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COMMUTATOR MEASUREMENTS ON POLARIZED ELECTRODES[1]

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In the usual commutator method of measuring overvoltage one segment of the commutator connects the polarizing current for a definite time interval and after breaking the current another segment connects the potentiometer for an equal time.[2] Unless the overvoltage be constant after disconnecting the electrolyzing current the potentiometer must, of necessity, be measuring an average of the potential and give a value without any meaning. This is, in fact, the case, for the potential at the electrode drops very rapidly as shown by the following measurements.

The commutator[3] used in this work differs from the usual construction in having only a point contact for the potentiometer connection. It is shown diagrammatically in Fig. 1.

It consisted of a two-piece shaft, the parts being insulated from each other by the hard rubber bearing C. The wheel A controlled the electrolyzing current and was made half of steel and half of hard rubber. A strip of phosphor bronze served as a brush (E)

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[1] Part of this work was done at the Electrochemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass., and part while the author was a Fellow of the National Research Council at the University of California, Berkeley, Cal.

[2] Newbery, *J. Chem. Soc.*, **105**, 2419 (1914).

[3] This commutator gives in effect, the same results that one would obtain with an oscillograph, except for the important difference that the oscillograph requires too much current from the electrode to be sure it does not thereby change the electrode potential. The measurements to be given are somewhat similar to those of LeBlanc ["Die Elektromotorische Kräfte und ihre Messungen mit Hilfe des Oscillographien," W. Knapp, Halle, **1910**] but differ in another important point, namely, that LeBlanc sent his current first one way, then after a pause reversed it. In the present work the current is unidirectional. LeBlanc's procedure is subject to the objection that with reversal of the current one can never be sure of saturating the electrode with only hydrogen or oxygen, but both must be present.

and was kept from vibrating by a sponge rubber damper placed as shown. The slip ring D was used as a return connection for the current. Connection was made to the potentiometer circuit by the point contact F on the hard rubber wheel B. This wheel could be turned on the shaft so that F might make contact at any desired phase relation with respect to the contact of the current on A. Thus by successive adjustments of B with respect to A (read on scale G) the overvoltage at any desired time after the current was made or broken could be obtained. The shaft could be run at any speed from one revolution in two minutes to 4000 revolutions per minute. It was found necessary to allow more time for the overvoltage to decrease to zero than for it to build up (see Fig. 2) and consequently the current must be broken for a longer time than it is on. This was done by a secondary contacting device geared to the above shaft (not shown in the figure) which allowed both commutator wheels to function only every ten revolutions. Thus with a shaft speed of one revolution per second the current would be on $^1/_2$ second and off $10^1/_2$ seconds. The contact point F was about 1 mm. in diameter and wheel B, 6 cm. in diameter. Therefore with a shaft speed of 31 revolutions per second, which was frequently used, the potentiometer contact was made for only 0.00017 of a second or less, at intervals of 0.032 second. This resulted in low sensitivity of the galvanometer so that even with a very good instrument, the potential could be measured at best to only 1 mv. The use of a condenser for storing up charge increased the sensitivity but slightly. The precision of 1 mv. is quite sufficient, however, for the present work.

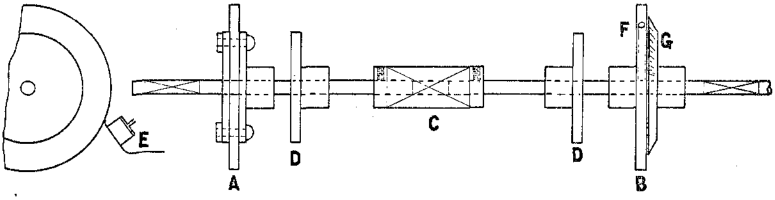

Fig. 1.—Commutator.

