HYDROGEN OVERVOLTAGE.

A Reply to Edgar Newbery.

By Duncan A. MacInnes.

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In a recent article, Newbery[1] has criticized the papers published, on hydrogen overvoltage, by MacInnes, Adler, and Contieri. The lack of agreement between this author and ourselves is, among other things, due to a difference in the use of the term "overvoltage." According to Newbery's implied definition the expression should be reserved for potentials determined by a commutator device, which periodically opens the exciting current at the electrode under examination and closes the potentiometer circuit connecting this electrode and a reference electrode. In the work of MacInnes and Adler,[2] and of practically every worker in this field, the exciting current remains flowing while the potentiometer measurements are made. Aside from the undoubted privilege of an author to define a term, within its range of meaning, in the sense most suitable for his purpose, I can find no precedents in the chemical literature for Newbery's objection to our use of the word.[3] In fact Newbery appears to be nearly, if not quite, alone in thus restricting the meaning of the term.

I will, therefore, use the term "overvoltage" in what follows as "the difference of potential that exists between a reversible hydrogen electrode and an electrode, in the same solution, at which hydrogen, H_2, is being formed from hydrogen ions."[4] The expression, "counter electromotive force" will be, in the lack of a better term, used for the potential obtained by a commutator device. The difference between overvoltage and counter electromotive force, in the senses just described, is Newbery's "transfer resistance."

My interpretation of Newbery's criticism is this, that the counter e. m. f. is more important and fundamental than the overvoltage since the latter is a combination of the counter e. m. f. and the "transfer resistance," the "transfer resistance" being, in turn, dependent upon the current density, the resistance of the electrolyte, the external pressure, etc. This is, of course, a criticism of all work on overvoltage not carried out with a commutator device. It is evident that the concept of "transfer resistance" should receive careful consideration.

The measurements by MacInnes and Adler were made with an apparatus shown diagrammatically in Fig. 1. Vessel C_1 held a rod of zinc, C_2 the

[1] This Journal, 42, 2007 (1920).

[2] Ibid., 41, 194 (1919).

[3] See, for instance, Caspari, Z. physik. Chem., 30, 89 (1899); Tafel, ibid., 50, 641 (1904); Lewis and Jackson, ibid., 56, 193 (1906); Thiel and Breuning, Z. anorg. Chem., 83, 329 (1913); Coehn and Dannenburg, ibid., 38, 609 (1901); Mott, Trans. Am. Electrochem. Soc., 15, 569 (1909); Rideal, This Journal, 42, 94 (1920).

[4] MacInnes and Adler, loc. cit.

electrode under observation, and C_3 the reference hydrogen electrodes. Between the electrodes in C_1 and C_2 was placed an adjustable source of potential opposite to, and slightly lower, than that naturally present between the electrodes.   Between the electrodes in C_2 and C_3 a potentiometer was connected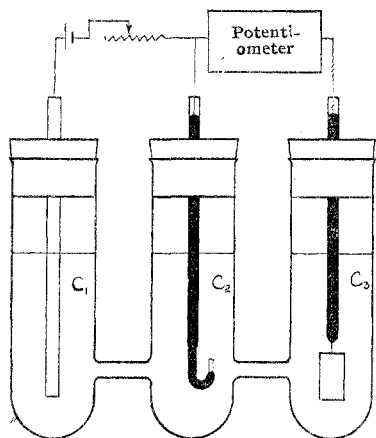 as shown.   Newbery contends that a film of gas forms over the electrode in C_2 producing an electrical "transfer resistance" at the surface.   Our experiments have shown, however, that gas does not cover more than a very small part of the electrode surface at the current densities of our experiments.   Gas evolution took place from one or two favored spots, apparently holding nuclei of the gas phase.   In the absence of these nuclei, gas evolution did not occur even at considerably higher voltages (see MacInnes and Adler, p. 200).   In fact, the continued evolution of bubbles appears to be a sensitive test for the presence of gas phase on an electrode surface.   This is precisely analogous to the gas evolution from a surface immersed in a supersaturated gas solution or in a superheated liquid.   The presence of a *gas* film covering any large portion of the electrode surface and of an ohmic "transfer" resistance due to such a film are, at least, open to serious question.[1]

Fig. 1.

