METALLISED GLASS OXYGEN ELECTRODES

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P.T.O.

(continued)

-SUMMARY-

Metallised glass electrodes with films of Pt, Ir, Pd, Os, Rh, Ru, Ag and Au in various states - bright, black etc. - have been studied as oxygen electrodes in the three electrolytes H_2SO_4, KCL, and NaOH. The use of oxygen or air electrodes for titration purposes has been extensively studied by others, and therefore little attention has been given to this aspect of these electrodes in this work, which has been chiefly confined to the search for a reproducible and accurate oxygen electrode.

Particular note was taken of the effect of the previous history of the electrode on the potential, but the history is not amenable to accurate measurement and no very definite results were obtained. No electrode was found which gave a reproducible, constant, thermodynamically reversible potential. On the other hand, the theoretical potential of the oxygen electrode was often exceeded, although only for very short periods of time as the potential fell rapidly, by freshly heated Rh and Ir electrodes. Although not at the reversible potential, potentials were also obtained which were reproducible within approximately 10 mv., e.g. Pd in KCL, Os in NaOH and H_2SO_4.

The electrodes were heated in vacuo to 400°C, in an effort to decompose any oxide films possibly present on the metallic surface. A very marked lowering of the initial potential was observed due to this treatment in neutral and acid solution, but the treatment had little or no effect in alkaline solution - with Ag and Rh there was very little effect in any electrolyte. A theory is developed to explain these latter results and the general behaviour of oxygen electrodes in undisturbed electrolyte. It is considered that no single theory proposed up to the present is capable of fully explaining the anomalies of the oxygenelectrode, but that a combination of several theories may do so - the ordinary oxygen potential being a "compromise potential".

The Motor Electrolytic Potential (M.E.P.), produced by relative motion between electrode and electrolyte, was also studied with these electrodes, since it appears to have considerable bearing on the constancy and reproducibility of the electrodes. It has been pointed out that there is no theory at present to account for the M.E.P. of gas electrodes as distinct from metal electrode M.E.P., and that even for metals there appears to be considerable confusion as to what the M.E.P. really is, and as to how it is to be measured. The M.E.P. of the Pt metals was found to vary widely, sometimes being positive and sometimes negative. By covering the electrode with a coating such as collodion, which is permeable to the electrolyte, the negative M.E.P. is rendered positive in all the cases tried. A theory is developed, based on that of Evans, and Müller and Konopicky, to explain the behaviour of these collodionised electrodes and the M.E.P. of oxygen electrodes in general.

INTRODUCTION.

The Irreversibility of the Oxygen Electrode:

The irreversibility of the oxygen electrode is well known, but the mechanism of this electrode is still a highly controversial subject. Although several theories have been proposed to account for the facts as at present known, none is yet generally accepted as true. In practice the result of this irreversibility is the low experimental values, for example, obtained for the oxy-hydrogen cell. The Hydrogen electrode, of course, giving the theoretical potential, the low values must be due to the oxygen electrode. The E.M.F. of this cell, calculated from the results of the classical experiments of Nernst and Von Wartenberg[1] on the dissociation of steam at high temperatures, is 1.232 - 0.00085 (t^0-17) volts. Lewis and Randall[2] give 1.22 volts as the average value for the O_2-H_2 cell as calculated from the data of Lowenstein[3], Langmuir[4], Lewis[5], Brofisted[6], Taylor and Hulett[7], and Nernst and von Wartenberg. Britton[8] has calculated the value to be approximately 1.22 volts from considerations of the potential of the Ag/Ag_2O/NaOH cell and the dissociation pressure of silver oxide. The generally accepted theoretical value is therefore approximately 1.23 volts, and this is the value used for the purposes of this investigation. The published experimental values for the O_2-Hgcell, however, are considerably lower than this figure, varying from 1.15 to 0.9 volts. Spielmann[9] gives a summary of the experimental values obtained for this cell by workers up to 1909, and the values all lie within the above limits. No further advance has been made since then as regards the attainment of the theoretical oxygen potential under ordinary conditions.

Continued .....

The Reversibility of the Oxygen Electrode and its use as an Indicator Electrode in Electrometric Titrations:

Haber and Fleischmann[10], Haber and Foster[11], and Haber[12] have used the oxygen electrode at high temperatures in fused glass, porcelain, NaOH and KOH as electrolytes, and they found that, at temperatures between 400 and 1000°C, the electrode gave values in accordance with thermodynamical theory. Baur[13] used an oxygen electrode in a molten eutectic of NaOH and KOH and Baur and Brunner[14] in carbonate melts at 500-600°C. It seems that at temperatures above 400°C the oxygen electrode is reversible.

Oxygen electrodes cannot be completely irreversible even under ordinary conditions. However, since they have been extensively and successfully used as indicator electrodes in electrometric titrations, where the use of hydrogen electrodes has to be avoided for various reasons. Being readily sensitive to changes of pH, they must have a certain degree of reversibility at any rate. Furman[15] has used oxygen electrodes for determining total acidity or alkalinity in the presence of chromate and dichromate by means of electrometric titrations. He later extended the work to air electrodes[16], using oxidising and non oxidising solutions, and found them quite satisfactory. Although the titration curves are not reproducible throughout their whole course, the break at the end point is quite definite and always occurs at the same point in the titration, thus furnishing an accurate method of determining acidity in solutions , where the use of Hydrogen electrodes is unpracticable. Arthur and Keeler[17] used an air electrode for controlling the

alkalinity of boiler feed water industrially.

Tilley and Halston[18] used the air electrode to follow the removal of ferric iron and alumina from copper sulphate solutions by precipitation with limestone, and a few other similar hydrolytic reactions. Van der Meulen and Wilcoxon[19] used a polished platinum wire as indicator electrode in titrating NaOH with standard acid. They stirred the solution mechanically and used no hydrogen gas, but found a sharp break at the end point. Under these conditions they were obviously using an air electrode, as the electrolyte would be in an air saturated condition. They attribute the potential, however, to selective adsorption of ions. Britton,[20,21,22], of all the workers in this field, has carried out probably the most exhaustive investigations on oxygen electrodes, as indicator electrodes in electrometric titrations. He followed the precipitation of Hg (ic), Cd, Pb, Ag, Cu (ic), V (ic), and Fe (ic) ions with NaOH and investigated the titration of various acids with NaOH. These experiments included titrations of chromic acid and organic di-basic acids. As a result of this work he found that, although two electrodes never give coincident curves, the oxygen electrode is quite satisfactory as an indicator of rapid changes in hydrogen ion concentration. Furman (loc. cit)calibrated his electrodes on an empirical pH scale, and Britton later improved the method to obtain greater accuracy throughout the titrations. Montillon and Cassel[23], and Brewer and Montillon[24], have used oxygen and air electrodes to determine the pH of plating baths especially where hydrogen electrodes are inapplicable, e.g. Ni and Co. plating solutions. (Ni and Co being lower than hydrogen in the electromotive series and therefore likely to plate

out on the electrode.) Calibrating their electrodes by means of buffer solutions, they claim to have determined the acidity with an accuracy of .1 pH. Popoff and LeHenry[25,26] used air electrodes in straight acid-base titrations, also in estimating acidity in presence of $KMnO_4$, phenol, varnish and cresol (hydrogen electrodes reduce the last three substances) and in the quantitative estimation of alkaloids, where they claim a greater accuracy than for any other method. Elder[27] discussed the titration of ferric iron with NaOH using an air electrode, and states that the apparent end point may be approximately 1p from the true end point, and that no direct determinations of pH can be made by air electrodes in such a solution. The variation of the end point he attributes to the fact that the platinum electrode is measuring principally an oxidation - reduction potential, the oxygen potential being suppressed. Butler and Armstrong[28] used bright platinum electrodes, polarised anodically for a short time, and then, momentarily, cathodically, in ordinary acid-base titrations, and claimed to have achieved a greater degree of reproducibility than in the case of ordinary oxygen electrodes.

Willard and Fenwick[29], Baylis[30], Parker[31], Kahlenberg and co-workers[32/34], Britton and Dodd[35], and Wolf[36], who gives further references to bi-metallic titrations, have used metals other than platinum e.g. tungsten to follow titrations, or to test pH and found them quite satisfactory. The explanation of why these electrodes function as pH indicators is, in all probability, that they too are acting in part at any rate as reversible oxygen electrodes, or metal-metallic oxide electrodes which are, in effect, oxygen electrodes, where the pressure of oxygen is determined

by the tendency of the oxide to dissociate into metal and oxygen. The well known antimony oxide electrode would also come under this category.

All this evidence points quite conclusively to the fact that, to some extent, the oxygen or air electrode is reversible, even under ordinary conditions. On the other hand the electrode is to a very large extent irreversible, as is shown by the fact that reproducible and constant potentials are not given even by the same electrode under, as far as possible, identical conditions. To explain this irreversibility and the many anomalies found when using these electrodes, various theories for the mechanism of the electrode have been proposed.

Investigations into the Mechanism of the Oxygen Electrode up to 1910:

In the early years of this century there existed in the main two theories, and to-day these remain essentially the same. Glaser[37], Wilsmore[38], Bose[39/41], and Briscoe[42], observed that an oxidising substance was present in the electrolyte around the electrode after prolonged use. This oxidising substance was supposed to be H_2O_2. As they found that addition of H_2O_2 lowered the potential of the electrode, the theory was advanced that the potential actually being measured was that of the free energy of formation of H_2O_2. Thus the low experimental values of the O_2-H_2 cell were accounted for. Bose assumed two modifications or isomers of H_2O_2, the one, a higher peroxide which would account for some of the high experimental values obtained, and the other a lower modification which was the product of the decomposition of the high peroxide. This decomposition was supposed to produce the drop in potential observed by Bose after anodic polarisation of the electrode.

Bornemann[43], however, although finding some evidence for the production of H_2O_2, was doubtful as to whether or no this substance was actually formed. Both Haber[44] and Lewis[45] suggested that the primary reaction in the O_2-H_2 cell was the formation of H_2O_2. This view has been strongly supported by Bancroft and Murphy[46], in recent years, who state, in a paper on "Oxidation and Reduction with H_2O_2", that, though it is not yet accepted, it is unquestionably the correct explanation.

The second, oxide, theory was investigated and supported principally by Lorenz and his co-workers[47/51]. Evidence for the existence of oxides on platinum had previously been brought forward by Lond, Ramsay and Shields[52,53] from considerations of the heat evolved by absorption of oxygen by platinum black, by Moehler[54] who obtained evidence of the existence of PtO on heating Pt in oxygen at 280°C for prolonged periods, and by Luther and Brislee[55] who found platinum passive under certain conditions, and attributed this passivity to the presence of an oxide film.