Some difficulty was encountered in securing sharp commutation. The corners of the current wave both when just starting and when first reaching the maximum current were slightly rounded off. This was not due to inductance, to any appreciable extent, as shown by tests, but depended on the brushes and commutator material. Steel commutators are better and more permanent than brass and the sponge rubber bumpers materially aided the commutation. As finally used the current built up to its maximum from zero in less than 0.003 of a second and dropped in a somewhat shorter time.

The details of the cell and electrodes used are all as described in a previous article.[4] The hydrogen overvoltages were measured in 2 *N* sulfuric acid, oxygen overvoltages in *N* potassium hydroxide and chlorine overvoltages in saturated potassium chloride solution. All measurements were made in a thermostat at 25°.

The procedure in making a run consisted in first determining how long the current must be on to insure reaching the maximum overvoltage, and running the shaft at the proper speed. Successive adjustments of the contact point F were then made around the entire 360° and the potentials measured, half of which gave the curve of increasing overvoltage as a function of the time and the other half for decreasing overvoltage.

[4] Knobel, Caplan and Eiseman, *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923).

The experimental data are shown graphically in Figs. 2, 3 and 4. In Fig. 2 the top dotted line shows the current-wave form. The overvoltage (the lower curve) is seen to rise very rapidly at first and approach asymptotically to a maximum value which it will hold as long as the current is on.[5]

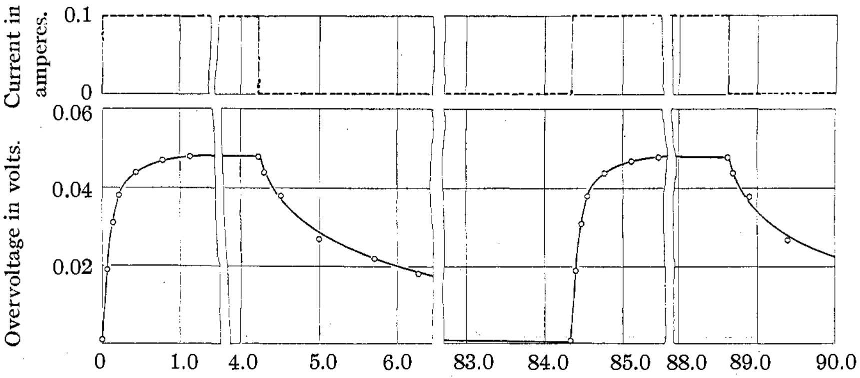

Fig. 2.—Current and overvoltage against time.

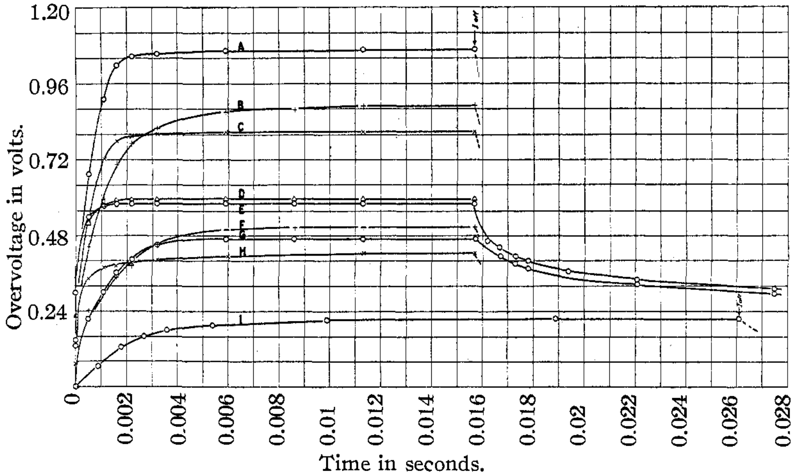

Fig. 3.—Curves of overvoltage against time. A. H_2 on Hg, 0.0075 amp./sq. cm. B. H_2 on Pb, 0.01 amp./sq. cm. C. H_2 on Ag, 0.1 amp./sq. cm. D. H_2 on Cu, 0.1 amp./sq. cm. E. H_2 on Ni, 0.1 amp./sq. cm. F. H_2 on Cu, 0.01 amp./sq. cm. G. H_2 on Ni, 0.01 amp./sq. cm. H. H_2 on smooth Pt, 0.01 amp./sq. cm. I. H_2 on smooth Pt, 0.001 amp./sq. cm.

