produces an ion or ions possessing high activity coefficients (such as, for example, the hydrogen ion).

8. At a given molal salt concentration, sodium chloride produces a greater dissociation of water than does potassium chloride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY COLLEGE OF THE SOUTH-WEST OF ENGLAND]

THE EFFECT OF SMALL ALTERNATING CURRENTS ON SOME POLARIZED ELECTRODES

BY S. GLASSTONE

RECEIVED SEPTEMBER 11, 1924 PUBLISHED APRIL 4, 1925

During the course of certain investigations[1] on the overvoltage of an electrode polarized by intermittent current, it was found that the potential of the electrode fell rapidly as soon as the polarizing current was switched off, but soon reached its normal value when the current was thrown on again. When the electrode was connected with the potentiometer system for the whole of a cycle, the potential recorded was the average of the varying potential of the electrode. This fact has an important bearing upon the measurement of electrode potentials under the influence of superimposed alternating and direct currents. Almost all of the workers[2] in this field have measured the potentials by the direct method, and have thus really measured the average of a varying potential rather than a definite value corresponding to an equilibrium condition. The only exception appears to be W. B. Jones,[3] who has shown that by superimposing alternating current upon direct current the potential of a lead cathode varies continuously throughout the whole of a cycle, and under some conditions even its sign may alter. It should also be pointed out that even though the actual sign of the electrode potential may not be reversed, yet since the direction of the current becomes reversed when the amount of alternating current exceeds the value of the direct current, the potential due to the resistance of the metal-gas-electrolyte system at the surface of the electrode will now act in the opposite direction, and thus cause an appreciable decrease in the average potential as measured by the direct method. All of the potentials recorded in the literature, except those of Jones, for the influence of alternating current on an electrode polarized by direct current are thus of uncertain value, and hence it seemed natural to question the belief that overvoltage may be reduced by the superposition of alter-

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[1] Glasstone, *J. Chem. Soc.*, **123**, 2926 (1923).

[2] (a) Ruer, *Z. physik. Chem.*, **44**, 81 (1903). (b) Von Wartenberg and Archibald, *Z. Elektrochem.*, **17**, 812 (1911). (c) Reitlinger, *ibid.*, **20**, 261 (1914). (d) Ghosh, THIS JOURNAL, **37**, 733 (1915). (e) Grube and Dulk, *Z. Elektrochem.*, **24**, 237 (1918). (f) Goodwin and Knobel, *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920).

[3] Jones, *ibid.*, **41**, 151 (1922).

nating current, especially as Goodwin and Knobel[2] state that in the case of a lead cathode in sulfuric acid "no effect (on overvoltage) is observed until the alternating current is large enough to cause some reverse current to pass through the cell." Alternating current of suitable magnitude is known to render active an electrode of iron or nickel that has been made passive by anodic polarization, but the factors operating here may be quite different from those at an electrode where hydrogen is being evolved.

Since the work of Jones[3] throws very little light on this particular problem, it seemed desirable to investigate the action of small alternating currents on an electrode polarized by direct current, under such conditions that no reverse current ever flowed through the electrolytic cell during the course of a whole cycle. The average potential of a polarized electrode could be measured by the direct method with simultaneous direct and alternating current; further, the potentials corresponding to the maximum and minimum current in the circuit could be determined with direct current alone. The arithmetical mean of these two latter values should give an approximate measure of the average potential that would be expected with superimposed alternating and direct current if the former exerted no specific effect on the electrode. A comparison of this calculated value with that experimentally determined should give a rough idea of the actual influence of alternating current on the polarized electrode. All of the measurements will include an error due to the resistance of a metal-gas-electrolyte system situated at the surface of the electrode, but it does not seem possible to eliminate or correct for this error unless one uses the very doubtful method employed by Jones.[3]

The Apparatus

The apparatus was arranged as shown in Fig. 1.

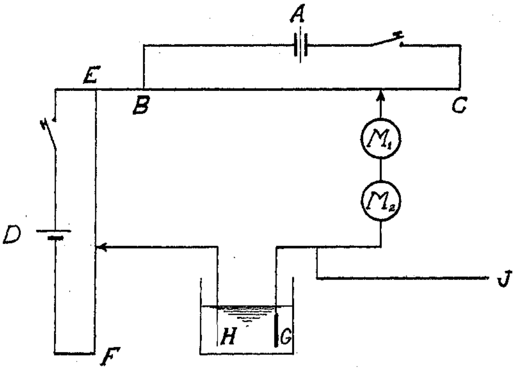

Fig. 1.

The source of alternating current (A) was the electric light mains (100 volts), which supplied symmetrical current of sinusoidal form at a frequency of 60 per second. The power factor of the lighting circuit varied continuously throughout the day, but did not appear to influence the results obtained. The current leads were connected across a resistance BC, which included two lamps; D was the polarizing battery of accumulators connected across the resistance EF. M_1 and M_2 were hot-wire and moving-coil ammeters, respectively, and G was the test electrode connected in the usual way by means of a Haber-Luggin capillary with a standard electrode (not shown); the other electrode in the electrolytic cell was always a short piece of platinum wire (H). *J* is the connection to the potentiometer.