Further, Newbery himself points out quite logically, in a paper referred to in his criticism,[2] that the existence of "transfer resistances" at the surfaces of electrodes means that all conductance measurements are in error since, if the supposed resistance exists only during the time that the current is passing, the errors resulting would not be overcome by the usual artifice of using an alternating current.   These transitory resistances are, according to this paper, of surprising magnitude, being as high as 1000 ohms for cells containing solutions whose resistances are of the order of 10 ohms.   Also, he finds that the "transfer resistances" are greatest at low current densities!   In one case mentioned 2 platinized electrodes,

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[1] An attempt was recently made in this laboratory, by Mr. W. R. Hainsworth, to determine whether the overvoltage readings of the apparatus represented in Fig. 1 are independent of the resistance of the circuit including the potentiometer and the electrodes in C_2 and C_3.   Capillary tubing of different sizes was placed between the vessels, without changing the readings, and finally, a large wide tube filled with electrolyte connected Vessels C_1, C_2 and C_3, again without effect.   In this apparatus the reference electrodes are apparently uninfluenced by the current passing between the electrodes in C_1 and C_2, at least for the current densities of our experiments.

[2] *Trans. Faraday Soc.*, **15**, 126 (1919).

2×1 cm. and 2 cm. apart, dipping into N sulfuric acid an arrangement having a resistance of about 4 ohms by the usual methods, gave a "transfer resistance" of *180 ohms* at the lowest current density (2 milliamperes). In view of these figures it would appear, if they have any basis in reality, that all electrolytic conductance work is subject to large errors. However, the precision with which conductances can be measured and the agreement of the results of numerous workers using quite different potentials, current densities, and electrodes, is strong evidence against errors due to such a source, and against the presence of "transfer resistances" of any appreciable magnitude. Also, the same author has published[1] results of conductance measurements carried out by determining the potential drop between 2 reversible electrodes in, and the current passing through, a solution of an electrolyte. These measurements were independent of phenomena occurring at irreversible electrodes. His results are, with one exception, within a few tenths of a per cent. of the accepted values, and the deviations, which are both positive and negative, are readily explainable by the errors of the method. Since the experiments just referred to were apparently designed to demonstrate the existance of "transfer resistance" errors, it does not appear that the author has proved his point.

Further, Eastman,[2] in a recent, very careful, investigation finds that the difference between the conductances determined by direct and alternating current measurements (using nonpolarizing electrodes) is of the order of 0.02–0.03% and that both agree with the results of Kohlrausch with about the same accuracy. Newbery's contention, which seems to me to be quite unjustified on theoretical grounds, that the effects of his "transfer resistance" would disappear if a pure sine wave were used, is, at least, unnecessary, since Kohlrauchs's results with an unsymmetrical current from an induction coil, agree, with the accuracy just stated, with Eastman's values using direct current and symmetrical alternating current. Clearly, then, the evidence from conductance measurements is against the presence at electrodes of "transfer resistances" of any appreciable magnitude.

The solution of the whole difficulty lies, I am convinced, in the realization of the facts (a) that the overvoltage is larger than the counter e. m. f. and (b) that the difference between the quantities is a potential and not a resistance. Also, it appears to me, that all the phenomena so far observed in this field, including those brought to light by Newbery's experiments, can readily be explained by the theory as originally advanced by MacInnes and Adler. According to them, "Hydrogen overvoltage is due, primarily, to a layer of supersaturated dissolved hydrogen in the

[1] *J. Chem. Soc.*, **113**, 701 (1918).
[2] THIS JOURNAL, **42**, 1648 (1920).