On breaking the current the overvoltage drops rapidly to approach asymptotically the zero equilibrium value. In Figs. 3 and 4 the entire curves

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[5] Excluding of course, the gradual rise in a matter of hours which takes place on some electrodes.

for decreasing overvoltage are not shown but they continue to drop slowly for a time interval 21 times as long as the time during which the current is on. The overvoltage does not always decrease to zero in the time allowed, whence all the curves of Figs. 3 and 4 do not start from zero. Where the slope is large this makes little difference and in other cases the true origin was found by fitting an equation to the curves and recalculating the origin for the purpose of later calculations.

All measurements were checked once and often three or four times. The reproducibility is not good in that the maximum overvoltage is apt to be variable, but the form of the curves is well reproduced and the data for any one run fall well on a smooth curve. Values for one run only are given rather than an average of several runs.[6]

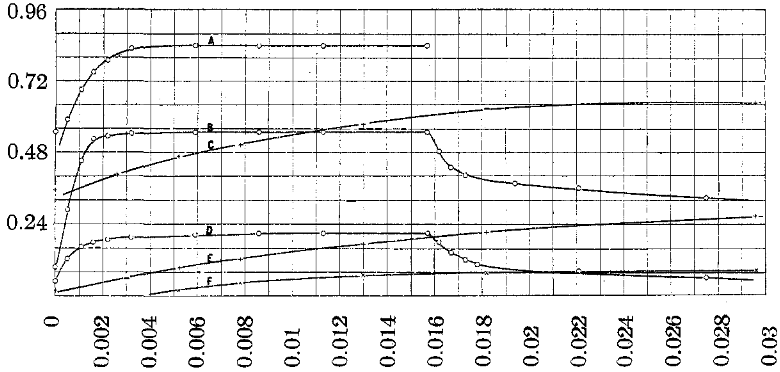

Fig. 4.—Curves of overvoltage against time. A. O_2 on smooth Pt, 0.1 amp./sq. cm. B. Cl_2 on carbon 0.01 amp./sq. cm. C. Cl_2 on smooth Pt, 0.001 amp./sq. cm. D. Cl_2 on smooth Pt, 0.01 amp./sq. cm. E. Cl_2 on carbon, 0.01 amp./sq. cm. F. Cl_2 on smooth Pt, 0.001 amp./sq. cm.

The forms of all the curves are very similar except that the times are different. Thus the maximum overvoltage on lead at a current density of 0.01 ampere per sq. cm. is reached in less than 0.01 second while for platinized platinum the time is about three seconds.

Discussion of Results

These data provide undeniable evidence that the usual commutator method of measuring overvoltage is incorrect for all overvoltages on account of the extremely rapid drop in overvoltage when the electrolyzing current is disconnected. For example, in the case of a smooth nickel electrode polarized at 0.1 ampere per sq. cm. to a maximum overvoltage of 0.597 volt, when the current is stopped, the potential drops 0.04 volt

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[6] Each run is an average, in a sense, in that the overvoltage is averaged for corresponding points on successive current and voltage waves.

in the first 0.0005 of a second—and 0.2 volt in about 0.003 of a second (See Fig. 3). The usual commutator[7] maintains connection to the potentiometer over rather more than 0.01 of a second in general—and hence must give an average of this rapidly changing potential and can have no meaning. The largest error will occur on smooth electrodes at high current densities and those showing a high overvoltage. On spongy electrodes, as platinized platinum, the curve for which is shown in Fig. 2, there is sufficient gas held by the sponge to keep the potential from dropping so fast, and it is probable that at high speed the usual commutator would in this case give nearly the maximum overvoltage. Newbery, in fact, gives results closely approximating those obtained by the direct method for platinized platinum, but very much lower values for smooth electrodes. The principal point of advantage[8] claimed for the commutator method is that it eliminates ohmic resistance drops but the above data indicate that there are no such drops with the direct method as used. If the maximum overvoltage included such a drop, the potential should drop vertically to some lower value when the current is shut off. This was never the case, as it is always possible to measure the overvoltage at every point from the maximum down. The first part of the decreasing overvoltage curve always had a slope larger than could be accounted for by an inductance lag. The requirements and discussion of the direct and commutator methods of measuring overvoltage given in a previous article[4] are therefore fully substantiated by experimental proof.

