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ELECTRODE POTENTIALS AND ADSORBED IONIC FILMS

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Introduction

This paper is an extension of the work begun by Tartar and Walker,¹ who concluded that the potential of the oxygen electrode is due to the preferential adsorption of ions from the solution. The reader is referred to this earlier paper for the significant references to the literature. The early work led to the hypothesis that the changeable ("drifting") potential of this electrode could be ascribed to the formation of various oxides of platinum. Van der Meulen² suggested that the potential might be due to the adsorption of ions. Richards³ concluded that the oxygen gas produces an effect in addition to that which might be due to platinum oxides.

If the potential of the oxygen electrode is due to the preferential adsorption of ions, there should be a film next to the metallic surface which differs in composition from the bulk of the solution. There should also be a potential gradient through this film. The experimental work presented in this paper was undertaken with the view of testing the validity of this hypothesis.

Experimental

Experimental Set-up.—The electrodes were made of platinum foil (0.0127 and 0.025 cm. thick) soldered to the end of square brass rods, 0.63 × 0.63 × 5.1 cm. The surface of each electrode was made smooth by polishing (grinding) on a bench plate, 10.2 × 15.2 cm. Two cast-iron bench plates were used which had been lapped together until the surfaces were very smooth and a very strong pull was required to separate the clean surfaces after they were pressed together. During the polishing of an electrode, the supporting brass rod was held in position by a "V" block, 5.1 × 5.1 × 10.2 cm., which had been ground against the bench plate. The first abrasive used was a fine valve-grinding material, which was followed by jeweler's rouge.

The electrodes were mounted on a microscope from which the eye piece and objective had been removed as shown in Fig. 1. The upper electrode bar was fastened

¹ Tartar and Walker, *THIS JOURNAL*, **52**, 2256 (1930).

² Van der Meulen, *Ind. Eng. Chem.*, **15**, 62 (1923).

³ Richards, *J. Phys. Chem.*, **32**, 990 (1928).

with sealing wax in the end of a glass tube which projected up through the barrel of the microscope. At the top, the glass tube was held by four screws which projected into the center of a hollow sulfur plug molded on the upper end of the microscope barrel. The lower end of this bar projected through and 1.9 cm. beyond a tightly fitting rubber stopper which fitted snugly into the barrel of the microscope.

The lower electrode bar was fixed by means of paraffin in a hole in the bottom of an electrode vessel so that the platinum surface was directly beneath that of the upper electrode, the two (platinum) surfaces being nearly parallel. These surfaces were finally made parallel by adjusting the four screws holding the glass tube. When the electrodes were quite close together and a strong light was focused on one side of the slit, interference bands were plainly visible through a traveling microscope focused on the opposite side. If the same number of bands was seen all along one side, those edges were considered to be parallel. The adjustment was continued until the edges of the four sides were parallel, thus making the electrode surfaces equidistant at all points.

The brass rods were covered with paraffin to prevent contact with the solution. The paraffin projecting beyond the edge of the platinum surface was cut away with a sharp blade so that the paraffin covered exactly to the edge of the electrode on all sides.

Electrical connection was made with a copper wire to the upper electrode by a few drops of mercury in the glass rod holding the electrode bar. A short length of copper wire was soldered onto the end of the lower electrode bar, this wire being connected to the lead to the potentiometer through a mercury cup.

The connection between the calomel half-cell and the electrode vessel was made through a flowing junction of the type used by Lamb and

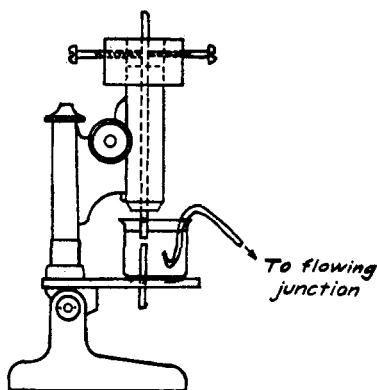


Fig. 1.—Apparatus for determining potentials.