Lorenz and his co-workers based their theory mainly on:

(a) The "resting points" found during the fall of the potential caused by the discharge of anodically polarised bright Pt electrodes; and

(b) The fact that when the pot. of various oxides or hydrated oxides of Pt were measured, they were found to agree very closely with the reported potentials of Pt surrounded by Oxygen, both measured against the hydrogen electrode. Their explanation was that the fall of potential occurred as the higher oxides decomposed into the lower ones - the "resting points" being the single potentials of the different oxides. They conclude from their results

that the higher the oxide and the higher the degree of hydration, the higher will the single potential become. Thus the potential of the oxygen electrode is really the single potential of oxides of Pt and the many differing values obtained are due to different oxides in different degrees of hydration. They were not able to find an oxide, however, with a high enough single potential to account for the values of over one volt which were often reported for the O2-H2 cell, e.g. Neale[56] 1.07 volts, Glaser[37] 1.08 volts, Crotogino[57] 1.06 volts, Wilsmore[38] 1.12 volts, Bose[39/41] 1.15 volts, Czepinski[58] 1.12 volts, Westhaver[59] 1.1 volts.

A summary of Lorenz's conclusions up to this point is given by Spiedmann[9]. Later Grube[60] reported the preparation of an oxide, PtO_3, giving a single potential of 1.5 volts. This potential falls very rapidly with the evolution of oxygen, as the oxide decomposes. He explains the depressing action of H_2O_2 on the potential as being due to the H_2O_2 discharging the PtO_3 and PtO_2 electrodes. Haber, Fleischmann and Foster[10/12] found that the oxygen electrode was thermodynamically reversible at high temperatures, and Haber[12] in the final paper, appears to favour the oxidation of the Pt by H_2O_2 as an explanation of the irreversibility of the oxygen electrode. Foerster[61], working on the Pt and Ir electrodes, explained his result on Lorenz's oxidic theory. He postulated that the Ir oxides were less stable than Pt oxides, thus explaining the more rapid fall of potential with Ir anodes. He affirms that the concentration of H_2O_2 in the electrolyte determines the concentration of the oxides, and therefore the potential of the electrode.

Bose[39] gives a bibliography of work on gas

cells up to 1900, and decides for the H_2O_2 theory[40,41]. Schoch[62] in a report of progress concerning work on the oxygen electrode up to 1910 sums up for the oxide theory, which theory certainly had the greatest weight of experimental evidence behind it.

Later Investigations conducted on the Oxygen Electrode:

From 1910 there was a gap, with the exception of the work of Grube and Dulk[63] who favoured the oxide theory, and no direct work appears to have been done on the theoretical oxygen electrode untilthe early twenties. These later workers, starting with Furman[15], were generally more concerned with making use of the electrode as a practical instrument in electrometric titrations, than with the theoretical reasons for it's irreversibility. Most of them seem to have agreed with Schoch's summing up[62] and accepted the oxide theory as it stood. Thus Furman[15,16] presumes the irrversibility to be due to oxide formation. Britton, with the evidence of his extensive work on electrometric titrations with the oxygen electrode[20,/22], attributes the irreversibility to "the tendency of the gas to combine with the Pt to form a series of oxides or perhaps of solid solutions[64]". He also recognizes the fact, however, that, to a large extent, the electrode is reversible, the oxygen ions being in equilibrum with the hydroxyl ions thus:

$$O'' + H_2O \rightleftharpoons 2OH'$$

Goard and Rideal[65] discuss the evidence for the oxide theory very thoroughly, and consider it highly probable that the anomalies of the oxygen electrode are due to solid solutions of oxides in the surface of the electrode. An electrode, pre-treated in $KMnO_4$ to control its oxygen content, was found to give a reproducible maximum potential in reducing solutions such as glucose. This was explained on the basis of oxides in solid solution in the surface

of the Pt.

Tammann and Runge[66], as a result of experiments on the effect of pressure on the oxygen electrode, decided that it was not reversible below 100°C, and that the potential could be explained satisfactorily on the basis of Lorenz's oxide theory. They suggest that it is probable that a reversible oxygen electrode could be attained at high temperature at which the oxides are decomposed. Von Maray Szabo[67] used a diffusion oxygen electrode similar to the diffusion hydrogen electrodes of Knobel[68] and Schmid[69], which consisted of hollow carbon rods plated with Pt, gas being led down the centre of the rod and allowed to diffuse through the metal. He explained his results on the usual electromotively active "primäroxyd" theory. Richards[70] found oxygen electrodes fairly steady in solutions of borates or phosphates and advocated an oxide theory in combination with the oxygen ion theory, i.e. the theoretical oxygen electrode. Most of the early workers considered the potential to be purely oxidic. Hoar[71] uses the oxide theory in a completely different manner. He asserts that the layer of oxide, as such, will not affect the potential or the electrode but applies the electrochemical theory of corrosion, as supported by Evans[72/74] and others, to the case of the oxygen electrode.

Some later workers, however, have supported the H_2O_2 theory. Tilley and Halston[18], because the oxygen electrode is sensitive both to oxidising agents and to the hydrogen ion concentration, come to the conclusion that the electrode is a combination of the H_2O_2 electrode and the theoretical oxygen electrode. As a result of the steady potential give by the oxygen electrode, when oxygen saturated electrolyte

flowed past the electrode at a uniform rate, Tartar and Wellman[75] supported the H_2O_2 theory in preference to the Pt oxide theory. They rejected the oxide theory because "It does not seem probable that a slight decrease in the rate of flow of the liquid past the electrode should permit the oxidation of the Pt with the possible formation of a higher oxide. Nevertheless, a shifting of the potential away from zero usually accompanied a decrease in the rate of flow of the solution". The concentration of H_2O_2 about the electrode would, of course, be influenced by the rate of flow, thus affecting the potential. Tartar and Wellman found, however, as the earliest workers had[37/42], that the addition of H_2O_2 to the electrolyte lowered the potential of the electrode. Consequently they state "It is not easily understood, however, why an increase in the rate of flow of the electrolyte past the electrode should shift the potential in the same direction as is caused by adding H_2O_2 to the electrolyte".

Later, as a result of the work of Tartar and Walker[76] this H_2O_2 theory was abandoned in favour of the selective adsorption of ions from the solution by the Pt. This theory was proposed by Van der Leulen and Wilcoxon[19], but Tartar and Walker were the first to develope it fully and to apply it to the oxygen electrode. The effect of oxygen on the electrode potential was explained as due to the modification brought about by adsorbed oxygen molecules on the preferential adsorption of the ions by the metal electrode. Further details of Hoar's[71] theory and that of Tartar and Walker are given later.

French and Kahlenberg[77], and Krueger and Kahlenberg[78] tried the effect of various gases, including H, O, N, He and A, on the potential of many metals including Pt., Ir, Au, Ag, and Pd in acid, alkaline and neutral electrolyte. They give no theory to explain their

results, but affirm that there is no such thing as a gas electrode; the potential depends on the gas, the metal and the electrolyte - they are gas-metal electrodes. The final potential depends partly, on the absorbing power of the particular metal for the particular gas, and partly on a gas film condensed on the electrode, the instability of the film providing the cause of the well known fluctuation of the potential of some gas electrodes. An oxidic theory would certainly agree that the potential depended on the metal from which the oxide was derived and also on the gas, providing it has an effect on the stability of the oxide. It is difficult to understand, however, how a simple oxidic theory could explain the immediate change of potential observed by the authors on tapping or jarring the electrode.

Reproducible and Constant Oxygen Potentials:

Throughout all these investigations a reproducible potential was attained only in a few cases under very special conditions with a limited application. Goard and Rideal[65] found a reproducible potential but only in arsenite, glucose or similar solutions, and after the electrode had been pre-treated in $KMnO_4$. Richards[70] obtained results reproducible to within one millivolt, but only in borate solutions and with "seasoned "electrodes, i.e. electrodes which had been alternately made anode and cathode several times and then left to acquire a steady potential in the electrolyte.

It seems to be slightly easier to obtain a constant potential with an electrode even though this potential may not be reproducible. Thus Tartar and Wellman[75] steadied the potential by keeping the electrolyte flowing at a uniform rate past the

electrode and Tartar and Walker[76] by stabilising the electrolyte round the electrode with Silicon powder or agar jelly. With the exception of a few isolated experiments on Ag, Au, Pd and Ir,[56,59,61,78] the only metal used by the large majority of workers has been Pt. Consequently, in the present investigation, it was decided to undertake a more comprehensive survey of the Pt metals than had yet been attempted in the hope that this might either lead to the discovery of a reversible, or at least a reproducible, oxygen electrode, or else provide data towards solving the problem of the mechanism of this electorde. Such a reproducible electrode, even if not giving the theoretical potential, would provide a very useful instrument for direct determination of pH in the cases where the hydrogen electrode is inapplicable.[15/36]

The two main sources of error in the direct determination of pH are:

(a) "Potential Drift", which involves change of single potential with time, and

(b) "Motor Electrolytic Potential" (M.E.P.), which involves change of single potential with relative motion between electrode and electrolyte. It was necessary therefore to study both of these factors with all the electrodes.

Again there is no generally accepted theory to account for either of these phenomena, although several have been proposed. The theories proposed to account for the irreversibility of the oxygen electrode in most cases cover the phenomenon of potential drift as well. For example, according to the oxide theory, the potential drift is due to the slow formation and decomposition of different oxides, and according to the adsorption theory it is

due to the slow adjustment of the outer edge of the ionic atmosphere surrounding the electrode.

The [illegible] of Oxygen electrodes:

The phenomenon of [illegible] has, with a few exceptions[75/79] been left entirely alone by investigators working on the theoretical oxygen electrode. Of these exceptions Tartar and Wellman[75] and Tartar and Walker[76] have not made a study of [illegible], but just offer tentative explanations based on their respective theories of the oxygen electrode, as to why relative movement of electrode and electrolyte should affect the potential. French and Kahlenberg[77], and Kreuger and Kahlenberg[78] have done some experimental work on the [illegible] of oxygen electrodes, and attribute it to the destruction of a condensed gas film usually present on the electrode. They say this effect may be brought into play merely by a patch of dirt on the electrode. This investigation is breaking almost unknown ground therefore, in tackling the phenomenon of oxygen electrode [illegible]. The subject of metal electrode [illegible], however, has been investigated by a number of workers, and a short resume of their theories will be given here. The experimental results obtained during this investigation, however, seem to show that oxygen electrode [illegible] is a phenomenon distinct, in many ways, from metal electrode [illegible], and possibly even from hydrogen electrode [illegible], as suggested by Newbery and Smith[79].

Billitzer[80] noticed the change in potential caused by movement of the electrolyte round a Hg electrode, in studying electrocapillary phenomena. Pionchon[81,82] found that if two Cu plates in water are connected through a sensitive galvanometer and the [illegible] allowed to become constant, on tapping the one plate the galvanometer shows a marked deflection.

He attributed this to the tapped plate losing copper ions more rapidly than the other. Newbery[83] observed the change of single potential with relative motion between electrode and electrolyte with electrodes of Fe, Ni, Co, Cu and Zn during overvoltage investigations.