electrolyte surrounding an electrode."[1]   Since the potential, in all prob-
ability, has its origin where the conductors change from ions to electrons,
emphasis was placed upon the dissolved hydrogen in the electrolyte rather
than that absorbed in the metal since in the latter the hydrogen is part of
a metallic conductor.   The gas phase can have only a secondary, though
important, effect, being nonconducting.   According to this hypothesis
hydrogen overvoltage does not differ from concentration polarization.
The magnitude of the effect lies, in all probability, in the fact that hy-
drogen, when dissolved, is not an electrolyte, and does not tend to migrate
away from the electrode.   Once formed it must be removed by diffusion,
stirring, or by formation of the gas phase.   The obvious difficulty with
this hypothesis is that for the higher overvoltages the concentrations (or
the pressures necessary to produce the concentrations) are inconceivably
great if computed from the usual Nernst equation.   However, we are
dealing here, not with pressures in the usual sense, but with "fugacities."[2]
The recent work on fugacities of ions shows that above moderate concen-
trations the ion fugacities increase much more rapidly than the ion con-
centrations.[3]   An investigation is now in progress in this laboratory to
determine whether, for high pressures of hydrogen, the fugacity differs
markedly from the pressure.   Until the results of this investigation are
at hand this part of our explanation must be of the nature of a hypothesis.
However, this hypothesis affords a ready explanation of all the phenomena
in this field, as I hope to demonstrate below.

According to this theory *all* the overvoltage is due to a layer of super-
saturated hydrogen solution, no part of the effect being assigned to
resistance.

There remains an important question.   Why does the overvoltage
differ from the counter e. m. f.?   According to Newbery the values of the
counter e. m. f. are determined by the decomposition potentials of un-
stable hydrides formed on the surface of the electrodes.   It is probable
that this explanation is the correct one for a great number of cases.   How-
ever, the fact must be recognized that the formation of these hydrides is
a consequence of, and in no way an *explanation* of, overvoltage.   In an
exactly analogous manner the deposition of metals above hydrogen in the
electromotive series results from, but does not explain, the failure of hy-
drogen to form gas at the reversible potential.   According to the hypothesis
advanced by MacInnes and Adler the deposition of metals high in the
electromotive series and the formation of unstable hydrides are both
due to the building up, during electrolysis, of a layer of dissolved hydrogen
of high fugacity.

[1] *Loc. cit.*, p. 207.

[2] Lewis, *Proc. Am. Acad. Sci.*, **43,** 259 (1907).

[3] See the compilation by Noyes and MacInnes, THIS JOURNAL, **42,** 243 (1920).

If the formation of hydrogen at an electrode is periodically interrupted by a commutator device, as in Newbery's work, this dissolved layer of hydrogen will begin to diffuse or be stirred away from the surface and the voltage will drop rapidly.   However, if the electrode surface contains an unstable hydride this will act as a reservoir of hydrogen of high fugacity, keeping the voltage from falling below the decomposition potential of the hydride until the exciting current is again applied.   The oscillograph work of Le Blanc[1] demonstrates that with an electrode at which gas is evolved, the potential drops rapidly, but by no means instantaneously, to a constant value of the counter e. m. f., after the exciting current is disconnected.   This relatively slow decrease of potential indicates the presence of material capable of yielding higher potentials than those of the unstable hydrides just referred to.

If a metal has a potential higher than hydrogen in the electromotive series the diffusion or stirring away of dissolved hydrogen from the surface may cause the potential to drop, when the exciting current is interrupted, until the metal of the electrode can form ions, after which no further decrease can occur.   For instance, when the exciting current is applied to an amalgamated zinc electrode in sulfuric acid the reactions occurring will be the deposition of nearby zinc ions (formed by "local action") and the discharge of hydrogen ions.   The open circuit voltage would, therefore, be expected to be that of the zinc, in sulfuric acid containing few or no zinc ions.   As a matter of fact, the potential of amalgamated zinc in fresh normal sulfuric acid against a hydrogen electrode in the same solution was found by the writer to be 0.84 volt, whereas Newbery's counter e. m. f. (or according to his definition "overvoltage") measurements yielded 0.88 to 0.70 volt.[2]   Further, Newbery gives 0.16 to 0.29 and 0.27 to 0.23 volt for the counter e. m. f. measurements of nickel and cobalt, respectively, whereas the "normal potentials" against a hydrogen electrode are 0.22 and 0.29 volt.   It seems nearly certain, therefore, that in these cases, and some others, the potentials that Newbery measured do not correspond to the decomposition of unstable hydrides, but are caused by the formation of ions by the metals themselves.

