any rate the value found experimentally is 36.6 which is very close to the value deduced by Jouquet from the first hypothesis.

In conclusion, I wish to express my thanks to Professor Nernst at whose suggestion this investigation was undertaken, for his interest and encouragement throughout the course of the work.

BERLIN. August, 1906.

THE POLARIZATION CAPACITY OF IRON AND ITS BEARING ON PASSIVITY.[1]

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Received August 29, 1906.

THIS paper contains an account of some measurements of the polarization capacities of iron electrodes. It was expected that a comparison of the capacity values in a number of different solutions would give some evidence for or against the oxide film explanation of passivity. As will be set forth below, the results found lead us to the conclusion that the oxide film theory is after all the correct explanation.

Finkelstein[2] measured the polarization capacity of iron in concentrated nitric acid by the same method that we have employed, with the same end in view, but came to the opposite conclusion. On the whole his capacity measurements, however, were not necessarily in conflict with the film theory, his main reasons for rejecting this theory being based on his measurements of the potentials of iron.

The method is that first used by Gordon,[3] at the suggestion of Nernst,[4] and later by Scott[5] and others in Nernst's laboratory. It is a comparison of the electrode capacity with that of a metallic condenser in the Wheatstone bridge, with a telephone receiver as the zero instrument. In most cases the method gives a sharp telephone minimum only for small measuring currents, near the limit of audibility of the telephone. In series with the metallic condenser it is necessary to have a variable resistance, in order to balance the resistance of the electrolyte, which is in series

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[1] Presented in abstract at the Ithaca Meeting of the American Chemical Society.

[2] Z. physik. Chem. 39, 91 (1902).

[3] Gordon: Z. Elektrochem. 3, 153 (1896); Wied. Ann. 61, 1 (1897).

[4] Nernst: Z. physik. Chem. 14, 622 (1894).

[5] Scott: Wied. Ann. 67, 388 (1899).

with the capacity of the electrodes. In some cases it is necessary to have a resistance also in parallel with the metal condenser, as a balance for the conductance in parallel with the electrode capacity; with some electrodes this parallel resistance is unnecessary. In the interpretation of the results of this paper, this parallel resistance is of special importance.

It has always been considered that the capacities given by this method may be either real electrostatic capacities, due to a high resisting film on the electrode, or only apparent capacities due to the changing of the electrode potential, resulting from concentration changes either in the solutions or electrodes. Aluminium, previously subjected to anodic polarization, affords a typical example of the first case, while mercury and platinum have been regarded as giving capacities due to concentration changes. The latter metals do not require any resistance parallel to the condenser, while the former *generally* does.

However, a good telephone mimimum without a parallel resistance does not necessarily mean that there is no high resisting film on the electrode. It may mean, just as well, that the resistance of the film is so high in comparison with the capacity that it has no appreciable effect on the telephone current. We have an example of this in the case of anodic films formed on aluminium; for the thinner films a parallel resistance is necessary, but for the thicker films the resistance is relatively so high as to have no noticeable effect on the telephone minimum. Thus, while the necessity for the parallel resistance can be explained only by the assumption of a high resistance film, its absence may denote either a film of still greater resistance, or, that the capacity measured is not due to a film at all, but to concentration changes.

The electrodes used were iron wires, about 0.8 mm. in diameter, prepared for standardizing work, and marked 99.6 per cent. pure. They were immersed in the various solutions to different depths. In most cases about 0.3 sq. cm. was covered by the solution. The values of capacities and parallel resistances given below are all reduced to values per square centimeter on a single electrode. On account of the action of certain solutions on the iron, the actual size of the surface of some of the electrodes is somewhat uncertain, so that the absolute values cannot be regarded as of great accuracy. The relative values for any pair of electrodes in different solutions generally agreed within a few per cent.

OBSERVATIONS.

Nitric Acid, Sp. Gr. 1.42.—In nitric acid, of the above concentration, five pairs of electrodes with surface areas varying from 0.12 sq. cm. to 0.3 sq. cm., gave capacities ranging from 58.7 to 66.0 Mf.; mean, 63.6 Mf.

This is in good agreement with the measurements of Finkelstein. His range of values is somewhat larger, but most of his results come within the above limits. Our observations differ from his in regard to the parallel resistance. He found no evidence of conductivity in parallel with the capacity and considered this partial proof against the so-called film theory. With electrodes as large as those used by Finkelstein, namely, 0.33 sq. cm. or more, we likewise found no improvement of the minimum on the addition of parallel resistance. However, with smaller electrodes (less than 0.2 sq. cm.) a parallel resistance always made the minimum much sharper. The amount of this resistance could not be determined very accurately. The resistance which was evidently too small differed from that evidently too large by about 20 to 25 per cent. Taking the mean of these two observed values, we found for electrodes 0.12 sq. cm. in diameter, in one case, 36 ohms per sq. cm.; and in another, 30 ohms per sq. cm. Electrodes 0.2 sq. cm. gave a resistance of 60 ohms.