Procopiu[84/87], however, was the first to undertake a detailed study of the phenomenon of metal electrode M.E.P., and he eventually proposed a theory depending on the disturbance of an ionic concentration gradient postulated to exist in the diffuse portion of the Helmholtz electrical double layer. Thushe identified his results with the well known electrokinetic potentials, and attempted to correlate his values of M.E.P. with Burton's[88] electrokinetic measurements, but not with complete success. His theory has, however, received support from other workers. Thus Bennewitz and Schultz[89], and Bennewitz and Bigalke[90] explain their results, obtained by scraping one of two silver electrodes in $AgNO_3$ with a movable diamond point, as due to the disturbance of the double layer of adsorbed ions at the metal liquid interface. Charnandarjan and Herwuschin[91,92] attribute their results to the same factors as give rise to electrokinetic potentials; Gheorghiu[93], and Fink and Linford[94] all find their results to be explainable on the basis of Procopiu's theory.

Another widely supported theory is that of "differential aeration" caused by motion. This was first proposed by Evans[72/74,95], and he has been supported by Müller and Konopicky[96], and from a slightly different standpoint by Koenig[97]. Very recently Kasper[98] has produced evidence in favour of Müller and Konopicky's idea of the mechanism of M.E.P. as opposed to the electrokinetic theory.

Mertz and Wellman[75] attempted an explanation

based on the MgO_2 theory of the oxygen electrode but found it incompatible with their own experimental results. Further and Walker[76] use their preferential adsorption theory to explain ... in very much the same way as Frumkin used the Helmholtz double layer to explain his results. The only apparent difference is that Further and Walker's theory allows for no double layer or ions against the electrode before arriving at the diffuse component of the Helmholtz double layer; also Further and Walker apparently postulate a concentration gradient extending considerably further into the solution than the diffuse component of the double layer is usually supposed to extend.

Whittum and Hunt[100] have applied their recently proposed theory of electromotive force[99] to the problem of ..., or, as they term it, electrokinetic potential. They propose what may be termed a modified double layer, in which the solution side consists of charged colloidal particles of the metal in the metal-liquid interface. Rapid rotation of the electrode forces the colloidal metal particles further out into the solution, where, in order to remain stable, they have to change their charge, either by accepting electrons from the metal or by adsorbing ions from the solution, or possibly by giving electrons to the metal or to ions in the solution. This exchange of electrons changes the potential.

Bowery and Smith[79] in the light of extensive work done recently on metal electrode ..., have put forward an oxidation-reduction theory, but found it quite inadequate to explain oxygen electrode ...

Material

The metals used were Pt, Pd, Os, Rh, Ru, Ir, ..., and Au in a number of different forms- bright

metal, oxidised metal, electrolytically deposited (black) metal and this black metal heated to give "greyed" electrodes. All the different forms of metal were used, as there is a decided difference of opinion among workers as to which is the form most satisfactory. For example, Richards[70] advised heavily platinised electrodes for the best results whereas Tartar and Wellman[75] apply only sufficient black to take the glint off the Pt and hold that bright Pt gives the better results.

Since it has been shown[67/69, 101] that gas electrodes attain equilibrium more rapidly when the metallic base is in the form of a thin film deposited on glass, or on a hollow carbon rod, most of the electrodes here described were plated on glass, though a few experiments were tried with metal sheetelectrodes. These metallised glass electrodes were used in the early years of this century by Cottrell[102], Luther and Brislee[55], Brislee[42], Westhaver[59] and Haber and Fleischmann[10]. Their use has recently been extended by Newbery[101], as a very cheap and durable form of metallic base for the hydrogen electrode.

The glass tubes to be metallised were 4-5 mm. external diameter, 12-14 cm. in length and sealed off at the one end. The sealed end was coated with metal for 20-30 mm., the thickness of the metallic film being of the order of 10^{-4} mm., as determined by a weighing method. In all cases the metals were plated on glass by dipping the glass tube into alcoholic salt solutions of the metals, and burning off in a bunsen flame. Contact with mercury inside the tube was made with a short Pt wire, which had been sealed through the end of the tube to be plated. The whole procedure has been described in detail by Newbery[101]. The

solution used for plating silver on glass was one of ammonic silver oxide in alcohol prepared as follows. Silver was precipitated from $AgNO_3$ with NaOH . The precipitate was washed, dissolved in as little ammonia (Sp. Gr. .88) as possible and the solution diluted with alcohol. The electrodes were made at once, and the excess solution was well diluted with water, and thrown down the sink, since the ammonic silver oxide, when dry possesses explosive properties.

The following are the details of the weighing method used in estimating the thickness of the metallic films. The only assumption made is that the densities of the films are the same as those of the respective massive metals.

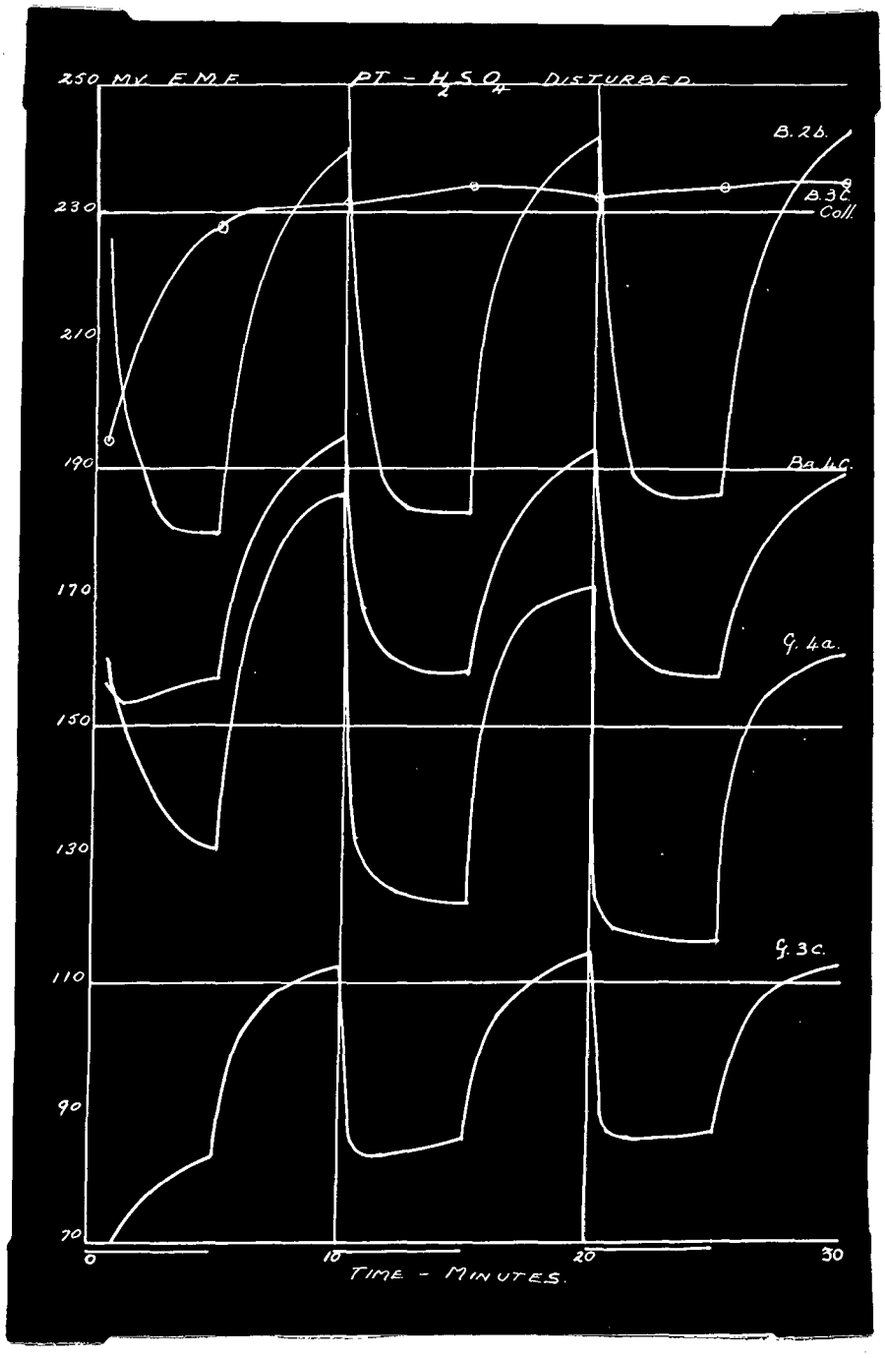
Small sample tubes 6 cms. long were sealed up at one end as in making the ordinary electrodes, but no Pt wire was sealed through. The tubes were then cleaned in hot NaOH, washed with H_2O and alcohol, dried and weighed. They were then heated and cooled several times and finally re-weighed. The heating hardly affected their weights at all. The metallic film was deposited as usual and the tubes weighed again. The weight of the metallic coats was determined, hence their volume and, on estimating the area of the surface, the average thickness of the film was calculated. This method, of course, only gives the average thickness since the film is likely to be thicker round the end of the tube, although rapid rotation during burning off minimises this to a large extent.
(See Table 1.)

The oxidised electrodes were made, where possible, by heating the bright metal to redness

TABLE I.

Metal	Wt. of glass tube.	Wt. tube + metal film.	Wt. metal film.	Density* of metal.	Vol. of film.	Area of surface.	Av. thickness of film.
Pt.	1.2244 gms.	1.2264 gms.	.0020 gms.	21.45 gms./cc.	.000093 c.c.	2.09 cm^2	3 10^{-5} cms.
Ir.	1.1534 "	1.1544 "	.0010 "	22.42 "	.000045 "	2.32 "	2 10^{-5} "
Pd.	1.1300 "	1.1336 "	.0036 "	11.64 "	.00031 "	3.18 "	1 10^{-4} "
Rh.	1.1145 "	1.1147 "	.0002 "	12.2 "	.000016 "	2.18 "	8 10^{-6} "
Ru.	1.0771 "	1.0782 "	.0011 "	12.32 "	.000082 "	2.61 "	3 10^{-5} "
Au.	1.0786 "	1.0833 "	.0047 "	19.3 "	.00024 "	2.90 "	8 10^{-5} "

* Values obtained from Mellor's "Inorganic & Theoretical Chemistry" vols. iii and xv.


250 MV. E.M.F.
Pt - H_2SO_4 DISTURBED.
B. 2b.
B. 3c.
Coll.
230
210
190
Ba. 4c.
170
G. 4a.
150
130
G. 3c.
110
90
70
0
10
20
30
TIME - MINUTES.