The considerations of the preceding paragraphs indicate clearly, I think, why the counter e. m. f. is nearly independent of the current density and the external pressure.   It is also evident that nothing valuable with regard to the relation of counter e. m. f. to valence, passivity, etc., need be lost by adopting the theory advanced by MacInnes and Adler.   Since, by our hypothesis, overvoltage is a concentration effect, it is equally obvious that the overvoltage should be dependent upon the current density.

[1] "Abhandlungen der Deutchen Bunsen-Gesellschaft," No. 3.
[2] Mem. Manchester Literary and Philosophical Soc., 61, (9) 3 (1917).

The influence of external pressure is more complicated, but, as is demonstrated in the earlier papers, follows directly from our theory.[1]

In conclusion, it is probable that I have not met, in detail, all of Newbery's objections to the theory proposed by MacInnes and Adler, and I am, naturally, in the dark as to the "many other" objections that he holds in reserve. However, enough is probably outlined above to indicate the fundamental difference of point of view upon which Newbery's aggressive criticism is based.
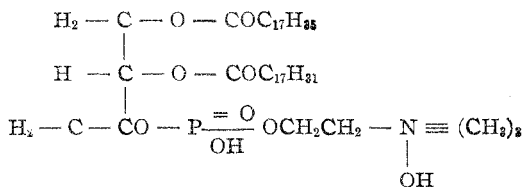
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THE QUANTITATIVE ESTIMATION OF PHOSPHATIDES.

BY D. H. BRAUNS AND JOHN A. MACLAUGHLIN.

The determination of phosphatides is often required in the analysis of foods and drugs. In the case of foods, phosphatides frequently serve as an index to the quantity of egg yolk in the food under examination. In the analysis of drugs, it is often necessary to determine phosphatides in order to establish whether or not statements made concerning the lecithin content of the preparation are warranted. Experience has shown that none of the methods hitherto proposed for the separation of phosphatides from such products is wholly satisfactory, for one reason or another. The investigation herein presented was undertaken for the purpose of devising a method which would be satisfactory. Since Maclean's[2] recent book, renders the publication of a bibliography superfluous, the references given in the present work have been limited to publications that offer suggestions of value for our particular purposes.

For the estimation of phosphatides we have considered 2 different phosphatides, first, lecithin, which is generally agreed to be a combination of glycerophosphoric acid, choline, oleic acid and stearic acid, and to have the formula $C_{44}H_{86}NPO_9$ or

$$H_2 - C - O - COC_{17}H_{35}$$
$$H - C - O - COC_{17}H_{31}$$
$$H_2 - C - CO - P\genfrac{}{}{0pt}{}{= O}{OH} OCH_2CH_2 - N \equiv (CH_3)_2$$
$$OH$$

[1] A forthcoming paper from this laboratory will deal with the question of the relation of overvoltage to pressure. For the present purpose it is sufficient to say that the results of Goodwin and Wilson, mentioned in our first paper, have been confirmed as to the direction of the effect. The excess pressure in small bubbles has been considered and must be taken into account for higher overvoltages. However, this extra pressure is very small for the comparatively large bubbles from platinized platinum electrodes, and it does not sensibly affect the computations published.

[2] H. Maclean, "Lecithin and Allied Substances, the Lipins," Longmans, Green & Co., London, 1918.