Activity coefficient	$\log f = \dfrac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$
Transference number of the barium ion	$t = \dfrac{1.4476}{1 + 0.07010\sqrt{c}} - 1$
Relative fluidity	$\varphi = 1 - 0.02013\sqrt{c} - 0.20087c$
Density	$d = 0.99707 + 0.18224c - 0.00421c^2$
Molal conductance	$\Lambda = 282.13 - \dfrac{636.3\sqrt{c}}{1 + 4.628\sqrt{c}} - 31.13c$

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THE OXYGEN ELECTRODE: AN ADSORPTION POTENTIAL

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The problem of the oxygen electrode arose, for the most part, from the study of the Grove cell: Pt, HNO_3, H_2SO_4, Zn. This cell gives, when freshly made, a potential of 1.6 to 1.7 volts. It is extremely sensitive to polarization effects, which change the potential over a considerable range and render it irreproducible. The cause of this polarization was supposed to be some reaction involving the transfer of oxygen from the gaseous tc an ionic or combined state. The outcome was that the study of the oxygen electrode was approached from the standpoint of polarization reactions.

One very prevalent explanation of the behavior of this electrode is the formation of various oxides of platinum and their hydrates; the so-called "oxide theory."[1] Another theory is that the potentials are due to the formation of unstable products in the electrolyte about the electrode.[2] The experimental work described in the literature just cited affords abundant evidence that the oxygen electrode is irreversible, and cannot be classed with the hydrogen electrode or metal electrodes against solutions of their ions. As a matter of fact, there is no experimental evidence to show that there is any chemical reaction at the electrodes.

Recently, efforts based upon purely empirical considerations have been made to use the oxygen electrode in electrometric titrations involving oxidizing solutions.[3]

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[1] G. Grube, *Z. Elektrochem.*, **16**, 621–632 (1910); R. Lorenz and co-workers *ibid.*, **15**, 206–212, 293–297, 349–355 (1909); F. Foerster, *Z. physik. Chem.*, **69**, 236–271 (1910); Spielman, *Trans. Faraday Soc.*, **5**, 88–102 (1909); G. Grube and B. Dulk, *Z. Elektrochem.*, **24**, 237–248 (1918); E. P. Schoch, *J. Phys. Chem.*, **14**, 665–677 (1910).

[2] F. Haber, *Z. Elektrochem.*, **7**, 441–448 (1901); E. Bose, *Z. physik. Chem.*, **34**, 726–730 (1900); E. Bose, *ibid.*, **38**, 23–26 (1901); Bornemann, *Z. Elektrochem.*, **15**, 673–679 (1910); G. N. Lewis, THIS JOURNAL, **28**, 164 (1906).

[3] N. H. Furman, *ibid.*, **44**, 2685–2697 (1922); Tilley and Ralston, *Trans. Am. Electrochem. Soc.*, **44**, 31 (1923); A. K. Goard and E. K. Rideal, *Trans. Faraday Soc.*, **19**, 740–747 (1924); W. T. Richards, *J. Phys. Chem.*, **32**, 990–1005 (1928).

Work in this Laboratory has shown[4] that the value and steadiness of the potential of the oxygen electrode are influenced markedly by the flowing of the electrolyte. Further investigations have brought the writers to the belief that these potentials are due largely, if not wholly, to the adsorption on the platinum of ions from the solution; an adsorption potential. The object of this paper is to present this explanation of the anomalous behavior of the so-called oxygen electrode.

Apparatus.—The apparatus used for all the experiments except those under reduced pressure was entirely analogous to that customarily employed for the measurement of hydrogen electrode potentials. Cells having a capacity of about 50 cc. were used with stoppers which provided for gas inlet and outlet, bridge connections and electrode. Bright platinum wire was used for the most part as electrodes, though some measurements were made with platinized wire and both bright and platinized foil. Commercial oxygen was used after being passed through acidified potassium permanganate, dilute sodium hydroxide and distilled water. The cells were supported in a thermostat which was maintained at a temperature of 25 ± 0.02°. The potentials were measured with a Leeds and Northrup student type of potentiometer, and a Leeds and Northrup lamp and scale galvanometer. Readings of potentials were made on neutral, acid and alkaline solutions. These were made using chemicals of "c. p. analyzed" quality. The potentials presented are referred to the standard molal hydrogen electrode, taking the value of the normal calomel electrode equal to -0.283 volt. They therefore represent the potential of the cell

$$\mathrm{Pt} - \mathrm{O_2}, \text{ electrolyte, } \mathrm{KCl}\ (1\ N),\ \mathrm{H^+}\ (1\ M),\ \mathrm{H_2} - \mathrm{Pt}$$

For the sake of brevity, readings have been reported at rather long time intervals. About twice as many readings were taken as appear in each table; the complete data are not essential to showing the characteristics of the various runs.