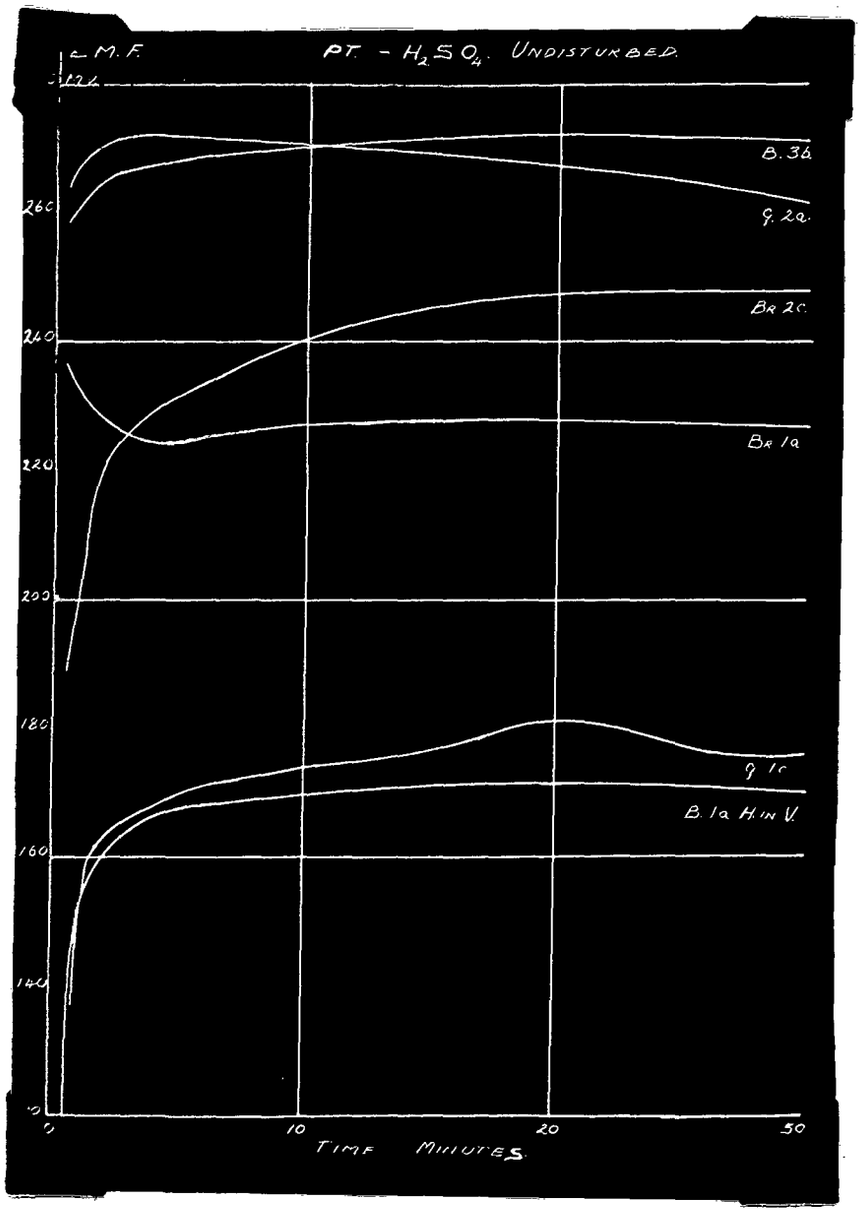
RESULTS.

PLATINUM.

This metal was used in the bright, black and grey forms. No visible oxidation took place during use or on heating to redness in the bunsen flame and cooling in air. Electrodes could usually be used immediately after electrolytic deposition of black metal without any untoward effects due to any hydrogen which might have been occluded during the process of deposition.

In H_2SO_4:-

Undisturbed electrolyte: The potential drift of bright Pt. electrodes in sulphuric acid is very irregular both in magnitude and direction. However, the electrodes usually settle down after 20 min. to give a fair constancy of approx. ± mv. Reproducibility is poor at 60 mv. A constancy of ± mv. works out as a potential drift of 12 mv. per hour which is approx. what Burman[15] reported for platinum in acid solution (5-10 mv. per hour). Continuous bubbling for the full 30 mins. gives a very similar curve to that given in a saturated solution. In the case of black Pt. the drift is nearly always in a more noble direction, and the constancy is about the same as for bright Pt. Reproducibility, however, is considerably better (10 mv.). Grey Pt. on the other hand is very irregular both in regard to the magnitude and the direction of potential drift, being considerably worse than bright Pt. in these respects. The reproducibility, too, is poor at 100 mv. Usually the grey electrodes are approx. 70 mv. less noble than black Pt. A black Pt. electrode heated in vacuo gave an initial potential approx. 100 mv. lower than ordinary platinum black, i.e. of the same order as the initial potential of grey platinum. In all cases the graphs of electrodes heated in vacuo are labelled H. in V.


E.M.F.
Pt. - H_2SO_4. Undisturbed.
1.226
B. 3a.
q. 2a.
Br 2c.
Br 1a
q 1c
B. 1a H in V.
260
240
220
200
180
160
140
0
10
20
30
Time Minutes.

ten minutes of each set of readings.

The figures that follow in the next section consist of a number of graphs, sufficient to show the general behaviour of each particular electrode - every experiment is not necessarily recorded in the graphs. Usually at least four different electrodes of each form of metal, black, bright, oxidised, and grey, were used at least twice in each electrolyte, both disturbed and undisturbed.

The nomenclature for these graphs is as follows. The numerals are simply a means of identifying which particular electrode is being used. The letters refer to the history of the electrode. The letter "a" refers to an electrode, which has been freshly heated and cooled, or plated, and used immediately. "b" refers to an electrode, which has been kept under distilled water for approximately 24 hours after first use. "c" refers to an electrode, which has been kept in air for approximately 24 hours after use. "d" refers to an electrode, which has been kept in oxygen for approximately 24 hours after use. The type of metal surface used is indicated as follows:-

G. = Grey metal, or, in the cases of Au and Ag, the H form.

Br.= Bright metal.

Ox.= Oxidised metal.

B. = Black metal, or, in the cases of Au and Ag, the R form.

Thus a graph designated 2t, G, 1, a., refers to electrode No.1 of the grey Pt electrodes, which has been used immediately after heating and cooling.

In obtaining the graphs for undisturbed electrolyte, E.M.F. readings were taken at the following time intervals:- 30 secs., 1 min., 3, 6, 10, 15, 25, 45 and 60 mins. For disturbed electrolyte the time intervals were:- 30 secs., 1 min., 2, 3, 5 min. and these were repeated each five minutes for the 30 mins.

The E.M.F. values shown in the graphs are all referred to the appropriate half cell, N Hg_2SO_4, N KCL or N HgO.

in the oxidising portion of the bunsen flame and cooling in air. The black electrodes were formed by electrolysing the aqueous solutions of the chlorides of the metals, using a bright metallised glass cathode, and an anode of the same metal where available. For Os and Ru black, a Pt wire anode was used, as massive pieces of these metals were not available. The table on the opposite page indicates the procedure which was followed in preparing the electrolytically blackened or roughened electrodes. (See Table 2).

The Os black was deposited on a base of bright Pt on glass, according to the directions of Weischede[103]. In the case of Ru , the anode solution was 4N. HCl, and was separated from the cathode compartment by an unglazed porcelain diaphragm. The cathode solution is first reduced to $RuCl_2$ and the colour changes from dark brown to green-blue, after which the Ru black is deposited. This procedure was that advocated by Lenchot and Schmid[104], and a similar method has recently been used by Godward and Wardlaw[105]. The deposition of Ir was attempted by Foerster's method[61], but the high current density required is not obtainable with metallised glass electrodes, so the resistance of the electrodes heats up the electrolyte too quickly. Weishover[59] also found great difficulty in iridising metallised glass electrodes. His method was tried, but gave very unsatisfactory deposits of a deep blue colour, which did not adhere well. The data subsequently given were obtained with these electrodes, but there appears to be no satisfactory method of depositing Ir black on metallised glass electrodes. The diagram opposite illustrates the potentiometric method of controlling the current

used in the deposition of Ag, Co, and Au, where low current densities were required. A and A' are moving contacts by means of which the current through the deposition cell and millimeter can be simply and accurately regulated.

Although air electrodes have been successfully used in titrations, they are, according tothe experience of Furman[15,16] and others, not as reliable as oxygen electrodes. Consequently, although a few preliminary experiments were tried with air instead of oxygen, the investigation as a whole was confined to oxygen electrodes. The original idea was that, should an electrode show good results in oxygen, it could be tried as an oxygen electrode later. No electrode, however, was sufficiently satisfactory in oxygen to warrant a trial in air. The oxygen used was obtained directly from an ordinary commercial cylinder, since French and Muelenberg[77] have found the use of carefully purified gas and metals to yield substantially the same results as those obtained with commercial materials. Richards[70] also used unpurified oxygen and obtained results reproducible to within one millivolt in specified solutions.

No thermostat was used, but the temperature during most of the investigation was 19° C ± 3 C$^{\circ}$. It was considered that a thermostat would be an unnecessary elaboration of apparatus, since the temperature coefficient of most electrodes is very small, and the irregular potential drift would mask any very slight change of potential due to small temperature variations.

The electrode vessels used were of the type illustrated in the Transactions of the Electrochemical Society Vol. 64, p. 99, 1933. A somewhat similar

type of electrode was used by Richards[70] in preference to the platinobrend type, because the latter took longer to give a sharp reproducible potential, in the case of the hydrogen electrode. Each electrode was used in the three solutions N/1 H_2SO_4, N/1 KCl & N/1 NaOH. A Tinsley Vernier potentiometer capable of reading to 0.01 millivolts was used for electrode potential measurements, although the experimental values were only read to the nearest millivolt.

The reference electrodes used were such as to eliminate any boundary potential difference:

Hg. Hg_2SO_4 N/1 H_2SO_4 for acid electrolyte.

Hg. Hg_2Cl_2 N/1 KCl for salt electrolyte.

Hg. HgO N/1 NaOH for alkaline electrolyte.

The theoretical E.M.F. of the oxygen electrode in N/1 H_2SO_4, N/1 KCl and N/1 NaOH measured against the appropriate half cell was calculated as follows:-

In H_2SO_4 The E.M.F. of the cell

H_2 / Pt / N/1 H_2SO_4/ N Hydrogen electrode

is, E = .058 log. H = .058 log. .510 = -.017 volts,

since the degree of dissociation of the H_2SO_4 = .51

The E.M.F. of the cell Hg./ Hg_2SO_4 / N H_2SO_4 / N H. electrode is .676 volts at 18°C as determined by Lamb[106].

Therefore the E.M.F. of the cell

Hg / Hg_2SO_4 / N H_2SO_4 / N H_2SO_4 / H_2 Pt.

is .675-.

= .693 volts.

The theoretical E.M.F. of the O_2-H_2 cell being 1.23 volts, the E.M.F. of the cell:-

O_2 Pt / N H_2SO_4 / N H_2SO_4 / H_2SO_4 / Hg.

is (1.23 - .693)volts

= .537 volts at 18°C.

In NaOh

The E.M.F. of the cell

Hg / HgO / N NaOH, H_2 at = .9265 volts at 18°C,

according to the work of Lewis and Randall[107].

