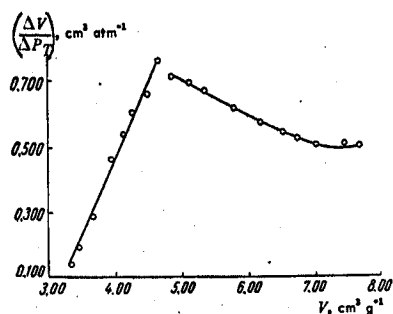




Mean compressibility of propane
at 100°C ($t_{\text{cr}} = 96.81^\circ\text{C}$).

of the compressibility curve near the maximum is clearly seen; there is a steep slope on the liquid side and a more gentle slope on the gaseous side (Figure)†.

It is not certain whether the maxima of $C_p(\partial V/\partial T)_p$ and $(\partial P/\partial V)_T$ coincide or not since the experimental evidence is contradictory^{2,3}; Rozen's theoretical argument concerning the fanwise divergence of the lines of the maxima⁴ is surely not very conclusive since it depends on various assumptions that have been previously discussed¹.

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THE APPLICATION OF THE φ SCALE OF POTENTIALS TO METAL OVERVOLTAGE

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Vagramyan and coworkers^{1,2} have stated that my theory³⁻⁵ regarding the role of surface charge in the electrodeposition of metals is erroneous, since:

(1) "... the deposition of metals of the iron group on mercury should be greatly facilitated, because its surface is positively charged and, according to Antropov, negatively charged ions facilitating the discharge of cations should concentrate at the mercury surface on the solution side.

† An unfortunate error occurs in Table 4 of Ref. 1, connected with the conversion of densities in Amagat units into specific volumes in $\text{cm}^3 \text{g}^{-1}$; v must be $0.98252 \text{ cm}^3 \text{g}^{-1}$ for $p = 66.7753 \text{ atm}$. This error was pointed out to me by Yu. D. Kolpakov and V. P. Skripov. Consequently two values near the maximum compressibility of xenon at 25° are incorrect. Fig. 7 is therefore also wrong; it should be an asymmetrical curve with a maximum (no abrupt decreases in compressibility).

Experiments show, however, that the reduction of metals of the iron group at a mercury cathode is much more difficult than ... at electrodes of the metals concerned" (Ref. 1, p. 817).

"The Table (a table of φ^0 potentials — L.A.) shows that the difference in the value of φ^0 for nickel and mercury amounts to about 1.4 V, i.e. that the reduction of nickel at a mercury electrode should be easier than the deposition of nickel at a nickel cathode ... Experiment shows, however, that the reverse is true" (Ref. 2, pp. 1741–1742).

(2) "An analogous contradictory result is observed in the electrodeposition of silver. Thus, according to recent data (reference is here made to a paper by Karpachev and Stromberg⁶ — L.A.), the zero charge of a silver surface is displaced to more negative values relative to the hydrogen electrode by 0.6–0.7 V. According to Antropov's ideas, positively charged ions with a marked retarding action on the reduction of silver ions should be adsorbed on the electrode surface. Experiment shows, however, that there is almost no overvoltage in the deposition of silver from solutions of its simple salts" (Ref. 1, p. 817).

These arguments are in fact irrelevant, since the theory with which the experimental data are compared bears no relation to my work³⁻⁵, and results from faulty reasoning by Vagramyan and his coauthors.

In my papers, as correctly stated by Vagramyan *et al.* (Ref. 1, p. 816; Ref. 2, p. 1741) the charge on a metal surface under electrodeposition conditions is estimated on the basis of the sign and magnitude of the φ^0 potential, defined as:

$$\varphi^0 = \epsilon^0 - \epsilon_{q=0}, \quad (1)$$

where ϵ^0 is the standard potential of the metal and $\epsilon_{q=0}$ its zero-charge point, expressed on the same arbitrary scale of potentials, for example the hydrogen scale†.