The investigations on the effect of removing dissolved gases from the electrolytes were conducted by means of the apparatus shown in Fig. 1. A water-jet filter pump was employed which reduced the pressure sufficiently to cause boiling of all the solutions used. A manometer, connected in the system, gave an average reading of 18 mm. The connecting bridge between the two cells was filled with a stiff agar jelly made with tenth molar potassium sulfate solution. This was found necessary to prevent sucking out of the conducting medium between the two cells. A similar jelly made up with molar potassium chloride was placed up to the stopcock in the connecting tube of the calomel electrode vessel. The stopcock was kept closed throughout the evacuation. Electrical contact could be readily maintained in this manner and the inconvenience and possible

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[4] Tartar and Wellman, *J. Phys. Chem.*, **32**, 1171–1177 (1928).

source of error associated with evacuation of the calomel electrode vessel were thus avoided.

Adsorption the Cause of the Potential.—The writers propose the following explanation to account for the potential of the oxygen electrode. The platinum preferentially adsorbs ions from the solution and thus produces a potential difference between the electrode surface and the bulk of the solution. To elucidate, let us suppose that there is in solution a uni-univalent salt, the cations of which are adsorbed by the electrode in greater amount than the anions, making the electrode positively charged with respect to the solution. The ions do not form two distinct layers at the surface of the electrode, the "electrical double layer" inference found many times in the literature, but are arranged so that the concentration of each ion gradually changes with increasing distance from the metal until they finally become the same as in the bulk of the surrounding medium. The diagram in Fig. 2 will probably aid in making the conception clearer. Between o and a, the cations are in excess; and between a and d, the anions. From o to d the number of cations is equal to that of the anions, but for a lesser distance o to b, the cations are in excess. The adsorption of ions by the metal produces a potential gradient between the surface of the electrode and the point d, the magnitude and the steepness of which depend entirely upon the excess of cations preferentially adsorbed. For a negatively charged electrode the arrangement of the cations and anions would be interchanged.

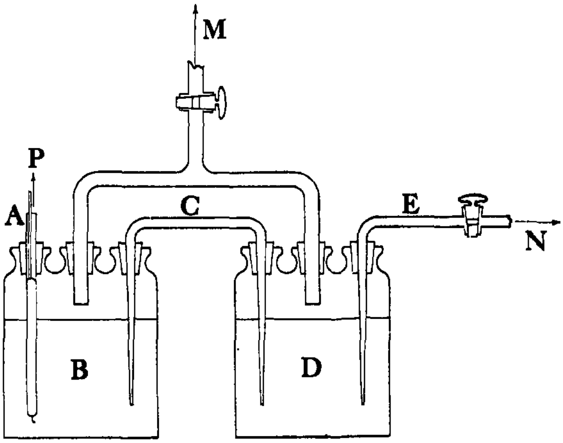

Fig. 1.—A, electrode; B, electrolyte; C, agar-filled bridge; D, KCl, about 1 *M;* E, connecting bridge filled with agar to stopcock; M, to manometer and suction pump; N, to normal calomel electrode; P, to potentiometer.

This concept of the potential of the electrode is consonant with the deductions of Debye and Hückel,[5] Gouy,[6] Powis,[7] McBain,[8] and Burton[9] regarding the distribution of ions in a Helmholtz double (?) layer.

The effect of the oxygen gas on the potential is due to its influence on the adsorption of ions. When the gas is dissolved in the solution, some oxygen molecules are adsorbed on the surface of the metal, thereby causing a change in the adsorption of ions from the electrolyte.

In support of the above explanation the writers submit the following evidences.

Evidence from the Drift of the Potential.—One characteristic of the electrode is that the potential changes or drifts with time. The rate of drift depends upon the electrolyte being greater with alkaline than with neutral or acid solutions Furman[3] states, and work in this Laboratory confirms his observations,[4] that the drift is from 30 to 60 millivolts per hour in alkaline solution and from 5 to 10 millivolts per hour in acid solution. Furthermore, the change is in a given direction for a particular electrolyte and is toward a greater potential difference between the electrode and the solution.