From this value the theoretical E.M.F. of the cell

O, at / N NaOH, H_2, Pt,

is 1.226 - .9265 volts = .0957 v. at 18°C.

In KCl:

Since KCl is a neutral salt, the E.M.F. of the cell

H_2 at / N KCl / N H_2 electrode is (.059 log 10^{-7})

= - 0.406 volts.

Taking the normal calomel electrode as .286 volts at 18°C

on the hydrogen scale, the E.M.F. of the cell

Hg / Hg_2Cl_2 / N KCl / N KOH / H_2 Pt

is .286 - (-.406)

= .689 volts at 18°C.

Therefore the E.M.F. of the cell

H_2 Pt / N KOH / N KCl / Hg_2Cl_2 Hg

should be (1.226 - .689) volts

= .541 volts at 18°C.

These figures, .689 volts in H_2SO_4, .606 volts in NaOH, and .541 volts in KCl, were the actual experimental values that would have been given by a truly reversible oxygen electrode. In comparing the values given in the different electrolytes, however, the E.M.F. of the cell was calculated to refer to a hydrogen electrode in the same electrolyte, i.e. in the case of acid the normal electrolyte .83 volts were added to the experimental values, and in the case of alkaline electrolyte .93 volts. All the values were then comparable. The hydrogen electrode to which the potentials of the respective cells were referred, could not always be one using the same base metal as that used in the corresponding oxygen electrode, since the results of Bowlby[101] show that some, at any rate, of these metals do not give the theoretical potential when used as hydrogen electrodes. Moreover, the object of this investigation was to enquire into the mechanism of the oxygen, not of the hydrogen,

electrode, and consequently all the values of the O_2-H_2 cell should be taken as referring to a theoretical hydrogen electrode in the same electrolyte. In order to check the theoretical calculations, direct measurements of the O_2-H_2 cell were made in all three electrolytes using platinised platinum electrodes. The values so obtained, i.e. by measuring an oxygen electrode versus a hydrogen electrode in the same electrolyte, checked with the calculated values within experimental error in all three electrolytes.

In studying the oxygen electrode without the presence of M.A.P., i.e. in undisturbed electrolyte, the solution was saturated before use by bubbling oxygen gas through for 30-40 minutes. The electrode was then placed in the quiescent electrolyte, and readings taken from that moment.

In the case of measurements taken in disturbed electrolyte, when M.A.P. was present, the electrolyte was not saturated beforehand, but bubbling was commenced at the moment that the electrode was immersed, and potentiometer readings taken from the same time. The rate of bubbling of oxygen was kept as near as possible to three bubbles per second throughout the investigation. The general procedure for runs in the study of M.A.P. was as follows. The bubbling of oxygen was continued forfive minutes and then shut off, the electrolyte remaining quiet for another five minutes, when bubbling was re-commenced. Alternate five minute periods of bubbling and quiet were continued for thirty minutes or, in some cases, longer.

In every case the electrode was completely immersed in the electrolyte. This was advocated by French and Kahlenberg[77] to obtain the greatest gas effect. Richards[70] states that the surface of the electrode should be kept as constant as possible, i.e. that the electrode should

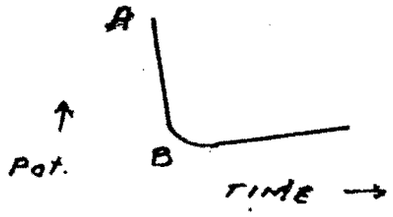
be totally inverted, he therefore advises against the Hildebrand type of electrode vessel.

In all cases the previous history of the electrodes was carefully noted and electrodes with various different histories were tested. Some were made and used immediately, some kept in air before use. After use, the electrodes were sometimes kept under distilled water, sometimes in air, and sometimes in oxygen, for approximately 24 hours before using again. Thus the behaviour of each metal was investigated under varying conditions, and the effect of these conditions on the potential could be observed.

It was found that Ru and Ru, as well as Os, oxidised very easily on heating, and consequently, on attempting to prey the black metal, an ordinary oxidised electrode resulted. It was therefore decided to heat the black form of these metals in vacuo, in attempt to obtain the grey form. A hard glass tube was fitted by means of a ground glass joint to a Toepler pump, and the pressure, after initially being considerably reduced with a water pump, was reduced to approximately 10^{-3} mm. with the Toepler pump. The electrodes were heated to 400°C and cooled in this tube and under the above pressure. The temperature was measured on a small thermometer lying alongside the electrode. On raising the temperature above 450°C approximately, the hard glass tube began to soften and collapse under the external pressure. The interesting results given by Os, Ru and Ru, suggested that the other metals might give similar results, and consequently Rt, Rh, Ir, Pd and Au were also heated in vacuo, in the re-planed or black form, except in the case of Ir, Rh and Au, whose roughened forms do not give as reproducible potentials as the bright metals.

In the following discussion of results, the e.m.f.

i. formed positive, which increases the potential in the direction of the theoretical oxygen electrode, i.e. in the more noble direction. In a number of cases the change du. to bubbling reverses in direction during the five periods, i.e. at first the potential falls (becomes less noble) and then rises as the bubbling continues, or vice versa. In view of this, the ..... is taken to be the maximum change observed, in the initial direction of the change.



The above shows the shape of a typical potential-time curve over five minutes of bubbling. The ..... here is the potential drop fro... -b.

Curves when ..... i in action are shown by double lines on the horizontal axis of the graphs.

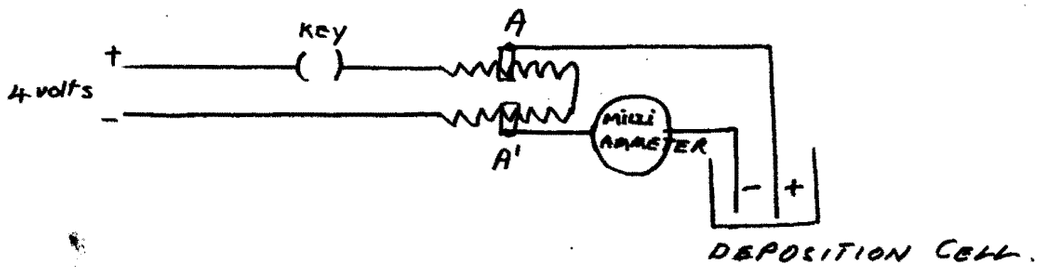
In studying ..... coil electrodes were collodionized i.e. they were given several liberal coatings of collodion, and used after the solvent has evaporated off. The collodion coating is, of course, porous so that the electrolyte still reaches the electrode. The ordinary potential of the electrode, as at first by Fredenhagen and Wahlenberg, is unaffected by the collodion. This procedure was adopted in an endeavour to eliminate the change of potential due to the mechanical disturbance of the electrolyte caused by bubbling.

For the purpose of this investigation the REPRODUCIBILITY of an electrode is taken as the difference in millivolts between the highest and lowest values observed, after thirty minutes in the electrolyte, with a number of similar electrodes, during their repeated use in the specified solution. The CONSTANCY of an electrode implies the ..... in ..... in millivolts, and, to put mild strain, during the last

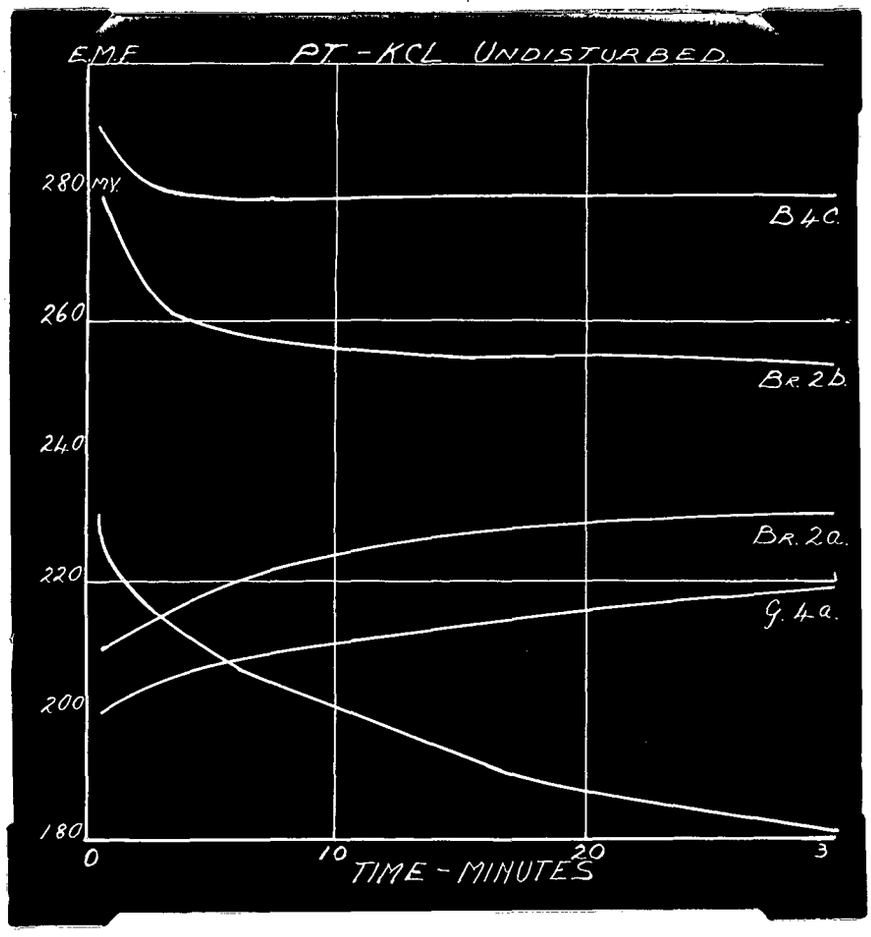
Table 4.