That we must have a parallel resistance for the smaller electrodes and not for the larger is, we presume, due to the greater density of the measuring currents with the smaller electrodes. Higher polarization probably reduces the resistance of the films; at all events, it brings their conductance into evidence. The higher resistance found for the larger electrodes indicates that the conductance increases with increased polarization of the measuring current. We take it that with the electrode larger than 0.3 sq. cm., the density of the measuring current being smaller, the parallel conductance was so high as to have no effect on the telephone current. Direct tests on the effect of varying the strength of the measuring current on a single pair of electrodes, as well as measurements of the capacity during polarization by a direct current, will probably give us more information in regard to the variations of this parallel resistance. Such experiments have not yet been made.

The capacity in fuming nitric acid was about the same as in nitric acid of specific gravity 1.42.

Dilute Nitric Acid.—Electrodes which had been made passive in concentrated nitric acid gave in dilute nitric acid, immediately after transference, the same capacity as in the concentrated acid. The capacity remained the same for a greater or less length of time, depending upon how long the iron had previously been in the concentrated acid. After a time, the capacity began to increase quite rapidly, going in less than one minute from the value for the concentrated acid to a pure resistance minimum, without any sign of capacity or polarization. *At the same time the dissolving of the iron in the nitric acid made itself evident.*

Before the increase of the capacity is noticeable, there is a decrease in the sharpness of the minimum, just exactly as would be the case if we had a film whose resistance decreased considerably before its thickness had suffered any appreciable change.

Ferrous Sulphate.—Immediately after transference from concentrated nitric acid, we found 58.7 Mf.; after standing ten minutes in the aqueous solution of ferrous sulphate, measurements showed 103 Mf. and 10 ohms. After transference from dilute nitric acid, 80 Mf. and 44 ohms.

After cathodic polarization, with the electrolytic precipitation of iron, there was a sharp resistance minimum without any sign of capacity. After anodic polarization at three volts, the following data were obtained: 120 Mf. and 8.6 ohms.

Ferric Chloride.—The capacity was so large in comparison with the parallel resistance that the latter determined, to a large extent, the position of the bridge minimum. The condenser improved the sharpness of the minimum but no reliable measurements of the capacity could be made. After cathodic polarization there was a sharp resistance minimum without the condenser. No signs of a minimum could be obtained with the condenser.

Hydrochloric Acid.—Electrode direct from air gave 240 Mf. and 4 ohms. Twenty minutes later, about 500 Mf. and 2 ohms.

The capacity soon became so large in comparison with the parallel resistance, that no reliable value could be obtained. The minimum was always better with the condenser than without it.

Sulphuric Acid.—In concentrated sulphuric acid a sharp minimum was not obtained. Approximate measurements gave 12 Mf. and 24 ohms.

In dilute sulphuric acid, one minute after transference from concentrated nitric acid, we found 136 Mf. and 3 ohms; five minutes later, 186 Mf. and 2 ohms; thirty minutes later, more than 400 Mf.

The parallel resistance was too small for accurate measurements. Electrodes directly from air gave 120 Mf. and 2 ohms. One minute after oxidation in Bunsen flame, 108 Mf. and 2 ohms; and after standing thirty minutes, about 200 Mf., resistance uncertain.

Sodium Sulphate.—The iron wire was made passive in concentrated nitric acid, transferred to the sodium sulphate solution and the following measurement recorded, 60 Mf. After fifteen minutes, 110 Mf. to 114 Mf.

After standing in dilute nitric acid for a time, and then transferring to the sodium sulphate, the capacity was at first very large but decreased too rapidly for us to follow with measurements. Finally it came to a nearly constant value at 113 Mf. and 4.7 ohms. After oxidation in Bunsen flame, 13 Mf. and 75 ohms.

When the electrodes were placed in the solution directly from air, the capacity was relatively small, but soon came to a constant at 110 Mf. and 9 ohms.

Potassium Nitrate.—Measurements were made in dilute potassium nitrate solution, after the iron electrodes were made passive in concentrated nitric acid, 62 Mf.; and after five minutes, 156 Mf. and 2 ohms.

Five minutes after transference from dilute acid to the potassium nitrate solution, these measurements were taken, 150 Mf. and 3.5 ohms. These values remained constant for forty-five minutes, when the observations ceased.

Taken from air and after one minute measured in the above electrolyte, the following was found, about 6 Mf.; and after five minutes, 14.4 Mf.; after four hours, 118 Mf. and 12.5 ohms. After oxidation in Bunsen flame, the first trial gave 3 Mf.; the second trial, 25 Mf. and 14 ohms. After two hours' anodic polarization of 0.5 volt, 76 Mf. and 11.00 ohms. After same polarization for twenty-four hours, 61.6 Mf. and 15.0 ohms. Thus by long-continued polarization the capacity was brought to the same value as in concentrated nitric acid.

Sodium Hydroxide.—With electrodes from the air, the minimum was so poor that no measurements were made. After anodic polarization of 1.5 volts for five minutes, we got 43.6 Mf. and 4.7 ohms. The polarization was continued for two hours and the capacity and resistance found to remain constant. Cathodic polarization made the capacity too large for the taking of accurate measurements, but not large enough to take resistance measurements without a condenser. After oxidation in a Bunsen flame, we found 3 to 4 Mf. and 30 ohms.

