals during deposition of metals takes place in regions whose thickness reaches several thousand atomic layers. This results from the intense movement of the electrolyte near the electrode and is associated with exceptionally complex hydrodynamic phenomena at the electrode surface during electrolysis. The simplified ideas of Antropov's analogy with the "anode grid" in triodes are inappropriate and cannot reflect the essential features of these phenomena.

Elementary calculation shows that the concentration of ions at an electrode surface is not as high as represented in Fig. 1. Thus in the case of divalent ions, when the potential differs from $\epsilon_{q=0}$ by 0.5 V (on the basis of an electrode capacitance equal to 18–20 μF cm^{-2}), the calculation shows that there is one ion for every 100 atoms on the surface†. Assuming that only a small fraction of the electrode surface is screened by foreign ions and that the ions, on the solution side at any rate, are hydrated and that the forces arising from their charges are compensated by the dipoles of the solvent, it is obvious that they cannot effectively hinder or facilitate the approach of the discharging ions to the electrode. Thus Antropov's theoretical views are extremely primitive and lack validity.

On what experimental data are Antropov's ideas based? There are insufficient data for metals of greatest practical importance to enable a table of zero-charge points to be constructed, but in 1953 Vasenin[5], a student of S.V. Gorbachev, put forward an original equation for calculating the zero-charge points of a number of metals:

$$\epsilon_{q=0} = 4.25 + 0.86\varphi. \qquad (1)$$

Antropov has made no allowance for the low accuracy of this equation, and has not verified it experimentally. He has merely modified it slightly, as he states, "to give better agreement with experimental data", and has calculated the zero-charge potentials for a number of metals[2]:

Fe (0.05), Co (-0.5), Ni (0.29), Cu (0.49).

On the basis of these and the above data, he constructed a graph relating the zero-charge potential to the electron work function for different metals (Fig. 2). Antropov[6] concludes that "most of the experimental data (irrespective of whether they relate to aqueous solution or to melts) lie with sufficient accuracy on the same straight line". Here he makes a serious error by comparing data for aqueous solutions with data relating to melts, for which there are no reversible standard reference electrodes[7].

On the basis of the data given in Fig. 2, and taking account of more accurate results for silver[8], it is possible to reach unambiguously the opposite conclusion, since most of the points do not lie on the same straight line. Nevertheless, Antropov[6] considers that the arbitrarily drawn line in Fig. 2 reflects the truth more accurately than

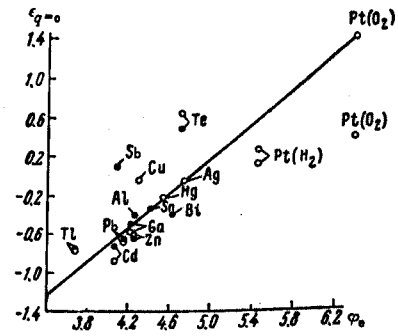

Fig. 2.

the experimental results: "... the accuracy of the measurement of $\epsilon_{q=0}$ and φ is small, and it is not known which of these quantities should be corrected in each individual case", or "we can say that for Sb, Cu, and Bi, the values found for $\epsilon_{q=0}$ differ considerably from the true values", *i.e.* Antropov[6] himself casts doubt on the reliability of the experimental data. The experimental data for the zero-charge points, given repeatedly in his papers, are not very accurate, as he himself admits (the errors are ± 0.2 V).

It is also impossible, on the basis of Eqn. (1), to obtain accurate information on the zero-charge points, since the accuracy of the determination of the electron work function[9] is 0.5 V. Thus the accuracy of both experimental and calculated data is low (the error amounts to 0.2–0.5 V). How then is it possible to make any definite statement regarding the signs of the charge on the surface of most metals, given by Antropov[4], when the error in the values on the φ scale, Ni -0.23 V, Fe -0.07 V, Co 0.24 V, Zn -0.13 V, Cu 0.22 V, and Sn 0.20 V, amounts to ~ ± 0.2 V? Even if it is assumed that his views are correct, how is it possible to explain the difference in the rate of reduction of ions, if the sign of the charge on the surface of these metals is not known reliably?

Let us take one further example to illustrate the reliability of experimental data on zero-charge points. The normal potential of a silver electrode can be determined with high accuracy (several tenths of a millivolt)[10]. For many metals, moreover, the normal potentials in aqueous solutions can be determined fairly accurately, but for the metals of the iron group and other readily passivated metals, determination of the equilibrium potential is difficult[11]. The determination of the zero-charge potential is difficult, however, even for silver, and the data obtained by different methods differ considerably. Thus adsorption measurements[12-14] give for silver ± 0.05 V; capacitance measurements give 0.05 V and -0.15 V; and observation of smoothing [electropolishing? (Ed. of Translation)][15] gives -0.3 V. Recently, Leikis[8] obtained -0.7 V for silver, using a capacitance method.

Thus for silver, which is a simple metal readily available for electrochemical study, the values of the zero-charge potential obtained by different authors differ by more than 0.7 V. What then can be said of the values of the zero-charge potential for other metals such as those of the iron group?