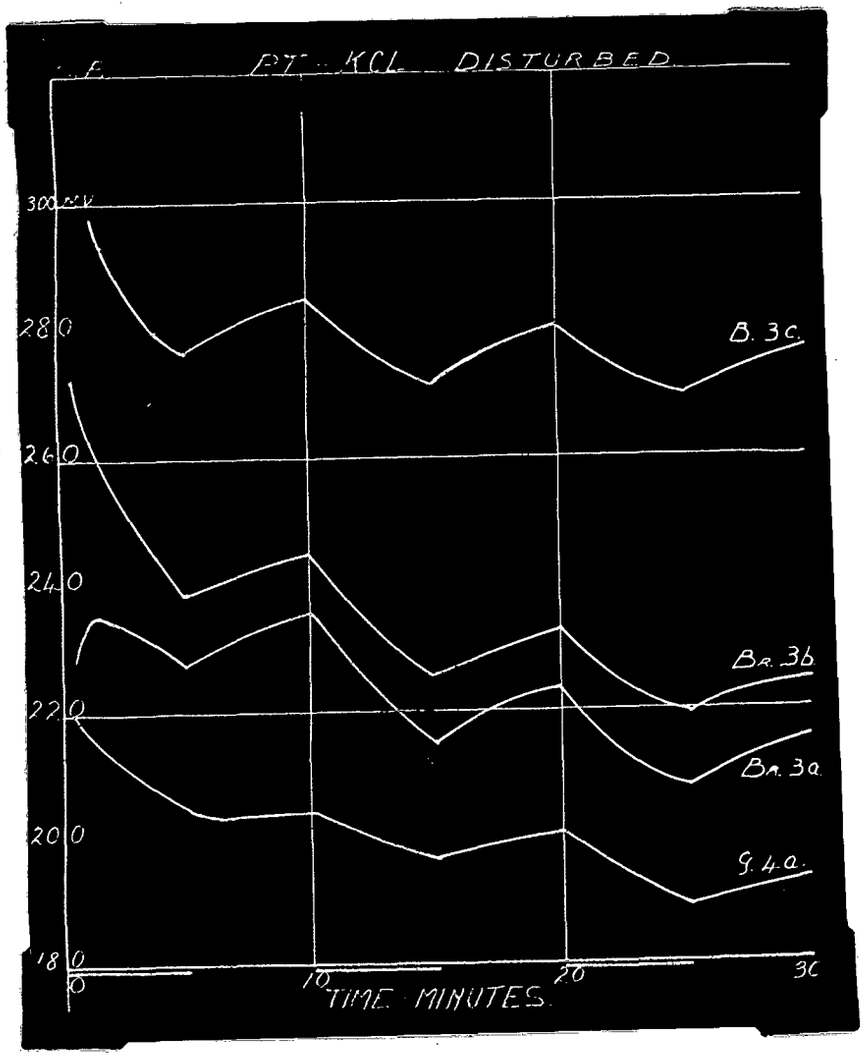
Metal	Electrolyte	Current or voltage applied	Cathode area
Pt	$S_2Pt(OH)_6$	4 volts for 30 secs.	2 sq. cms.
Pd	$S_2Pd(OH)_6$	4 volts for 30 secs.	"
Au	$K_2Au(OH)_6$	4 volts for 10 secs.	"
Ag	cyanide plating bath	10 milliamps. for 30 sec.	"
Rh	K_3RhCl_6	4 volts for 30 secs.	"
Os	$K_2OsO_4Cl_2$	4 milliamps. for 15 min.	"
Ru	K_2RuCl_5 in N. HCl.	150 milliamps.	"

METHOD of CURRENT CONTROL.



Disturbed Electrolyte: Here reproducibility is poor for all three forms of metal. The curves, however, are all regular except during the first period of bubbling, when L.E.P. may be either positive or negative. For the bright electrodes it is always negative, but grey electrodes kept in air and freshly blacked electrodes give a positive L.E.P. at first, changing in the second period of bubbling to negative. All the electrodes give a regular negative L.E.P. by the second period of bubbling. The L.E.P. of black electrodes increases slightly with time but the values given by grey and bright electrodes decrease with time. The general trend of the curves is away from the theoretical oxygen potential, but again freshly blacked Pt. and grey Pt. kept in air are exceptional - they tend to drift towards the theoretical oxygen potential. The average L.E.P. of black Pt. is -50 mv., of grey -40 mv. and of bright -27 mv. Whereas keeping under distilled water reduces the L.E.P. of bright electrodes, it increases that of black by 50%. Keeping in air nearly halves the L.E.P. of grey electrodes. Again grey electrodes are less noble than black (approx. 100 mv.). On one bright Pt electrode the rate of bubbling was accidentally allowed to slow down, and it was found that the potential started to rise while still bubbling. On increasing the rate to 3 bubbles per sec., the potential fell again as usual. This is referred to in discussing the results. Among the black Pt L.E.P. curves is one which is quite different from all the rest. That is the one given by a collodionised electrode - L.E.P. is almost eliminated but a small positive effect of 2 - 3 mv. still persists. Nevertheless, an L.E.P. of -50 mv. has been reduced to +2 mv. simply by covering the electrode with a porous, non-conducting coating. The graphs of collodionised electrodes are labelled "coll.".


E.M.F
PT - KCL UNDISTURBED.
280 MV.
260
240
220
200
180
B 4 C.
BR. 2 b.
BR. 2 a.
G. 4 a.
0
10
20
3
TIME - MINUTES


E.
PT - KCL DISTURBED.
300 MV
280
260
240
220
200
180
B. 3 c.
BR. 3 b
BR. 3 a
G. 4 a.
0
10
20
30
TIME MINUTES.

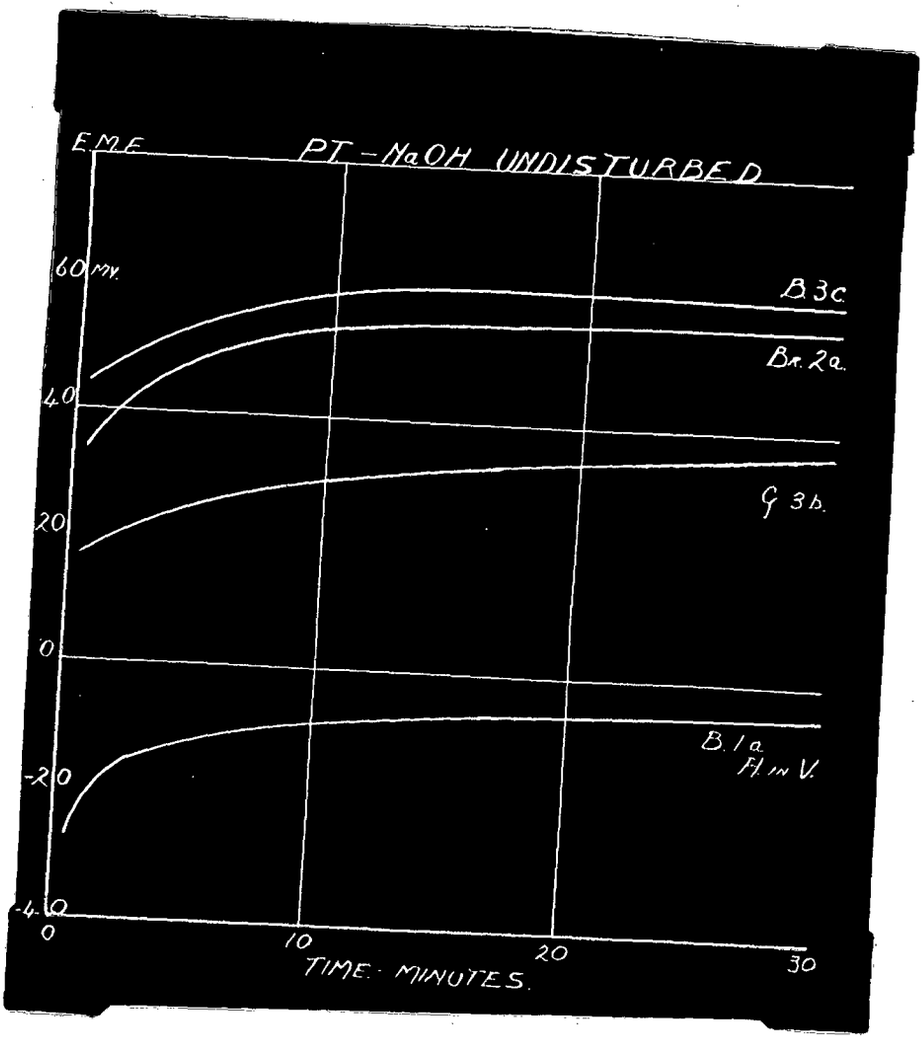
In KCl.:-

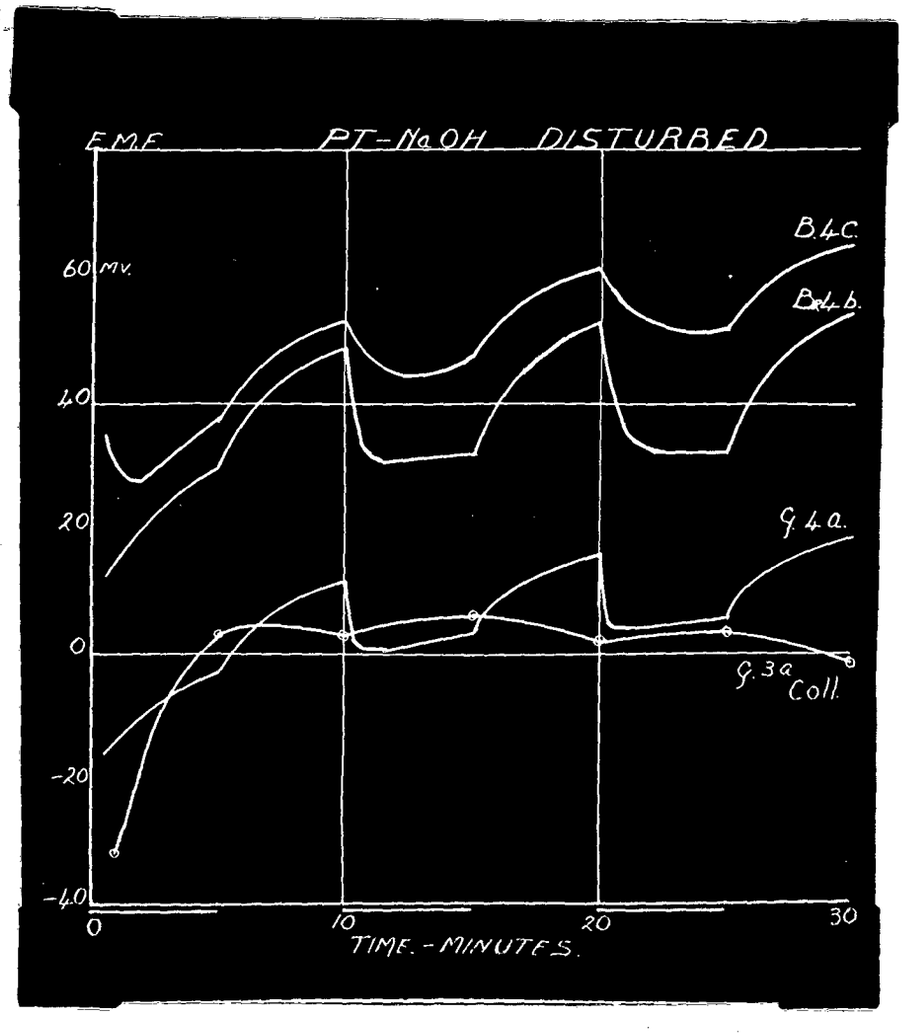
Undisturbed electrolyte. In all forms of the metal potential drift may occur in both positive and negative directions. Whenever, for the sake of brevity, the terms positive and negative are used in this connection, they are to be taken to mean "towards a more noble potential" and "towards a less noble potential" respectively. Constancy is approx. 2 mv. throughout, although black electrodes usually give the lowest values. Reproducibility for black and bright electrodes is 50mv. The grey electrodes, on an average, give a potential 90 mv. lower than the black, their reproducibility being approx. 90 mv. On heating a black Pt electrode in vacuo it gave an initial potential approx. 250 mv. below that of the average black electrode. After 30mins. the potential was still over 100 mv. lower than the usual potential of black Pt at the corresponding time.