By definition, φ^0 is the standard potential of a metal, relative to its zero-charge point, and corresponds to a system consisting of a metal in a solution of a salt of the same metal, with the metal ion activity equal to unity. The potential ϵ' of any metal, for example mercury, immersed in a solution of a salt of another metal, for example nickel, obviously cannot be equal to the standard potential ϵ^0 of the first metal, in this case mercury; ϵ' is usually much more negative than ϵ^0 (according to the familiar Nernst formula). From this it follows that the potential of mercury on the φ scale, derived from the ϵ potential [see Eqn. (1)] cannot be equal to φ^0 , but is equal to:

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

which has nothing in common with its standard potential φ^0 , used by Vagramyan and coworkers in the formulation of their first conclusion. The unjustified use of φ^0 in the comparison of overvoltage at solid cathodes and a mercury cathode is thus one of the reasons why the first objection of Vagramyan and coauthors to my views must be regarded as erroneous.

† In the more general case we must use the quantity φ corresponding to specific electrolysis conditions — electrolyte composition, temperature, etc. As I have pointed out⁵, the use of φ^0 is a slight simplification, which is however admissible as a first approximation, since the activities of the metal ions in the solutions generally used for metal electrodeposition do not differ greatly from unity.

Another reason is related to the fact that the deposition of iron, nickel, and cobalt, which are almost insoluble in mercury, takes place, even when mercury cathodes are used, mostly not on mercury but on the corresponding solid cathodes. Under such conditions the charge on the mercury surface (its φ potential), even when defined correctly, naturally cannot play any part in the electrodeposition of these metals. The difference in overvoltage for the electrodeposition of, for example, nickel on nickel and on mercury, is here related to the form — compact or dispersed — in which the metal is deposited at the cathode. It is surprising that Vagramyan and coworkers, while recognising the specific character of the deposition of the metals of the iron group on mercury in this respect, have considered it possible not only to compare metal overvoltage with the values of φ^0 but also to reach certain theoretical conclusions on this basis.

With reference to the second objection to my views, the following points may be noted. The charge of a metal surface is determined not by the potential of zero charge, as stated by Vagramyan and Popkov (Ref. 1, p. 817), but by the value of φ or the φ^0 potential, as they correctly wrote one page earlier while discussing Eqn. (1). It can readily be seen that, contrary to Vagramyan and Popkov's assertion, at the new zero-charge point ($\epsilon_{q=0} = -0.7$ V) the value of φ^0 determining the charge of the silver surface will not be negative, but actually more positive [$\varphi^0 = 0.8 - (-0.7) = 1.5$ V] than that for the value which I adopted: $\epsilon_{q=0} = -0.05$ V [$\varphi^0 = 0.8 - (-0.05) = 0.85$ V]. No retarding action by cations is to be expected here, in spite of Vagramyan and Popkov's statement, and the discharge of silver ions should proceed without hindrance, as found experimentally. It is quite clear that Vagramyan and Popkov's reasoning has nothing in common with my views, but results from a confusion between the φ^0 potential and the zero-charge point $\epsilon_{q=0}$.

It is noteworthy that when Vagramyan and coworkers are not occupied in refuting my views, but are merely giving experimental results, their data agree fairly well with conclusions reached on the basis of the application of the φ scale of potentials. Thus the measurements of the cathodic potentials for the deposition of certain metals from their sulphate solutions, carried out by Vagramyan and Popkov, led them to the conclusion that metal overvoltage decreases in the order:

Ni, Co, Fe, Cu, Zn, Cd, Tl, Sn. (A)

The order of increasing positive values of φ^0 for these metals, however, is

Ni, Fe, Co, Zn, Cu, Bi, Sn, Cd, Pb, Tl, Ag, Hg. (B)

It can readily be seen that the order (A) corresponds on the whole to the more general order (B). Exceptions are Zn, which should precede copper, and Sn, which should precede cadmium. For these metals, however, most published values of the overvoltage are higher than those obtained by Vagramyan and Popkov. The parallelism in the cathodic and anodic overvoltages, established by Vagramyan

and Popkov, also agrees with my views, and may be explained by the fact that adsorbed anions should accelerate, and adsorbed cations retard, the passage of positively charged metallic ions through the double layer, irrespective of the direction in which this transfer is taking place.