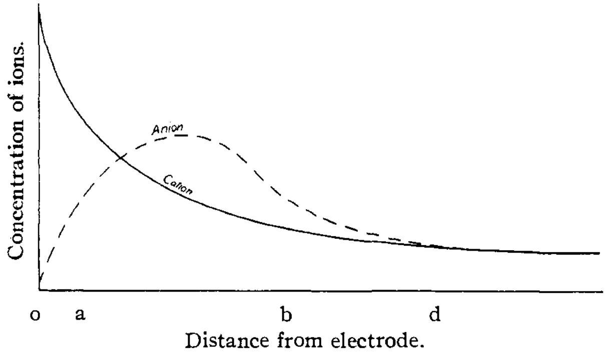

Fig. 2.

This uni-directional drift may be considered as a consequence of the slow adjustment in the outer fringe of the ionic layer, *i. e.*, of the part b to d, Fig. 2. This is substantiated by the fact that with time, the drift becomes appreciably slower and the potential approaches a steady value. This time element is not surprising when it is considered that the ionic layer throughout which the potential gradient exists is probably many ions deep, and the forces holding the outermost ions in position become very weak.

[5] Debye and Hückel, *Physik Z.*, **24**, 185 (1923).

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

[7] Powis, *Trans. Faraday Soc.*, 11, 160 (1916).

[8] McBain, *J. Phys. Chem.*, **28**, 706 (1924).

[9] Burton, "Colloid Symposium Monograph," Chemical Catalog Co., New York, 1926, Vol. IV. p 132.

Influence of Movement of Electrolyte upon the Steadiness of the Potential.—It has been shown by Tartar and Wellman[4] that the potential becomes more steady, ceases to drift, when there is a uni-directional flow of the electrolyte past the electrode. The potential becomes fairly constant for a given electrode in a given solution provided the rate of flow remains unchanged. This phenomenon can be explained as being due to the effect upon the distribution of the ions from the surface of the electrode. In the region a, Fig. 2, the distribution is maintained by electrical forces sufficiently great to be but little influenced by the movement of the electrolyte. Forces of less magnitude operate in the region b to d, which are more easily overcome by the movement of the solution. Thus the flow gives a shearing force opposing the electrical forces tending to maintain the potential difference from o to d and the fringe, say b to d, is swept away. This results in a more constant potential and the elimination of the drift.

Effect of Jarring the Electrode and of Small Electric Currents.—With some solutions the potential shifts markedly when the electrode is gently tapped. This effect may be accounted for in the same way as that produced by the movement of the electrolyte. The tapping moves the electrode with respect to the solution, thereby producing a change in the arrangement of the ions, particularly in the outer portion of the ionic layer (b to a).

Difficulty was experienced in reading the potentials in neutral and acid solutions. The potentiometer could be set anywhere within a range of 40 to 60 millivolts and the galvanometer show no deflection if the connecting key were tapped frequently enough. This apparent "balance," obtained both above and below the actual potential, is due to modifications in the ionic layer by the small electric current to and from the electrode when the potentiometer was "off balance."

Evidence from the Effects of Gases Other than Oxygen.—It has been suggested earlier in this paper that the influence of the oxygen gas on the value of the potential is due to the modification of the electrode surface by the adsorption of oxygen molecules. This modification is not limited to oxygen alone but should occur with other gases as well. Accordingly, investigations were conducted with nitrogen and hydrogen.

In the case of hydrogen, a neutral electrolyte was used, *viz.*, a saturated solution of potassium sulfate. The electrode was of bright platinum, which accounts for the difference between the type of readings obtained and that usually associated with the hydrogen electrode. Table I gives a set of readings, together with notations indicating manipulations of the gas and the electrode. The data show that the potential drifted markedly and was extremely sensitive to the effects of jarring and of other disturbances in the immediate vicinity of the electrode. This would indicate that hydrogen gas has a very pronounced modifying influence on the adsorption of ions by the platinum—an indication which is hardly more than would be expected in view of the relatively high adsorption of hydrogen itself on platinum. Hence the potentials are of an electrode which is functioning in part only as a hydrogen electrode, and where the predominating influence is still that of ions adsorbed from solution.