† In these calculations it is assumed that all the cations (in the case of $\varphi < 0$) in the double layer are foreign ions, *i.e.* are not reduced at the electrode. If some of these ions are the discharging ions, which is more likely, this ratio will be even smaller.

There have been no studies on electrode processes with an accuracy of the measurements as low as this, and it is strange that Antropov has tried, on the basis of these inaccurate data, to explain experimental results on metal overvoltage, obtained with far higher accuracy.

Antropov, replying to Popkov, Klimasenko, and Vagramyan, puts forward a dual viewpoint. On the one hand he attributes the difference in the overvoltage of metals to the sign and magnitude of the charge on the electrode surface, and on the other hand he formally does not deny the part played by passivation and other factors. It should be noted that the electrostatic forces acting on an ion near the electrode are far weaker than in the chemisorption of foreign species. The latter, being firmly bound to the electrode surface, alter its nature and influence the rate of electrode processes. If Antropov had considered this, he would not have written[6] that "... passivation theory cannot explain without further assumptions the difference in the polarisation values and the structure of the deposits for metals of the iron group and metals such as lead, silver and some others. If the values of the zero-charge points of these metals are taken into account, it is possible to obtain a definite interpretation of this phenomenon".

Antropov considers that the experiments carried out by Popkov *et al.* are not related to his work, since these authors did not take account of the difference between ϵ^0 and ϵ', where ϵ^0 is the normal potential of the electrode, *i.e.* for an activity of the metal ions equal to unity, and ϵ' is the equilibrium potential of the metal under the given experimental conditions.

If Antropov had attached any great importance to this argument, he should first of all have abandoned his views on the relationship between the charge on the surface and the magnitude of the polarisation of the electrode, since the charge on the electrode surface is determined from the value of ϵ^0, and in the electrodeposition of most metals the concentration of ions at the electrode surface decreases to zero, since the greater part of the polarisation is concentration polarisation. In the experiments with a mercury electrode (designed to verify the theory), even when the mercury ion concentration is very high, there is a decrease in the concentration of ions at the electrode surface during electrolysis.

It should also be pointed out that, according to Antropov's ideas, the rate of reduction of metal ions depends not on the concentration of discharging ions in the double layer, as follows from the laws of the kinetics of electrode processes, but on the nature of the film formed on the electrode surface (cationic or anionic grid). For example, in the case of a cationic film, the discharge of metal ions is retarded until the discharging ions have penetrated through the film, after which reduction takes place much more rapidly. The surface concentration of the discharging ions does not determine the rate of the process.

Antropov also considers that, when comparing the rate of reduction of metal ions with the sign of the charge on the metal surface, it is not necessary to keep the same concentration of ions for ϵ^0 and ϵ'. Thus in the Table‡, which is taken from Antropov's paper (his symbols)[2], the values of the potential $\Delta\epsilon_1$, obtained from ϵ^0, are compared with the potential $\Delta\epsilon_2$, for which the concentration of ions in the electrolyte is quite different from that for the conditions under which the normal potential ϵ^0 is measured.

‡ In different papers Antropov gives different values of the potential on the φ scale for a given metal.

In the Table $\Delta\epsilon_1$ is the same as the potential on the φ scale, *i.e.* the value of the charge on the metal surface in the "equilibrium" state, and $\Delta\epsilon_2$ is the same potential when current is passing. ϵ_i is the cathodic potential during the reduction of the metal ions at the current densities used in industry, where, as pointed out above, the concentration of metal ions differs considerably from that corresponding to ϵ' and ϵ^0. Thus it is strange that Antropov should assert that we have not allowed for the difference between ϵ' and ϵ^0. The reference to the fact that in our experiments mercury ions are absent, so that the charge on the electrode may have a fairly high negative value, is incorrect, since acidic solutions always contain mercury ions formed by dissolution of its oxides. Although the activity of the solution will not be equal to unity, nevertheless, considering that the potential of mercury has a high positive value, that change in the concentration of the ions cannot significantly influence the electrode potential, and that the presence of more negative ions (nickel) does not influence the potential of mercury, it can be assumed that under these conditions the charge on the mercury remains positive.

According to Antropov's views, in the reduction of nickel ions on mercury, *i.e.* on a positively charged surface, we should expect them to be more readily discharged, but this is not confirmed experimentally. Both at the start of the process, when the nickel is deposited on a mercury electrode, and subsequently, when the nickel is deposited chiefly on nickel, the discharge of nickel ions is hindered. Moreover the high overvoltage for the deposition of metals of the iron group on mercury is not related to the solubility in mercury of the metal being deposited, as we have already point out[16].

Antropov states[4] that "... when the potentials of metals change very slightly with change in the concentration of the solution and the current density, the sign of the charge on the metal, determined by the sign of the φ potential, will remain unchanged, even for a fairly marked change in the conditions under which the metal–solution system exists". When dealing with this question as regards our experiments, Antropov contradicts himself.