Larson,⁴ which served to keep a steady liquid-liquid potential and to prevent contamination of the electrolyte.

The electrode vessel was made from an ordinary 400-cc. Pyrex beaker which had a hole drilled through the bottom and which was cut off about 3.8 cm. from the bottom. The cell was covered with a sheet of rubber dam which was punctured in four places to allow the entrance of the upper electrode, the gas inlet, the bridge, and a thermometer.

The distance between the electrodes was changed by means of the fine adjustment screw of the microscope, one complete revolution of which moved the upper electrode 0.50 mm. The distance moved could be measured to 0.003 mm.

The potentials of the cell

Metal, gas, electrolyte, KCl (1 mole per liter), HgCl (s), Hg

were read to 1 millivolt with a Leeds and Northrup student type potentiometer. The potentials reported have been calculated to the normal hydrogen reference electrode, taking the potential of the normal calomel electrode to be -0.282 volt.⁵ The potential of the cell was considered positive when negative electricity flowed from right to left.

The whole apparatus was so arranged that it could be placed completely in a water-

⁴ Lamb and Larson, *THIS JOURNAL*, 42, 229 (1920).

⁵ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923, p. 407.

tight iron box and the entire box submerged in the thermostat, which was held at $25 \pm 0.1^\circ$. The small changes in temperature had so small an effect that some of the experiments were made without having the box submerged, in which case the temperature of the electrolyte was read at frequent intervals.

The oxygen was purified by bubbling successively through 7 *N* sodium hydroxide solution, 7 *N* sulfuric acid solution and distilled water. It was then passed through the electrolyte at the rate of approximately 8 cc. per minute. This was considered fast enough to prevent any diffusion of air through the gas exit tubes into the electrode vessel.

All salts were recrystallized twice, with the exception of the aluminum sulfate, which was of "C. P. Analyzed" quality.

Experimental Procedure

The platinum electrode surfaces were cleaned with alcohol to remove traces of paraffin, then with dichromate cleaning solution until the surfaces drained evenly when covered with distilled water. After thoroughly rinsing the electrode vessel first with water and then with the electrolyte to be used, the rubber dam was put in place, fastened with rubber bands and the vessel filled with the solution. The gas was then started bubbling and the thermometer and bridge were put in place.

The electrodes were next brought together until the potential between them fell abruptly to zero and the zero point was noted on the fine adjustment screw of the microscope. The upper electrode was moved a definite distance from the lower electrode by the use of the fine adjustment screw. When the potentials had either become constant or showed only a slight gradual drift, the upper electrode was moved a definite distance nearer the lower electrode and the potentials read until they were steady or showed only a slow steady drift. The upper electrode was then moved again a given distance nearer the lower electrode and the potentials read as before. By this procedure the upper electrode approached the lower one by steps until they touched; then the upper electrode was separated from the lower in the same steps by which it had approached.

The potential of each electrode was determined against the normal calomel half cell, and the potential between the electrodes was taken as a check. A resistance of 10,000 ohms was connected in series with the galvanometer to prevent too much current passing through the electrodes.

Experimental Results

The above procedure was carried out at 25° under oxygen at atmospheric pressure using the following electrolytes: 0.20 *M* boric acid containing 0.01 *M* potassium chloride (the potassium salt added to increase the conductivity), 0.056 *M* disodium hydrogen phosphate, 0.01 *M* potassium dihydrogen phosphate, 0.01 *M* copper sulfate, 0.01 *M* lead nitrate, 0.01 *M* aluminum sulfate and 0.01 *M* nickelous chloride.

Many experiments were tried using different electrodes and electrolytes prepared at different times. In some cases months elapsed between the repetition of experiments. It is unnecessary for the purpose of this paper to give all the tabulated data. It will suffice to give the graphic presentation of the results from typical experiments which were carefully checked by repeated repetition.

Figure 2 shows the way in which the potential of platinum changes with the distance between electrodes in the boric acid solution. The arrows

indicate the potential immediately before change of distance and the figures along the curve give the distance between the electrodes at any time. When the electrodes were changed from 0.3 to 0.005 mm. apart, the potential changed from -165 millivolts to $+70$ millivolts, and then when they were separated to 0.4 mm apart the potential returned to -168 millivolts. Further separation of the electrodes induced relatively little change in potential.