TABLE I

POTENTIAL WITH BRIGHT PLATINUM IN SATURATED POTASSIUM SULFATE IN THE PRESENCE OF HYDROGEN GAS

Time, min.	Potential, volts	Manipulations	Time, min.	Potential, volts	Manipulations
0	−0.368	Hydrogen bubbled in	102	0.367	
10	+ .162		105	.352	Hydrogen bubbled directly on electrode
30	.207	Electrode shaken			
40	.257		107	.382	
50	.182		110	.362	
80	.312		115	.342	Electrode shaken
100	.337	Hydrogen bubbled directly on electrode	130	.427	

The second gas (nitrogen) was chosen because of its inertness and comparatively low adsorption on platinum. By analogy, we expected that the potential with this gas would drift more slowly than with either oxygen or hydrogen. The data, which appear in Table II, seem to bear out this prediction.

TABLE II

POTENTIAL WITH BRIGHT PLATINUM IN SATURATED POTASSIUM SULFATE IN THE PRESENCE OF NITROGEN GAS

Time, minutes	0	5	10	15	35	65
Potential, volts	−0.395	−0.383	−0.338	−0.328	−0.300	−0.386
Time, minutes	95	125	190	310	370	
Potential, volts	−0.278	−0.265	−0.248	−0.223	−0.193	

The readings were continued for periods up to twenty hours without a definite cessation of the drift, though the rate of change became extremely slow. For the first 300–400 minutes the potential seemed to be affected but little by external disturbances, but thereafter became much more sensitive. A similar run was conducted with normal sulfuric acid and nitrogen gas, which gave the same type of results; *e. g.*, at the end of nine hours the potential was still drifting at the rate of 12–13 millivolts per hour.

Evidence from Potentials in the Absence of Gases.—If the suggested interpretation of the effect of gases on this potential is correct, the characteristic drift should exist when no gas is present. To show this, investigations were conducted using the apparatus already described and shown in Fig. 1.

Previous to evacuation, the electrolyte was saturated with the desired gas and readings of potential taken for some time. Oxygen, hydrogen and nitrogen were used. The electrolyte was a saturated solution of potassium sulfate, so that no difficulty arose due to changes in concentration during the course of evacuation. Table III gives a summary of these results.

TABLE III

POTENTIALS WITH BRIGHT PLATINUM IN SATURATED POTASSIUM SULFATE DURING REMOVAL OF DISSOLVED GASES

Time, min.	Potential, volts (satd. with oxygen)	Potential, volts (satd. with hydrogen)	Potential, volts (satd. with nitrogen)
0	. .	. .	−0.179[d]
20	. .	. .	−0.174
30	−0.377[a]	+0.339[c]	.166[b]
50	.381	.427[b]	.164
80	.381[b]	.172	.161
100	.372	.132	.160
130	.340	.107	.158
160	.338	.008	
220	.336	−0.083	
280	.331	.113	
340	.324 .278 (5.5 hours)	.157 .163 2 hours	

[a] Oxygen bubbled in. [b] Evacuation begun. [c] Hydrogen bubbled in. [d] Nitrogen bubbled in for seven hours.

These data indicate that the cessation of the drift appears to be in no way hastened by the removal of dissolved gases from the electrolyte. Similar work of more limited extent was performed with saturated oxalic acid as the electrolyte with confirming results.

Evidence from Potential with "Immobile" Electrolytes.—If the ionic layer is of the thickness suggested, it should be possible to stabilize it by making the electrolyte less mobile or else by packing a sufficiently finely divided material about the electrode.

An attempt to steady the potential in this way was made by imbedding the electrode in finely powdered silicon dioxide covered with the electrolyte. Bright platinum electrodes were used. Oxygen was bubbled continuously through the electrolyte with the tip of the gas inlet tube below the surface of the powdered material and at a distance of not more than 8 mm. from the electrode. Neutral, acid and alkaline solutions of varying normalities were used in order to determine the dependence of the steadiness of the potential upon the concentration. In general, the more concentrated solutions gave the more stable potentials but the difference in the type of readings was not sufficiently pronounced to warrant the inclusion of all the data. Hence, potentials for only one concentration of each electrolyte will be reproduced. In each case a series of readings in the same electrolyte and without the silicon dioxide was taken simultaneously and the results of these are also given in Table IV.