Many experimental facts indicate that Antropov's view of the relationship between the charge on the surface and the magnitude of the overvoltage is incorrect. One well-known fact is sufficient. The zero-charge points of metals, according to Antropov, have the same values for aqueous solutions and for melts. It might therefore be possible to verify the relationship between the charge on the surface and the magnitude of the overvoltage in melts also. It is known, however, that metals of the iron group are deposited from melts without overvoltage. Where then in this case is the screening action of cations assumed by Antropov's theory?

It is surprising that several years ago Antropov attributed the low overvoltage (3–5 mV) for the deposition of

TABLE.

Potential	Fe	Co	Ni	Zn	Cu	Cd	Pb	Ag
$\Delta\varepsilon_1=\varepsilon^0-\varepsilon_{q=0}$	−0.46	−0.23	−0.57	−0.13	−0.15	0.5	0.56	0.75
$\Delta\varepsilon_2=\varepsilon_i-\varepsilon_{q=0}$	−0.82	−0.02	−0.99	−0.19	−0.23	0.48	0.54	0.74

silver to the charge on its surface ($\epsilon_{q=0}$ = 0.05 V). Later, after a new value had been obtained for the zero-charge potential ($\epsilon_{q=0}$ = -0.7 V), *i.e.* when the magnitude of the charge [the zero-charge point? (Ed. of Translation)] had been changed by 700 mV, he again attributed the low overvoltage of silver to the charge on its surface. This naturally raises the question of whether the magnitude of the charge on the surface of the metal has any influence on the overvoltage and whether this viewpoint is worthy of further consideration.

From the above it follows that Antropov's views regarding the influence of the charge of an electrode surface on the overvoltage of metals are based on an incorrect scientific theory and unreliable experimental data, and are therefore unjustified.

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RECOMBINATION OF RADICALS FROM DIFFERENT TRACKS DURING RADIOLYSIS AND HOMOGENEOUS KINETICS. II. APPLICABILITY OF ALLEN'S MODEL

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During radiolysis radicals are distributed non-uniformly in the solution, but in calculations for concrete cases this distribution is assumed to be uniform. To estimate the error introduced thereby, we shall examine first, as before[1], a solution with radicals of one kind, namely $H^\cdot$ atoms. This case is realised in practice, for example, in the radiolysis of an acid solution of $FeSO_4$, in which $OH^\cdot$ radicals do not accumulate in the bulk†, because of the rapid reaction $Fe^{2+} + OH^\cdot$, and therefore do not participate in any other reaction. The $H^\cdot$ atoms in this solution do accumulate, because the reaction with the acceptor (H^+ ion) is slow, and participate in two competing reactions: (1) recombination $H^\cdot + H^\cdot$ with rate constant k; (2) capture $H^\cdot + H^+$ with rate constant k_A.[1,2] The concentration c of the atoms changes from a maximum (at the sites where the spurs are generated) to a minimum value.

In the steady state we note the instantaneous distribution of c in a certain volume of the solution and then plot the elements of this volume as abscissa in order of decreasing values of c. We then plot the values of c, corresponding to each volume element, as ordinate and obtain the distribution curve $c(w)$‡, whose shape does not depend on time.

To plot the $c(w)$ curve, we must first examine the generation of a single spherical spur with an effective radius R_0, containing n_0 $H^\cdot$ atoms. For simplicity, we shall replace the Gaussian distribution of the radicals in the spur by a uniform distribution and assume that the radius of the spur increases according to the equation

$$r^2(t) = R_0^2 + 9.5Dt. \qquad (1)$$

Eqn. (1) follows from the requirement that the rate of recombination in a spur with volume $v = \frac{4}{3}\pi r^3$ and a radical concentration n/v should be the same as the rate of recombination in a spur containing the same number of radicals, at the instant of generation, having a Gaussian distribution such that the root mean square distance of the radicals from the centre of the distribution is the same in both spurs. The decrease of the quantity n in a spur having a uniform concentration is given by the following expression:

$$\frac{dn}{dt} = -2kv\left(\frac{n}{v}\right)^2.$$

On solving Eqn. (1), we obtain

$$n = n_0 \frac{1}{1 + L(1 - R_0/r)}, \qquad (2)$$

where $L = 0.1\,kn_0/DR_0 = 0.23$ is a constant calculated in the previous paper[1].

We now introduce a spherical volume V (with radius R) of a single spur whose lifetime is T. Consider 1 cm³ of the solution in which the formation of spurs began. Suppose that in 1 sec ν spurs are formed, the radius of each increasing according to Eqn. (1). At a certain moment T the entire volume of the solution becomes filled with atoms and the individual spurs vanish. The quantities T and V

† We shall distinguish radical reactions "in the spur" (track) and "in the bulk". The quantitative determination of the fraction of the solution occupied by the spurs and by the "bulk" is given in the text.

‡ The letter w denotes a variable volume, read off from the origin of the coordinates, when the distribution of the volume elements of the solution is plotted along the abscissa axis in the way indicated above.