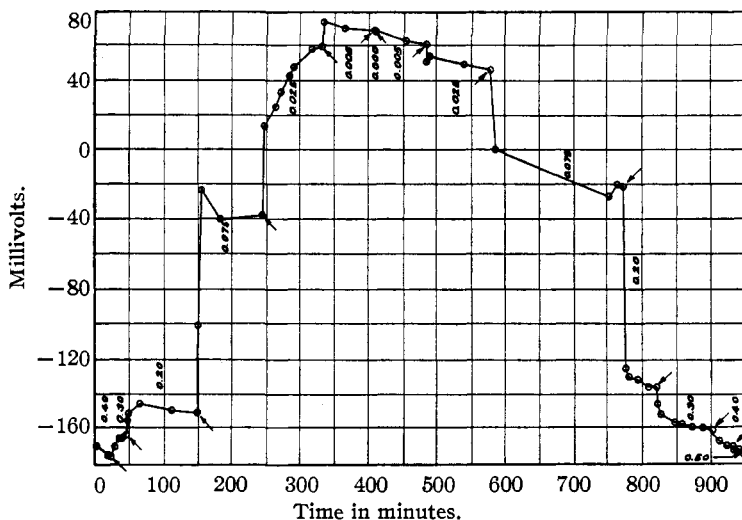


Fig. 2.—Potential of bright platinum electrode in 0.20 *M* boric acid solution containing 0.01 *M* potassium chloride per liter.

In Fig. 3 the steady potentials in the boric acid solution are plotted against the distance between the electrodes, Curve 1 representing the potentials as the electrodes were brought together, and Curve 2 the potentials as the electrodes were separated. The curves show a greater change of potential per unit change of distance when the electrodes are close together.

The change of potential with the distance between electrodes in the disodium hydrogen phosphate solution is graphically represented in Fig. 4. The potentials are plotted against the distance between the electrodes in Fig. 5. The potential does not change until the electrodes are about one-fifth as far apart as they were in the boric acid solution, when the potential began to be affected.

Figures 6 to 10 inclusive, depict the change in potential as the electrodes were brought together in the other solutions. These experiments are not as complete as those previously described since it was considered sufficient to show that the potential changes with the distance. The order of magnitude of this distance at which the potential starts to change

is apparent from a consideration of the experimental points plotted and the general nature of the curves for the more complete experiments.

It was found that when one of the platinum electrodes was replaced by a gold electrode in the boric acid and disodium hydrogen phosphate solutions, the gold electrode showed a similar change of potential with varying distance between the electrodes.

It was found in the case of the solutions of copper sulfate, aluminum sulfate and nickelous chloride that air could be used instead of oxygen with analogous results.

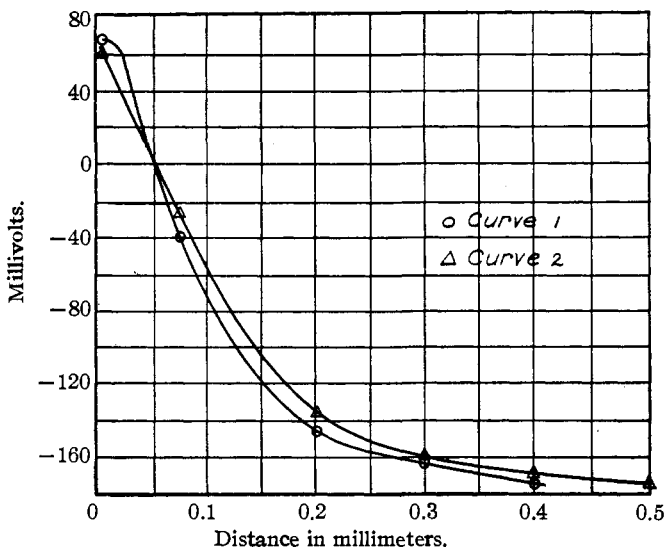


Fig. 3.—Relation between potential and the distance between electrodes in 0.20 M boric acid solution containing 0.01 M potassium chloride per liter. O, Curve 1; Δ, Curve 2.