DISCUSSION.

The measurements show that, in general, the polarization of iron electrodes can be balanced by a condenser, *with a resistance in parallel.* Only four exceptions to this were found, in dilute nitric acid and in ferrous sulphate and ferric chloride after cathodic polarization, the iron behaved as a non-polarizable electrode; with the larger electrodes in concentrated nitric acid, the parallel resistance was not necessary.

We found the parallel resistance necessary, however, with the smaller electrodes in concentrated nitric acid, and the smaller the electrode, the less the resistance per square centimeter. We conclude that failure of the method to give evidence of parallel conductivity in the case of large electrodes was due to the conductance being so small as to have no appreciable effect on the telephone current. *Since the resistance in parallel with the condenser can only be interpreted as being due to a poorly conducting film, we hold that our results present very strong evidence in favor of the film theory.*

Probably the most surprising thing in connection with the results, is that in neutral and acid solutions, where iron is active, we found the capacity of the same order of magnitude as in the concentrated nitric acid. In the latter the capacity is about 60 microfarads while in sodium sulphate, after treatment with dilute nitric acid, as well as after being made passive in concentrated nitric acid, the capacity soon came to about 110 microfarads. In dilute sulphuric acid, soon after immersion from air, with gas bubbles being evolved on the iron, the capacity was only 160 microfarads. The difference between active and passive iron is not shown so much in the magnitude of the capacity as in that of the parallel resistance. It seems that in most solutions iron is covered with an oxide film, comparable in thickness with that formed in concentrated nitric acid, but in the latter electrolyte its resistance is much greater.

Our results are, in most respects, a confirmation of the views on the question of passivity lately expressed by Haber and Goldschmidt,[1] whose paper came to our notice after the greater number of the above measurements had been completed. They have shown that the assumption of an oxide film, not perfectly continuous, but full of pores, and the presence of such a film in solutions where iron is only partially passive, does away with most of the objections to the film theory of passivity. The pores, assumed by them, readily explain the parallel conductivity, which we have found. It is not necessary to assume metallic conduction for the film to account for the results of Finkelstein, as we have shown that his measurements are not contradictory to the idea of a film of high resistance. The greater conductance found by us for larger densities of measuring current, we conceive as being due to an enlargement of the pores, although the formation of higher oxide threads with metallic conduction would also explain the phenomena.

Apparently the strongest argument against the film theory is that due to the observations of Müller and Königsberger,[2] who found no difference in the reflecting power of active and passive iron. Our results confirm the supposition of Haber and Goldschmidt, who infer that Müller and Königsberger were measuring the reflecting power of an oxide film in all cases, and naturally found it the same.

Finkelstein sees in the fact that the capacity of iron in concentrated nitric acid is near that of platinum (bright), after it has been heated in a flame, an argument against the film theory and in favor of the idea that the capacity is due to concentration changes, which has heretofore been considered the case with gold

[1] Z. Elektrochem. 12, 49 (1906).

[2] Physik. Z. 5, 413, 797 (1904); 6, 847 (1905).

and platinum. We consider it more probable, in view of the still larger capacities which we have found with parallel conductance, and in view of the fact that Scott found the capacity for gold (10.3 Mf. sq. cm.) almost the same as that for aluminium (10.6 Mf. sq. cm.), where there certainly is such a film, that gold and platinum, likewise, are covered with an oxide film, which is at least the main factor in determining their capacity. From the very irregular values of capacities found for platinum, except after it has been heated in the flame, it appears as if such heating produces a very regular film, which slowly changes when left standing in air or in solution.

The capacity of platinized platinum is many times larger, but it is not at all improbable that here, too, the size of the capacity is largely determined by such a film. By this assumption a number of facts can be explained, which are hard to reconcile with the heretofore accepted theory that the capacity is due to changes in concentration of gas occluded in the electrode. A few of these facts we shall merely mention, as a discussion of this point would carry us far beyond the intent of this paper. Scott found no change in the capacity of platinized platinum with change in pressure, although he used pressures as high as 800 atmospheres. It has recently been shown by several different methods that platinized platinum, saturated with oxygen, does not give the correct potential value for an oxygen electrode.[1] Gordon,[2] as well as Wien,[3] found an apparent increase in the resistance of an electrolytic cell subjected to alternating current polarization, even when this polarization was balanced by capacity or inductance.

CENTRAL UNIVERSITY.
DANVILLE, KENTUCKY, July, 1906.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ABSORPTION COEFFICIENTS OF URANIUM COMPOUNDS.

BY HENRY M. GOETTSCH.

Received August 4, 1906.

IT WAS first stated by Mme. Curie[4] that the radioactivity of

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[1] Lewis: This Journal, 28, 158 (1906).

[2] Gordon: Loc. cit.

[3] Wien: Wied. Ann. 58, 37 (1896).

[4] Thèse, Paris, 1903: Chem. News, 88, 98 (1903).