In this connection the following points may be noted.

1. I have never stated that the charge on the surface, i.e. the magnitude of the φ potential of the metal (and not the zero-charge point $\epsilon_{q=0}$, as assumed by Vagramyan *et al.*), is the only factor determining the kinetics of the electrodeposition of metals. On the contrary, I have always pointed out that allowance should be made for other factors — the ratio of the bond energies of the ion in solution and in the metal, passivation effects, the sorption of hydrogen, etc. In some cases these factors may even predominate. The particular attention paid in my papers to the charge on the metal surface, reflected in the value of the φ potential, is due not only to the important part which it plays in the kinetics of electrodeposition but also to the fact that this factor has not been taken into account in most work on the electrocrystallisation of metals. The surface of the metal being deposited has always been assumed to be negative, merely because the deposition of metal is taking place at the cathode. This is of course incorrect, and these ideas cannot provide a reliable guide for the research worker, particularly in the search for additives capable of influencing the electrodeposition of metals.

2. The simple relationship which I have postulated between the values of φ^0 and the overvoltage of metals assumes that the kinetics of electrodeposition are determined by the discharge of the metal ions. Only in this case can we expect that cations will increase, and anions decrease, the metal overvoltage. The fact that most metals show a regular decrease in overvoltage with increase in the positive value of the φ^0 potential provides proof of the applicability of the concept of retarded discharge to the cathodic deposition of metals. It should, however, be remembered that, for a sufficiently high positive value of the φ^0 potential, the activating action of the anions may be so great that discharge will proceed without any retardation. All deviations of the potential, when current is flowing, from the equilibrium value must be due to other factors, such as crystallisation retardation. The arrangement of the metals with respect to overvoltage, which should here be very small, will now not be simply related to the φ^0 potential. This is probably realised in the case of the cathodic deposition of metals such as mercury (where crystallisation retardation is also excluded), cadmium, thallium, and silver, which have extremely high positive φ^0 potentials.

3. Although the comparison of the values of φ with the overvoltage at solid cathodes and a mercury cathode, in the form in which this has been done by Vagramyan and coworkers, is without significance, the comparison can be made for metals soluble in mercury. It is necessary, however, to remember the following points. (a) The potential of a mercury electrode under these conditions is not equal to the standard potential of mercury, but is determined by the activity of the metal ions in solution and the activity of its atoms in the amalgam. (b) The zero-charge potential of a mercury electrode, under the conditions of metal deposition on the mercury, is not equal to the zero-charge point of pure mercury, but is determined by the composition of the resulting amalgam. (c) The energy gains for discharge on the metal concerned and on the amalgam may be different, and this will be superimposed

† The above assertion by Vagramyan and Popkov that the charge on the silver surface is negative, since its zero-charge point is equal to -0.7 V on the hydrogen scale, is contrary to the physical significance of the potential of zero charge; $\epsilon = \epsilon_{q=0}$, irrespective of whether it is positive or negative, corresponds to an uncharged metal surface.

on the effect associated with the value of $\phi_{Hg/M}$. 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"

A. T. Vagramyan

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 Frumkin¹ 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, electro-deposition of metals, etc.) on the basis of the charge on the electrode surface², whereas Frumkin considers that this charge is important only in some cases.

The idea of the zero-charge potential arose in connection with electrocapillary phenomena³. 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. Frumkin¹ 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:

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

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 $\phi > 0$, the surface of the electrode is positively charged, and when $\phi < 0$, 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.

Antropov⁴ 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

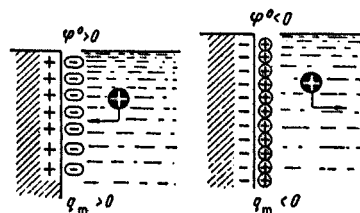


Fig. 1.