If the potentiometer was placed several tenths of a volt "off balance" and the key tapped, the potential of the electrodes was changed. The change in potential back toward its original value could easily be followed. Figure 11 is a graphic representation of the change of the potential between two platinum electrodes in the boric acid solution when such procedure was followed. The potential was changed 50–75 mv. but regained its former value in about three minutes. When the disturbing current is reversed the potential changes the same amount in the opposite direction, which would be expected if the film contains a preponderance of one ion near the surface of the electrode.

In some experiments there was no apparent change of potential with distance but this does not necessarily mean that no ionic film was present. It may have been too thin to measure with the apparatus used. A list

of these experiments emphasizes the importance of oxygen: (a) hydrogen substituted for oxygen in the disodium hydrogen phosphate, sodium di-

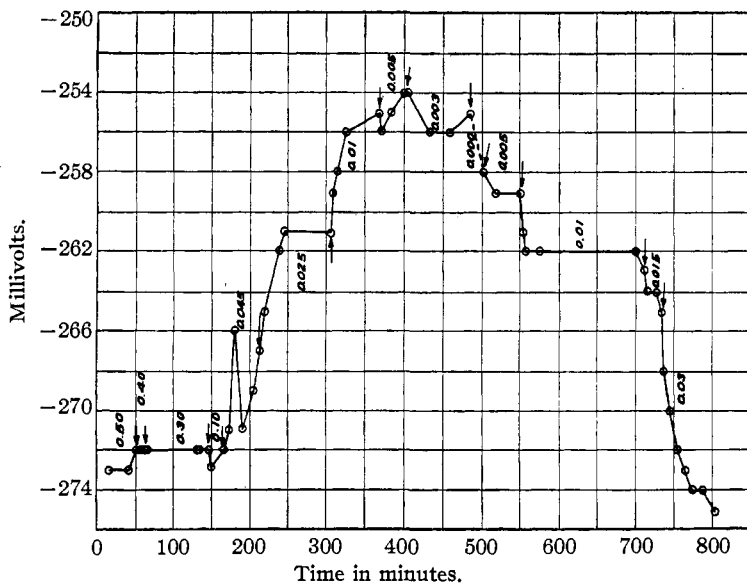


Fig. 4.—Potential of bright platinum electrode in 0.056 *M* disodium hydrogen phosphate solution.

hydrogen phosphate and boric acid solutions; (b) carbon dioxide substituted for oxygen in the sodium dihydrogen phosphate, and boric acid solutions; (c) nitrogen substituted for oxygen in the boric acid, and sodium dihydrogen phosphate solutions; (d) solutions of potassium chloride, potassium sulfate, sulfuric acid and sodium hydroxide, all under oxygen.

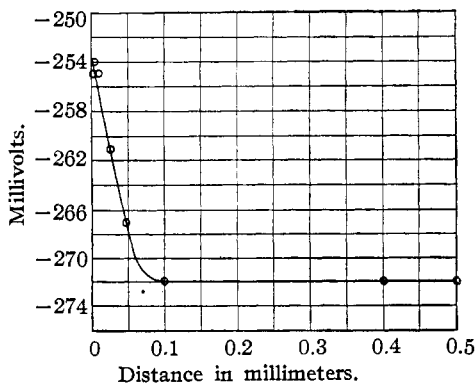


Fig. 5.—Relations between potential distance between electrodes in 0.056 *M* disodium hydrogen phosphate solution.

its surface. This effect supports in a striking manner the hypothesis advanced by Tartar and Walker¹ that the potential is due largely to the

Discussion

The data presented above show that in the presence of air or oxygen over the electrolyte, the potential of a flat platinum electrode may be changed by placing a similar electrode near

its surface. This effect supports in a striking manner the hypothesis advanced by Tartar and Walker¹ that the potential is due largely to the

preferential adsorption of ions by the electrode. Positive or negative ions are adsorbed in greater quantity at the electrode surface and, as a result, the concentration of each ion gradually changes with increasing distance from this surface until they finally become the same as in the bulk of the solution. In this layer or film there is a potential gradient due to the uneven distribution of positive and negative ions.