Quantity of Adsorbed Gas

These data also provide means of making an approximate estimate of the quantity of gas on the electrode when it is polarized. When the electrode has its equilibrium potential, equal to zero, there exists some concentration of gas in moles per sq. cm. of electrode surface which may be designated by the symbol H_a. (We will speak of hydrogen only and assume it to be present as monatomic gas.) When the current at a density I amperes per sq. cm. is applied this gas concentration will start to build up at a rate proportional to the current or

$$\mathrm{d}\,H_a/\mathrm{d}t = k_1 I \qquad (1)$$

where k_1 equals $1/96{,}500 = 1.037 \times 10^{-5}$ moles per coulomb. As soon as a measurable concentration over the equilibrium quantity is reached, the gas will be lost by diffusion and reaction of the atoms to form molecules. For the first part of the curve, however, Equation 1 will be approximately correct and exactly so at the first instant. Integrating Equation 1 we obtain

$$H_a = k_1 I t + H_a' \qquad (2)$$

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[7] For example, as used by Newbery, Ref. 2.

[8] See Newbery, *Trans. Faraday Soc.*, **15** (1919); THIS JOURNAL, **42**, 2007 (1920).

which is the equation for gas concentration as a function of time and current and in which the integration constant, H_a', is equal to the initial equilibrium concentration of gas.

To bring in the overvoltage E, we must make some assumption regarding the relation between the concentration of gas H_a, and its pressure P. It has been usual to assume that the two are directly proportional, but Haber and Russ,[9] for example, as well as others, have found that this gives quite inconsistent results in treating the relation of current density and overvoltage. An equation of the form suggested by Freundlich[10] for the adsorption of gas on charcoal, etc., namely,

$$P = k_2 H_a^m \tag{3}$$

where k_2 and m are constants, is probably more nearly applicable, as the present case is apparently one of adsorption. Even this equation is probably not closely obeyed for any large range of polarization (and concentration change) but the exponent m, which is larger than one, gives the correct trend. For the present discussion we will assume only that m is approximately constant for the concentration range covered by the first few points on the overvoltage-time curve.

Using Equation 3 then to introduce the concentrations of Equation 2 in the general equation for overvoltage,

$$E = \frac{RT}{F} ln \frac{P}{P'} \tag{4}$$

where P and P' represent pressures of monatomic hydrogen at any particular overvoltage and at equilibrium, respectively, we obtain

$$E = \frac{m\,RT}{F} ln \left(\frac{k_1 I\, t + H_a'}{H_a'}\right) \tag{5}$$

By grouping constants this may be written

$$E = S \log (t + z) + \text{constant} \tag{6}$$

where

$$z = H_a'/k_1 I \tag{7}$$

If now the logarithm of t plus an empirically determined constant z is plotted against E, a straight line should result for the first part of the curve—that is, as long as the approximation involved in Equation 2 is good. Referring to Fig. 5 in which the data for platinized platinum at 0.01 ampere per sq. cm. have been used, Curve A is the result when z is taken equal to zero (too small), Curve C when z is 0.8 (too large) and Curve B when z is taken as 0.4. In the last case a straight line can be drawn through the first four points. Furthermore, this straight line intersects the axis of zero overvoltage at a point which is equal to the logarithm of the chosen value for z, as it must to satisfy Equation 6. By

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[9] (a) Haber, *Z. physik. Chem.*, **32,** 193 (1900). (b) Russ, *ibid.*, **44,** 641 (1903). (c) Haber and Russ, *ibid.*, **47,** 257 (1904).