This arrangement was preferred to the one used by some previous workers, for example, Reitlinger,[2c] and Grube and Dulk,[2e] in which the test electrode is duplicated and the alternating current applied to these only, while the direct polarizing current is applied to both of these and to a third electrode. Examination of the arrangement of the apparatus shows that there will be an unequal distribution of current at the two electrodes unless special precautions are taken to obviate this, as in the rather complicated arrangement used by Jones.[3] The solid electrodes used in this work were all of 1 sq. cm. area, while the mercury electrode had an exposed area of 10 sq. cm., connection being made by means of a platinum wire fused into a glass tube. The electrolytes used were *N* sodium hydroxide solution and *N* sulfuric acid.

Experimental Method

The electrode G was first polarized with direct current alone for ten minutes; the alternating current was then switched on, and the resistances BC and EF so adjusted that the average current as indicated on the ammeter M_2 was always 0.12 amp. The average potential of the test electrode and the reading on the ammeter M_1 were then recorded for two different values of alternating current; from the readings of the two ammeters the values of the maximum and minimum currents in each cycle were calculated on the assumption that the alternative current was sinusoidal, and the overvoltages measured with direct current alone equal in amount to these values.

Results

Rows I and II give the overvoltage corresponding to the maximum and minimum current in each cycle, and Row III gives the arithmetical mean of these values. In Row IV is given the actual average potential measured

TABLE I

RESULTS

CATHODIC OVERVOLTAGES IN *N* SODIUM HYDROXIDE SOLUTION

	Lead		Nickel		Copper		Tin	
I	1.38	1.42	0.74	0.82	1.06	1.10	1.32	1.43
II	1.24	1.18	.54	.43	0.83	0.75	1.20	1.10
III	1.31	1.30	.64	.62	.94	.92	1.26	1.26
IV	1.27	1.23	.63	.61	.92	.86	1.18	1.11
	Iron		Cadmium		Antimony		Platinum	
I	0.69	0.70	1.05	1.11	1.20	1.27	1.02	1.17
II	.63	.60	0.80	0.66	0.93	0.80	0.78	0.68
III	.66	.65	.92	.88	1.06	1.03	.90	.92
IV	.66	.64	.90	.85	1.05	1.02	.83	.72

TABLE I (*Concluded*)

	Aluminum		Zinc		Silver	
I	0.78	0.80	1.28	1.32	0.78	0.80
II	.66	.60	1.10	1.00	.68	.62
III	.72	.70	1.19	1.16	.73	.71
IV	.71	.69	1.17	1.14	.71	.62

CATHODIC OVERVOLTAGES IN N SULFURIC ACID

	Lead		Nickel		Copper		Tin	
I	1.31	1.33	0.53	0.55	0.78	0.82	0.98	1.01
II	1.20	1.18	.45	.40	.65	.57	.83	0.75
III	1.25	1.25	.49	.47	.71	.69	.91	.88
IV	1.10	0.99	.47	.44	.66	.59	.86	.77

	Iron		Cadmium		Antimony		Platinum	
I	0.78	0.81	0.80	0.83	0.89	0.92	0.72	0.74
II	.68	.64	.70	.66	.81	.75	.64	.60
III	.73	.72	.75	.74	.85	.83	.68	.67
IV	.71	.67	.77	.74	.84	.80	.60	.52

	Aluminum		Zinc		Silver		Mercury	
I	1.20	1.25	1.02	1.04	0.58	0.60	1.22	1.24
II	1.00	0.92	0.94	0.89	.48	.42	1.16	1.12
III	1.10	1.08	.98	.96	.53	.51	1.19	1.18
IV	1.12	1.03	.98	.94	.48	.40	1.15	1.09

ANODIC OVERVOLTAGES IN N SODIUM HYDROXIDE SOLUTION

	Lead		Nickel		Copper		Iron	
I	1.21	1.24	0.82	0.85	0.83	0.85	0.57	0.59
II	1.08	1.04	.75	.70	.76	.73	.52	.49
III	1.14	1.14	.78	.77	.79	.79	.54	.54
IV	1.06	0.98	.80	.75	.76	.69	.54	.52

	Cadmium		Platinum	
I	1.18	1.22	1.44	1.48
II	1.04	0.98	1.28	1.20
III	1.11	1.10	1.36	1.34
IV	1.05	0.90	1.09	0.96

ANODIC OVERVOLTAGES IN N SULFURIC ACID

	Lead		Nickel		Iron		Platinum	
I	1.00	1.02	0.76	0.78	0.82	0.84	1.12	1.15
II	0.98	0.96	.69	.66	.75	.73	1.05	1.00
III	.99	.99	.73	.72	.78	.78	1.08	1.07
IV	.99	.99	.72	.67	.74	.62	1.02	0.91

with simultaneous alternating and direct current; a comparison of this value with that in Row III gives the specific influence of alternating current on the overvoltage at a particular electrode. The direct current used was always 0.12 amp., while the maximum amplitude of the alternating current was 0.07 and 0.10 amp. in two series of experiments given in the first and second columns, respectively, for each electrode.