When two similar electrodes are made to approach each other, there is no change in the potential until the outer edge of the ionic layer of one electrode comes in contact with the edge of the film around the other electrode. When the two electrodes are made to approach each other sufficiently closely for the two films to interpenetrate, there is a change of potential due to the change brought about in the distribution of ions between the two electrodes.

The potential-distance curves give an idea of the potential gradient. In every instance the slope is greater near the surface of the electrode,

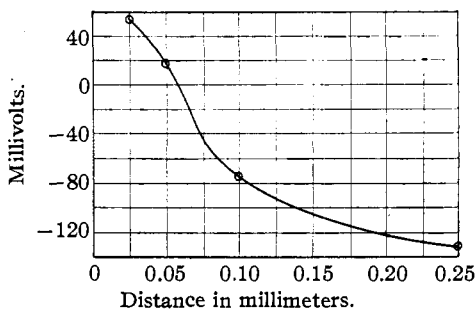


Fig. 7.—Relation between potential and distance between electrodes in 0.01 M lead nitrate solution.

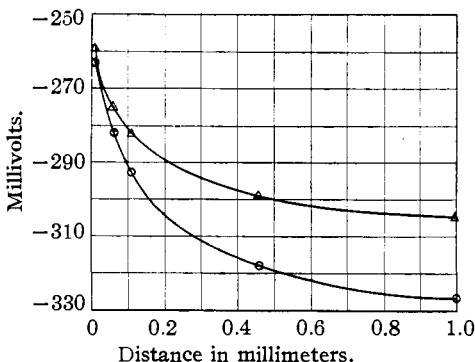


Fig. 6.—Relation between potential and distance between electrodes in 0.01 M copper sulfate solution.

thus showing that the gradient is steepest in this region. This fact also is consonant with the interpretation of the potential as given above.

The observed return of the potential of a given electrode to nearly the same value for a fixed distance between the electrodes indicates that the potential gradient is due to an approach to an equilibrium of some kind in the solution near the electrode. The fact that the poten-

tial is not precisely reproducible at a given distance is not incompatible with this conception. If the potential be due to the uneven distribution of positive and negative ions from the electrode surface, any change in the surface, the gradual adsorption of impurities from the solution, such as dissolved glass, any formation of platinum oxides or the influence of small convection currents in the electrolyte should modify the potential.

The data on the time of recovery of the potential after the momentary passage of a small electric current affords an idea of the time required for the ionic layer to readjust itself. Since the same value of potential is

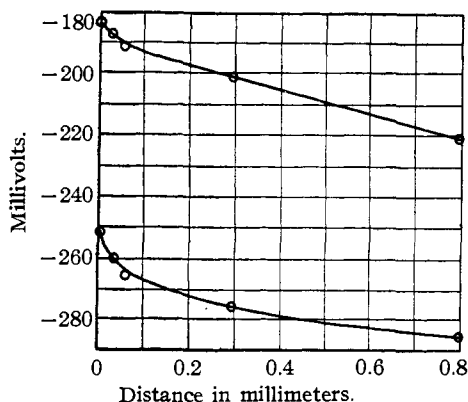


Fig. 8.—Relation between potential and distance between electrodes in 0.01 *M* aluminum sulfate solution.

regained, it is improbable that the condition of the electrode surface is changed. Evidently the transient current displaces the potential gradient in the ionic layer and a brief time is necessary for it to regain its former position.

The curves in which the potential is plotted against the distance between the electrodes show that the change begins when the electrodes are from 0.1 to 0.5 mm. apart. This is the thickness of two ionic layers of films; each one, therefore, must be from 0.05 to 0.25 mm. thick. This is of

the order of 10^6 molecules thick! Different solutes give different values.