Disturbed Electrolyte: In this electrolyte the E.M.F. curves are quite different from those in sulphuric acid. The trend of all the curves is in the less noble direction. During the first period of bubbling E.M.F. may be positive or negative. The average value for the E.M.F. is approx. -13 mv. for all forms of metal. The previous history of the electrodes has, in this case, little effect on the E.M.F. Reproducibility for the black and bright forms is 50 mv., but for the grey is over 100 mv. Grey electrodes give final potential values approx. 70 mv. below the black.

In NaOH:

Undisturbed Electrolyte: The curves in all cases are very regular and the same in general shape. Potential drift is always in a positive direction. Constancy is good throughout at 1 - 2 mv. and reproducibility fair at 20 - 30 mv. Grey electrodes are slightly less noble than black (approx. 30 mv.). A black electrode heated in vacuo gave an initial potential 70 mv. lower than the ordinary air-treated black electrodes.

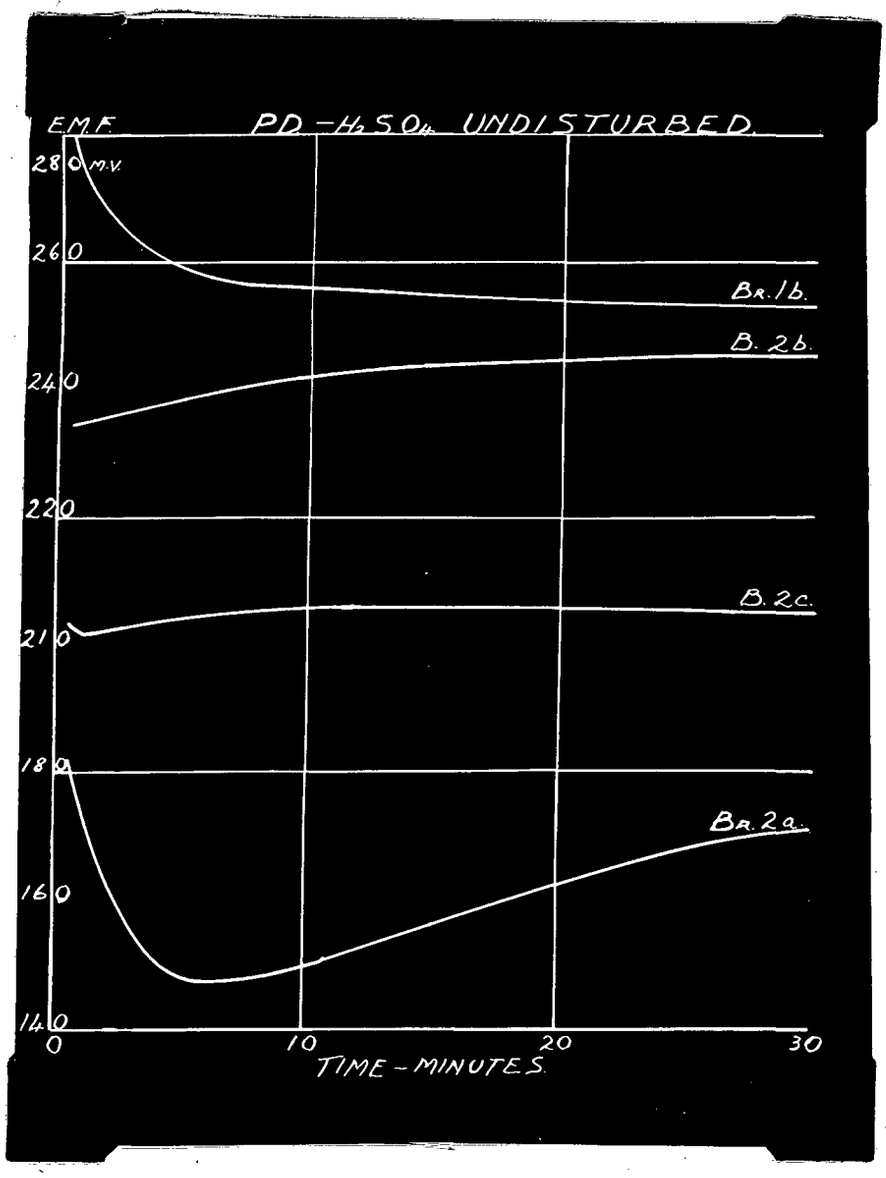

E.M.F.
Pt - NaOH UNDISTURBED
60 mv.
40
20
0
-20
-40
B.3c.
Br. 2a.
G 3b.
B. 1a.
H. in V.
0
10
20
30
TIME. MINUTES.

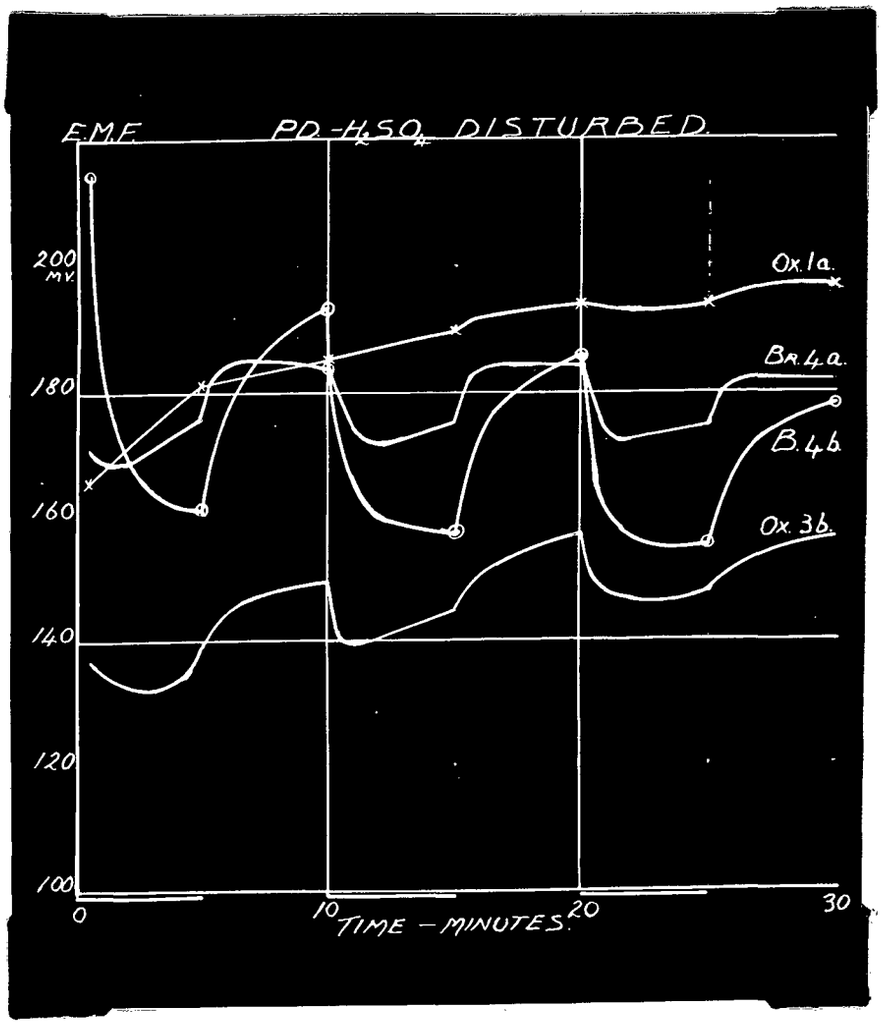

E.M.F.
Pt - NaOH DISTURBED
60 mv.
40
20
0
-20
-40
B.4c.
Br.4.b.
G. 4a.
G. 3a.
Coll.
0
10
20
30
TIME. - MINUTES.

Disturbed Electrolyte: Again all curves are similar and regular, although the first period of bubbling usually gives a positive E.M.F. Average E.M.F's are:- black and grey, -10 mv. and bright -19 mv. Previous history has no marked effect on E.M.F. With the bright electrodes E.M.F. increases with time, but the E.M.F of the other forms remains more or less constant. All the curves have a general trend in the more noble direction. Grey electrodes are approx. 30 mv. lower than the black. It was observed that in all cases the potential, which at first falls on bubbling, begins to rise towards the end of the five minutes. A collodionised grey Pt electrode gave an E.M.F. of +2 mv. - another big change from -10 mv.

Palladium.

This metal was used in the bright, oxidised and black forms. The oxidised form is a purplish-blue in colour, and has lost the bright polish of the bright form. On heating a black electrode it oxidises readily and an ordinary oxidised electrode results, consequently Pd was one of the metals heated in vacuo in an effort to grey the black form. The black remained apparently unchanged by this treatment. In all cases Pd black electrodes must be kept in air or oxygen for approx. 24 hours before being used as oxygen electrodes, in order to allow dissolved hydrogen to oxidise. Since they have stood for 24 hours in the air, these electrodes are denoted, in the graphs, with the letter "A", having not been previously used as oxygen electrodes. Oxidised electrodes, in all electrolytes, usually show potentials 20 - 40 mv. lower than bright ones. In no case could any difference be noted in the appearance of the electrode after it had been used.


EMF
Pd-H2SO4 UNDISTURBED.
280 M.V.
260
240
220
210
180
160
140
Br. 1b.
B. 2b.
B. 2c.
Br. 2a.
0
10
20
30
TIME - MINUTES.