Discussion

Although the results given above cannot by any means be regarded as exact overvoltages, since they include the errors inherent in the direct method of measurement, yet inasmuch as the measurements were carried out with direct current and with superimposed alternating and direct currents under similar conditions, they should give some information on the matter under discussion, namely, the effect of alternating current on overvoltage. In the following cases only, of those examined, does a small alternating current cause any appreciable lowering of overvoltage: platinum, tin, lead and silver cathodes in sodium hydroxide solution; copper, platinum, tin, lead, silver and mercury cathodes in sulfuric acid; copper, platinum, cadmium and lead anodes in sodium hydroxide, and platinum and iron anodes in sulfuric acid. In all of the other cases there is either a doubtful lowering of overvoltage, or else the alternating current of small amplitude appears to have no effect at all.

Ghosh[2d] has suggested that alternating current lowers the mechanical resistance which causes the accumulation of gas inside the electrode, this accumulation being responsible for overvoltage. Bancroft[4] thought it possible that electrical stress tends to remove the active gas, which is the cause of overvoltage, from the surface of the electrode. Experiments by the present author have indicated that when there is a sudden discharge of current in a circuit; for example, when a circuit containing a large self-inductance is suddenly broken, the potential of the electrode falls more rapidly than it does when the circuit is broken under normal conditions. It thus appears that electrical discharges aid those processes that tend to remove electromotively active material from the electrode, and alternating current may act in the same way. It is possible that the rapid variation in the value of the current, when alternating and direct currents are superimposed, causes a diminution in the tensions at the metal-gas-electrolyte interfaces, with the result that bubble formation takes place more readily. In this way the accumulation of active material at the electrode is to some extent prevented, and hence the overvoltage reduced. An investigation of the influence of alternating current on the minimum or bubble overvoltage would be of some interest, and it is hoped to undertake this at a later date.

If the considerations discussed at the beginning of this paper apply to a platinum anode, then it appears that many of the conclusions of Grube and Dulk[2e] may be invalidated. According to these authors, oxygen can be liberated at a platinum anode in acid or alkali at potentials lower than the theoretically reversible values, by superimposing large alternating currents on the direct polarizing current. As has been pointed out above, the potentials measured were average values over a whole cycle during

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[4] Bancroft, *Trans. Am. Electrochem. Soc.*, **29**, 309 (1916).

which large positive and negative currents were in the circuit, and during which time the sign and magnitude of the electrode potential probably changed. It therefore appears impossible to say at which potential the oxygen was liberated, and in the absence of evidence to the contrary it is simpler to assume that this gas was liberated when the potential of the electrode was equal to or greater than the reversible value. The same argument applies to the results of Goodwin and Knobel[2f] in connection with the liberation of hydrogen at a lead cathode in sulfuric acid.

Summary

The reasons are outlined for believing that many of the potentials given in the literature, which purport to indicate the influence of alternating current on overvoltage, are of doubtful value. The effect of small alternating currents on cathodic and anodic overvoltage has been measured approximately for a number of different metals in *N* sulfuric acid and *N* sodium hydroxide solutions. The results indicate that only in a limited number of cases does alternating current of small amplitude reduce the polarization at such electrodes. A possible explanation for the effect of alternating current in lowering overvoltage in some cases is discussed briefly.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

THE FREE ENERGY OF SULFURIC ACID IN AQUEOUS SULFATE SOLUTIONS

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RECEIVED OCTOBER 1, 1924 PUBLISHED APRIL 4, 1925

The free energy of dilution of sulfuric acid in aqueous solutions may be computed accurately at concentrations above 0.01 *M* concentration from measurements of the electromotive forces of cells of the type,

$$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg$$

where *m* is the molal concentration. These cells have been studied by Brönsted[1] who extended his measurements over a considerable concentration range and at different temperatures, Lewis and Lacy,[2] and more recently by Randall and Cushman.[3] The results of these studies along with freezing-point measurements and the vapor-pressure measurements of Brönsted[1] have been employed by Lewis and Randall[4] for their computation of the activity coefficients of this acid.

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[1] Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

[2] Lewis and Lacy, THIS JOURNAL, **36**, 804 (1914).

[3] Randall and Cushman, *ibid.*, **40**, 393 (1918).

[4] Lewis and Randall, (a) *ibid.*, **43**, 1112 (1921). (b) "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 355.