The writers realize that this thickness of the ionic layer is essentially unheard of in the literature. There is, however, much evidence to support the idea that the oft-mentioned Helmholtz double layer may be many molecules deep. McBain⁶ has shown that Helmholtz' original assumptions regarding the thickness of the adsorbed double layer are not valid.

Debye and Hückel⁷ and also Gouy⁸ have deduced equations which indicate that the outer Helmholtz double layer is of greater than molecular dimensions.

Burton⁹ in his derivation of an equation for electroendosmose, has found it necessary to assume a value of unity for the ratio of the thickness of the Helmholtz double layer

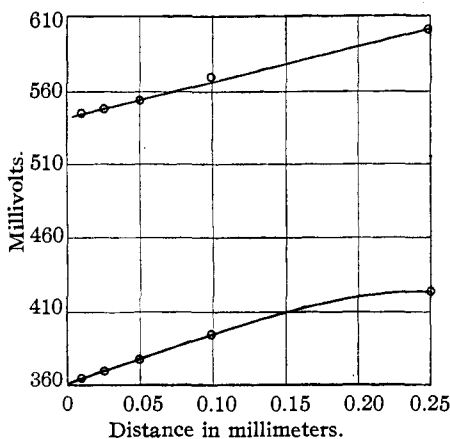


Fig. 9.—Relation between potential and distance between electrodes in 0.01 *M* potassium dihydrogen phosphate solution.

⁶ McBain, *J. Phys. Chem.*, **28**, 706 (1924).

⁷ Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

⁸ Gouy, *J. phys.*, [4] **9**, 457 (1910).

⁹ Burton, "Colloid Symposium Monograph," 1926, Vol. IV, p. 132.

to the perpendicular distance one must proceed from the wall in order to come to the place where the liquid has attained the average velocity; and Morrow¹⁰ in his study of the flow of water through a pipe arrived at the idea that the maximum velocity of the liquid is not attained at a distance less than 0.5 cm. from the surface of the pipe.

The work of McBain and his co-workers¹¹ on the surface conductivity of solutions of electrolytes in contact with glass is particularly significant in connection with the experimental results reported in this paper. They find that in a capillary space of less than 0.01 mm.

thickness, half of the conductivity is surface conductivity due to a greater concentration of ions. The writers believe that the measurement of the

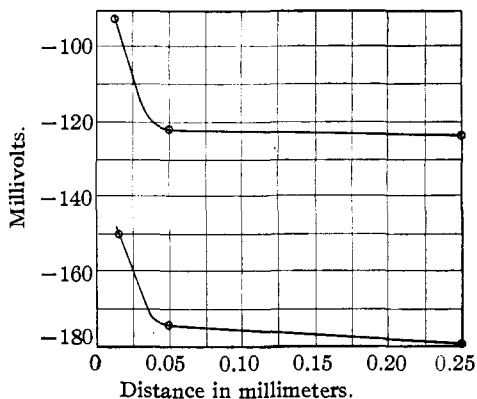


Fig. 10.—Relations between potential and the distance between electrodes in 0.01 M nickelous chloride solution.

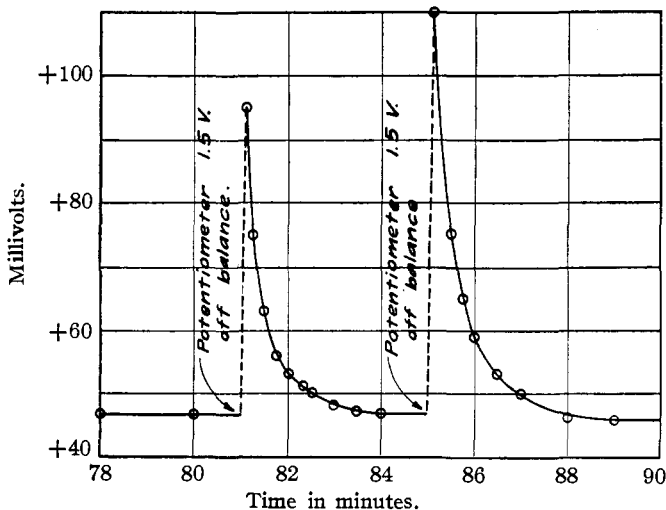


Fig. 11.—Change in potential difference between two electrodes when a sharp electrical impulse is sent through the cell.

change of potential near the surface is a much more sensitive method of measuring the thickness of the adsorbed ionic layer.