[10] Freundlich, "Kapillarchemie," Akad. Verlag., Leipzig, **1922,** p. 151.

these two criteria it is possible to determine the value of z quite closely and when obtained we can calculate H_a by Equation 7.

Curve B must deviate, of course, from a straight line at higher overvoltages, when the gas concentration has built up, but *if* there were no loss of gas by reaction or otherwise, Curve B would continue straight to the maximum overvoltage. The intersection of this straight line and the maximum overvoltage at D gives the time (t_0) therefore necessary to put on the electrode the maximum quantity of gas which it does finally hold. That is, t_0 is the time necessary to saturate the electrode, if the rate of increase of concentration were constant and the same as the initial rate. The value t_0, obtained graphically, multiplied by the current density and k_1 the number of moles per coulomb discharged, gives therefore the concentration of gas on the electrode when it has its maximum overvoltage.

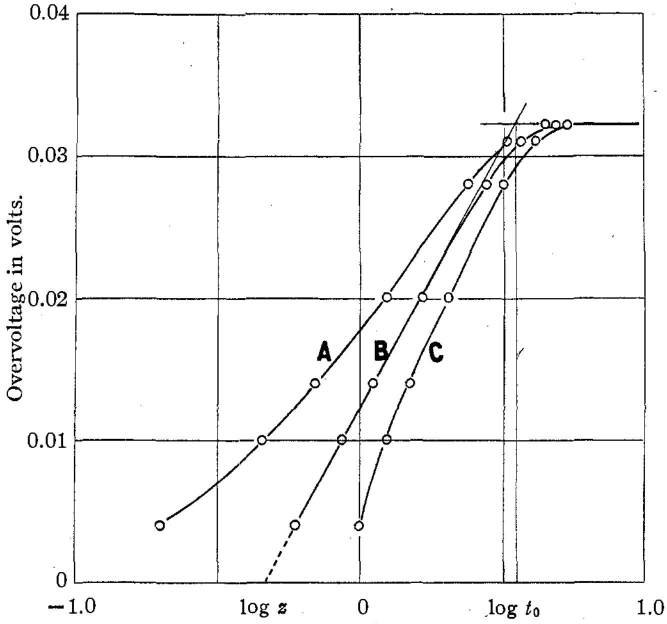

Fig. 5.

Notice that in this treatment it is assumed only that (a) monatomic hydrogen is the electromotively active substance (but if it were diatomic hydrogen the values would be only halved and the order of magnitude not changed); (b) an equation of the form of Freundlich's obtains for the relation between concentration and pressure; but this latter assumption need only apply for the first few points, that is, for a limited gas concentration range.

The results obtained by this method of treating the data are given in Table I.[11] The concentrations H_a and H_a' are in moles per sq. cm., the area being the superficial area of the electrode surface. The precision is admittedly poor, probably not better than ±50% but the order of magnitude is of interest. One conclusive result is the enormously larger concentration of hydrogen on platinized platinum than on the other electrodes, all of which are smooth. A monomolecular layer of hydrogen consists of 1.6×10^{-8} to about 2×10^{-9} moles per sq. cm., depending on whether a square of 10^{-8} cm. on a side is allowed to each atom, or there are assumed to be as many hydrogen atoms as metal atoms in the surface. It appears, therefore, that on all the smooth electrodes there exists from 0.1 to 0.01 molecular layer at equilibrium, which increases to nearer a molecular layer where polarized. This result, it is believed, is in accordance with modern ideas on adsorption.[12] The similarity in the values for the various electrodes (except platinized platinum) is not surprising because they were all smooth (polished with No. 0000 emery paper) and are not in the sponge form used as catalysts. It would appear