TABLE IV

POTENTIALS WITH BRIGHT PLATINUM IN NEUTRAL, ACID AND ALKALINE ELECTROLYTES WITH AND WITHOUT SILICON DIOXIDE POWDER

Time, min.	Potential in electrolyte without powder, volts	Potential in electrolyte with SiO_2 powder, volts	Time, min.	Potential in electrolyte without powder, volts	Potential in electrolyte with SiO_2 powder, volts	Time, min.	Potential in electrolyte without powder, volts	Potential in electrolyte with SiO_2 powder, volts
	$M/10$ K_2SO_4			N H_2SO_4			N KOH	
10	−0.490	−0.516	10	−0.814	−0.696	10	+0.159	+0.119
30	.458	.515	20	.818	.683	30	.153	.116
75	.435	.516	60	.816	.683	100	.146	.114
105	.425	.516	140	.825	.683	130	.144	.113
120	.433	.515	210	.811	.683	160	.142	.113
165	.428	.518				210	.140	.113
190	.430	.518						
300	.432	.521						

The results show that in all cases the addition of the powdered material had a stabilizing influence, more so in the alkaline and acid solutions than in the neutral. The above experiments were repeated with a coarser medium employed as a stabilizer, namely, Ottawa sand. It was found that this material had the desired effect in the alkaline and acid solutions but was of little assistance in the neutral electrolyte. Three sets of readings are given in Table V. It will be noted, however, that while the presence of the sand does not render the potential with the neutral electrolyte steady, it does stop the tendency to drift continuously.

TABLE V

POTENTIAL WITH BRIGHT PLATINUM IN NEUTRAL, ALKALINE AND ACID ELECTROLYTES IN COARSE SAND

Time, min.	Potential in $M/10$ K_2SO_4, volts	Potential in N KOH, volts	Potential in N H_2SO_4, volts
10	−0.602	+0.103	−0.730
20	.592	.106	.690
80	.583	.103	.701
100	.581	.100	.702
130	.583	.100	.702
160	.581	.100	.702
180	.582	.098	.702
210	..	.098	.702

The effect of powdered silicon dioxide on the potential with *platinized* platinum electrodes in alkaline and acid solution was observed; it was found that with this type of electrode surface the amount of stabilization produced in this manner was negligible.

Further experiments were made by placing bright platinum electrodes in agar jelly containing the electrolyte; tenth molar potassium sulfate and tenth normal sulfuric acid were used. The potentials were very steady and did not drift. Because of the indefinite nature of the agar jelly, it is not possible to say that the steady potentials were due wholly to the stabilization of the ionic layer.

Evidence from the Effect of Substances Reducing Interfacial Tension.—Another method for showing the role played by adsorbed ions in producing these potentials was based on the effect obtained when the interfacial tension between the electrode and the electrolyte was reduced. Two types of substances were employed; one polar and the other non-polar. These were potassium pelargonate and amyl alcohol, respectively. Since the former would interact with the acid solution, readings were taken with it only in neutral and alkaline electrolytes. The data appear in Table VI. The concentration of the pelargonate was about 0.25 g. per 100 cc. of electrolyte.

TABLE VI

POTENTIALS WITH BRIGHT PLATINUM IN NEUTRAL AND ALKALINE ELECTROLYTES WITH POTASSIUM PELARGONATE

Time, minutes		15	75	135	195	250	255
Potential, volts	in $N/10\,K_2SO_4$	−0.566	−0.566	−0.566	−0.566	−0.566	−0.566
	in $N/10\,KOH$	+0.181	+0.203	+0.205	+0.205	+0.205	+0.205

In the case of amyl alcohol, all three electrolytes were used, and were made about 1% with respect to the amyl alcohol. Table VII contains readings taken in this manner.

TABLE VII

POTENTIALS WITH BRIGHT PLATINUM IN NEUTRAL, ACID AND ALKALINE ELECTROLYTES WITH AMYL ALCOHOL

Time, min.	Potential in $N/10\,K_2SO_4$, volts	Potential in $N/10\,H_2SO_4$, volts	Potential in $N/10\,KOH$, volts
10	−0.561	−0.752	+0.154
60	.558	.749	.151
90	.554	.750	.148
200	.550	.750	.147
300	.549	.751	.146

The experiments with amyl alcohol were repeated with platinized platinum with even more gratifying results; *e. g.*, in the case of sulfuric acid ($N/10$) the potential showed no change whatever, after the first twenty minutes, during 500 minutes of observation.

Summary

1. The behavior of the oxygen electrode has been explained as being due largely to the adsorption of ions; an adsorption potential.

2. Experimental evidence has been presented to support this explanation.

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