¹⁰ Morrow, *Proc. Roy. Soc. (London)*, A76, 205 (1905).

¹¹ McBain, Peaker and King, *THIS JOURNAL*, 51, 3294 (1929); McBain and Peaker, *J. Phys. Chem.*, 34, 1033 (1930).

Thus far the writers have made only qualitative tests of the thickness of the ionic layers in the case of a metal in contact with a solution of one of its salts. These preliminary tests indicate that the films do exist in certain cases. In this connection it is noteworthy that Euler and his co-workers¹² have found that silver powder or foil will adsorb a large percentage of silver ions from a dilute solution of silver nitrate. These results indicate that a metal electrode in a solution of one of its salts may be in contact with a layer in which the concentration of ions is different from that in the bulk of the solution.

The effect of the oxygen gas on the potential seems to be due to its influence on the adsorption of ions. The writers are of the opinion that when this gas is dissolved in solution, some of the oxygen molecules are adsorbed on the surface of the metal, thereby causing a change of adsorption of ions on this surface. Richards³ has stressed the great influence of oxygen and has found the platinum oxide theory of the potential insufficient to account for its magnitude. It is noteworthy, too, that Kahlenberg and French¹³ have found that the potential of an aluminum electrode in an aqueous solution of potassium chloride is markedly affected by the presence of oxygen and that the values are caused by oxygen adsorbed by the surface of the metal.

The fact that the writers did not obtain with the other gases, films which were thick enough to measure should not be taken to mean that thin adsorbed films were not formed. In fact, the behavior of the potential indicated that such films were present. The work of Kahlenberg and French¹³ using different metals in potassium chloride solution with different gases showed effects which may be considered to be indicative of the presence of adsorbed ionic layers.

The existence of a thick adsorbed film offers an explanation of the facts which have been recorded¹⁴ regarding the change in potential when the electrolyte is moved with respect to the electrode. The adsorbed film would be disturbed by any movement of the electrolyte and this would modify the potential gradient.

The fact that the potential is mainly due to an adsorbed ionic layer is not incompatible with the theory that platinum oxides may have an influence. The unsteadiness or drift of the potential of the oxygen electrode is due largely to the adsorbed film and this depends on the surface. If any oxide were formed as has been suggested by several workers¹⁵ the change in the surface would undoubtedly modify the adsorption.

¹² Euler and Hedelius, *Arkiv. Kemi. Mineral. Geol.*, **7**, No. 31 (1920); Euler and Zimmerlund, *ibid.*, **8**, No. 14 (1921); Euler, *Z. Electrochem.*, **28**, 446-449 (1922).

¹³ Kahlenberg and French, *Trans. Am. Electrochem. Soc.*, **54**, 163 (1928).

¹⁴ Schmid and Winklemann, *Helv. Chim. Acta*, **13**, 304 (1930); St. Procopiu, *J. chim. phys.*, **27**, 29-35 (1930); **19**, 121-134 (1921); Mashimo, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **2**, 341 (1917).

¹⁵ Grube, *Z. Electrochem.*, **16**, 621 (1910); Lorenz, *ibid.*, **14**, 781 (1909); **15**, 151 (1910); E. P. Schoch, *J. Phys. Chem.*, **14**, 665 (1910).

The writers have considered well other hypotheses to account for the variation of the potential with distance between the electrodes. While none have proved sufficient, some discussion of the most likely one of them may add to the completeness of this paper.