TABLE I

RESULTS

Metal	Current density Amps./sq. cm.	H_a' Moles per sq. cm.	$E_{max.}$ Volts	H_a at $E_{max.}$
Ag[a]	0.1	1.3×10^{-10}	0.807	1.57×10^{-9}
Ag[a]	.01	1.0×10^{-10}	.584	1.9×10^{-9}
Ag[a]	.001	1.9×10^{-10}	.362	1.7×10^{-9}
Ni[a]	.01	2.6×10^{-11}	.469	3.5×10^{-10}
Ni[a]	.001	2.6×10^{-11}	.264	2.2×10^{-10}
Hg[a]	.0075	9.4×10^{-12}	1.066	1.4×10^{-10}
Hg[a]	.00075	9.7×10^{-12}	0.909	1.7×10^{-10}
Cu[a]	.1	$3. \times 10^{-11}$	.597	4.2×10^{-10}
Cu[a]	.01	2.4×10^{-11}	.506	4.9×10^{-10}
Pb[a]	.01	1.6×10^{-11}	.890	3.5×10^{-10}
Pb[a]	.001	2.1×10^{-11}	.914	2.5×10^{-10}
Pt (smooth)[a]	.01	5.2×10^{-11}	.424	1.2×10^{-10}
Pt (smooth)[a]	.001	5.2×10^{-11}	.214	9.0×10^{-11}
Pt (platzd.)[a]	.1	1.5×10^{-7}	.048	6.7×10^{-7}
Pt (platzd.)[a]	.01	5.2×10^{-8}	.0322	3.9×10^{-7}
Pt (smooth)[b]	.01	9.3×10^{-12}	.209	2.6×10^{-10}
Pt (smooth)[b]	.001	1.5×10^{-11}	.087	1.9×10^{-10}
Carbon[b]	.1	1.4×10^{-9}	.549	2.8×10^{-9}
Carbon[b]	.01	8.3×10^{-10}	.318	5.0×10^{-9}
Pt (smooth)[c]	.01	4.4×10^{-13}	.84	1.5×10^{-10}
Pt (smooth)[c]	.001	2.0×10^{-12}	.666	1.2×10^{-10}

[a] Hydrogen. [b] Chlorine. [c] Oxygen.

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[11] A few values are included for which the experimental data are not given.

[12] Langmuir, THIS JOURNAL, 37, 1162 (1915).

that a complete monomolecular layer of hydrogen atoms would be very unstable and only at the highest current densities would enough hydrogen ions be discharged to maintain the layer.[13] The situation may also be described by saying that the hydrogen atoms cannot come nearer together than about 10^{-8} cm., without immediately coupling to form hydrogen molecules.

These concentration values give a new viewpoint of the mechanism of gas overvoltages. It has been customary to assume[14] that when the overvoltage changes by, say 1 volt, and the fugacity of hydrogen by approximately the ratio 10^{17} to 1 (from Equation 4) the concentrations of gas are also in approximately the same ratio. This necessitates the presence of either extremely large concentrations on the one hand, or extremely small concentrations on the other, both of which are quite inprobable. The present work indicates that the concentration ratio is only about 100 to 1 for the above pressure ratio, a result which fits Freundlich's equation (qualitatively) and allows reasonable concentrations at all polarizations.

Summary

By a specially designed commutator, curves of overvoltage against time, both for increasing and decreasing overvoltage, have been obtained.

The results indicate, without room for doubt, that the usual commutator method of measuring overvoltage is incorrect.

By a graphical treatment of the data, approximate values for the gas concentrations on the polarized electrodes have been obtained. It appears that on smooth electrodes the adsorbed hydrogen is present as about 0.01 of a molecular layer at low polarizations, approaching a molecular layer at high polarizations.

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[13] We are speaking here of a layer in one plane; on platinized platinum the gas layer has a considerable depth.

[14] Ref. 9c. Tafel, *Z. physik. Chem.*, **50**, 641 (1905). Lewis and Jackson, *Proc. Am. Acad.*, **41**, 399 (1906).