The experimental results reported above could conceivably be explained by supposing a reaction occurring at the electrode, in which case the proximity of another electrode would change the rate of diffusion of the reacting substance to the electrode, or the rate of diffusion of the product of the reaction away from the electrode, or both. Any change in these rates of diffusion should cause a change in the potential of an electrode. Even in the light of the work of Pennycuick¹⁶ and of Kolthoff,¹⁷ who have shown the possibility of the formation of an acid of platinum under certain conditions, the authors believe that the hypothesis of an adsorbed ionic film is preferable to that of a reaction at the surface. The results of three additional experiments are submitted which confirm this belief.

In the first experiment, the lower electrode (Fig. 1) was encased in a bakelite sheath which extended 1 cm. above the electrode surface. The upper electrode fitted into this as tightly as was compatible with easy movement of the electrode. This formed a small cell which held less than 0.5 cc. Since any substances used or formed by a reaction at the surface must diffuse out of or into this small cell, it was thought that change in the distance between the electrodes could have very little effect if the potential be due to a reaction. The experiment was run with 0.0388 *M* Na_2HPO_4 under air and with 0.1974 *M* H_3BO_3 (0.01 *M* KCl) under oxygen. In each case there was a change in potential with change of distance between electrodes. In the phosphate solution the potential was affected when the electrodes were 0.05 mm. apart, which is of the same order as the distance between the electrodes at which the potential was affected without the Bakelite sheath. With the boric acid solution, the electrodes were 0.2 mm. apart, which is approximately one-half the distance between the electrodes in the experiment without the Bakelite.

In the second experiment, the upper electrode (Fig. 1) was replaced by a flat, polished quartz disk (23 mm. in diameter) sealed on the end of a glass rod by means of paraffin. It was found that the potential of the electrode changed in the 0.0388 *M* Na_2HPO_4 (under air) when the electrode was 0.1 mm. from the quartz. This is of the same order as the distance between two platinum electrodes in the same solution. The potential of the electrode in 0.1974 H_3BO_3 (0.01 *M* KCl) under oxygen changed when the electrode was 0.2 mm. from the quartz. This is about one-half the distance between two platinum electrodes when the potential begins to change in the same solution.

¹⁶ Pennycuick, *J. Chem. Soc.*, 2600 (1927); 551 (1928); 2108 (1928).

¹⁷ Kolthoff, *THIS JOURNAL*, 51, 2888 (1929).

In the third experiment, one electrode was placed opposite a flat disk of Bakelite in the boric acid solution under oxygen. It was found that the potential was affected when the electrode was 0.2 mm. from the Bakelite and when brought up against it the potential changed 147 millivolts. This distance is also of the order of one-half that between two electrodes when the potential was affected in the same solution.

Summary

It has been shown that when two parallel platinum electrodes are brought together in certain solutions in contact with oxygen or air, the potential changes with the distance between the electrodes. This phenomenon is considered supporting evidence to a theory that the potential is due in part to an adsorbed ionic film extending from the electrode a measurable distance out into the solution.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE HEATS OF VAPORIZATION OF SOME ORGANIC COMPOUNDS

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The electrical method for the determination of heats of vaporization which was developed in this Laboratory,¹ has been further improved by changes in both design of apparatus and technique of operation. In this article we shall briefly describe these changes, and give the results of new determinations.

The method (for complete description see original article) consists essentially of a determination of the exact time necessary for the vaporization of a predetermined definite weight of liquid contained in the vaporizing tube (B, Fig. 1) by a precisely maintained supply of electrical energy passing through the heating coil, L, the tube containing the liquid being suspended in a vapor thermostat to prevent heat losses. The vaporizer tube, B, is nearly filled with the liquid being studied and a portion of the same liquid is placed in the "boiler" below, containing the heating coil, H. Vapor rises from the boiling liquid below and completely envelops the vaporizer tube, the excess passing out at the top of the chamber, C, into the outer chamber, D, and thence back through the condenser and trap to the "boiler" below.

The liquid in the vaporizer is heated by a current maintained at exactly 1 amp. and after thermal equilibrium has been established throughout the

¹ J. H. Mathews, *THIS JOURNAL*, **48**, 562 (1926).