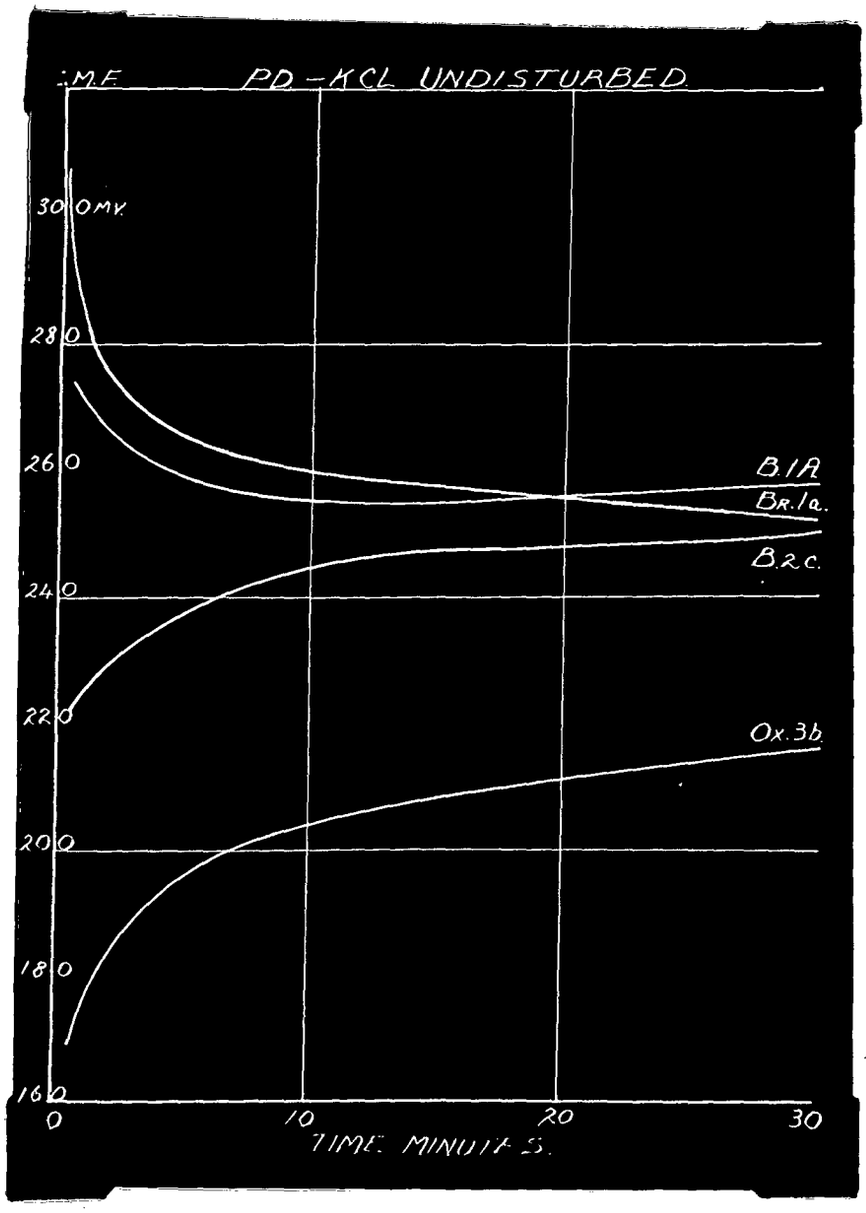

EMF
Pd-H2SO4 DISTURBED.
200 MV.
180
160
140
120
100
Ox. 1a.
Br. 4a.
B. 4b.
Ox. 3b.
0
10
20
30
TIME - MINUTES.

In H_2SO_4:

Undisturbed electrolyte: The potential drift of bright electrodes varies a lot. It may be either towards or away from the theoretical oxygen potential and the direction of drift may reverse during the 30 mins. The constancy varies from 6 mv. for freshly made electrodes to 3 mv. or less for ones which have been kept under distilled water after use. The black electrodes are much more regular, once the dissolved hydrogen has been eliminated, and the constancy is excellent at 0 - 1 mv. Reproducibility for both forms, however, is very poor. Continuous bubbling for the full 30 mins. gave a curve analogous to those given in electrolyte saturated with oxygen.

Black electrodes heated in vacuo started at a potential of -.09 volts referred to the normal Hg_2SO_4 electrode, whereas the average potential of the ordinary black electrodes is approx. .210 volts positive to the normal Hg_2SO_4 electrode. After 30 mins. the potential of the heated in vacuo electrodes rose to +.03 volts and one of the electrodes, after standing in air for 23 hours, gave a potential only 5 mv. more positive. This was assumed to be due to the Pd not being rapidly oxidised at ordinary temperatures. In order to test this, an electrode was heated and cooled in air to obtain a visible oxide coating. On immersion in the electrolyte, the oxidised electrode immediately gave a potential of .18 volts referred to the normal Hg_2SO_4 electrode, that is, the usual potential of visibly oxidised electrodes.

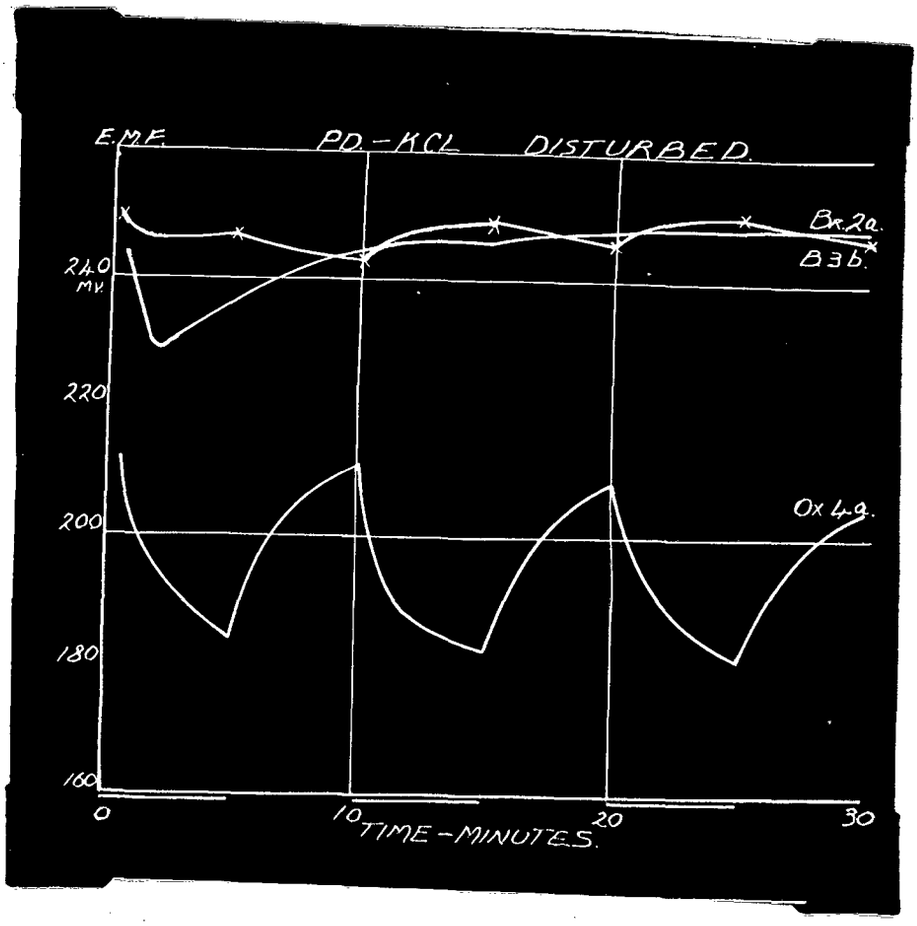
Disturbed Electrolyte: Black electrodes give a large M.E.P. of -24 mv.; whereas bright and oxidised electrodes average -10 mv. The previous history of electrodes has little effect on the M.E.P., but one or two oxidised electrodes were found which gave very low positive values.

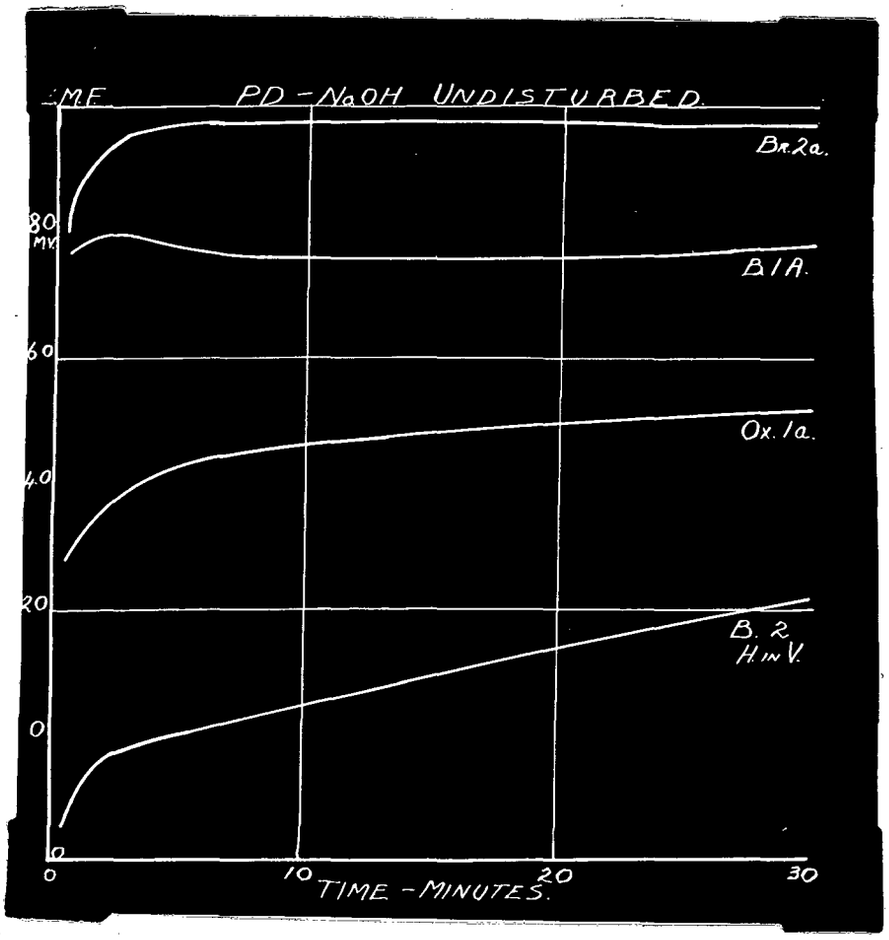

:ME PD-KCL UNDISTURBED
30 OMH
28 0
26 0
24 0
22 0
20 0
18 0
16 0
B.1A
Br.1a.
B.2c.
Ox.3b
0
10
20
30
TIME MINUTES.

This may be due to a thick porous coating of oxide acting as the corrosion coating does in other cases, by preventing mechanical disturbance of the solution immediately around the electrode. Reproducibility is very poor in all cases. The general trend of the curves may be in either direction, but it is never a very decided trend in any case. The first period of bubbling usually follows the second and third periods as regards the sign of e.m.f. With all forms the E.M.F, in general, decreases slightly with time.

In KCl:

Undisturbed electrolyte: In this electrolyte Pd black electrodes and the bright electrodes to a somewhat lesser extent, give extraordinary reproducible results. In eight experiments using three different black electrodes with various histories, the potentials all lay within a compass of 15 mv. after 10 mins. in the solution. After 30 mins. the reproducibility was 12 mv. The constancy was obviously therefore very good as well. If such reproducibility can always be relied on it would enable pH determinations to be made to within .2 pH units around the neutral point. Oxidised electrodes give a very much worse reproducibility - 30 mv. The constancy for freshly oxidised electrodes is good but after keeping in air or under distilled water it deteriorates to 3 - 4 mv. Black and oxidised electrodes drift towards the theoretical oxygen potential, but bright Pd. may drift either towards or away from it. A black electrode heated in vacuo gave an initial potential 240 mv. below the usual initial potential of black electrodes, but rose steadily throughout the 30 mins., at the end of which period it gave a potential still 160 mv. below the usual final potential.

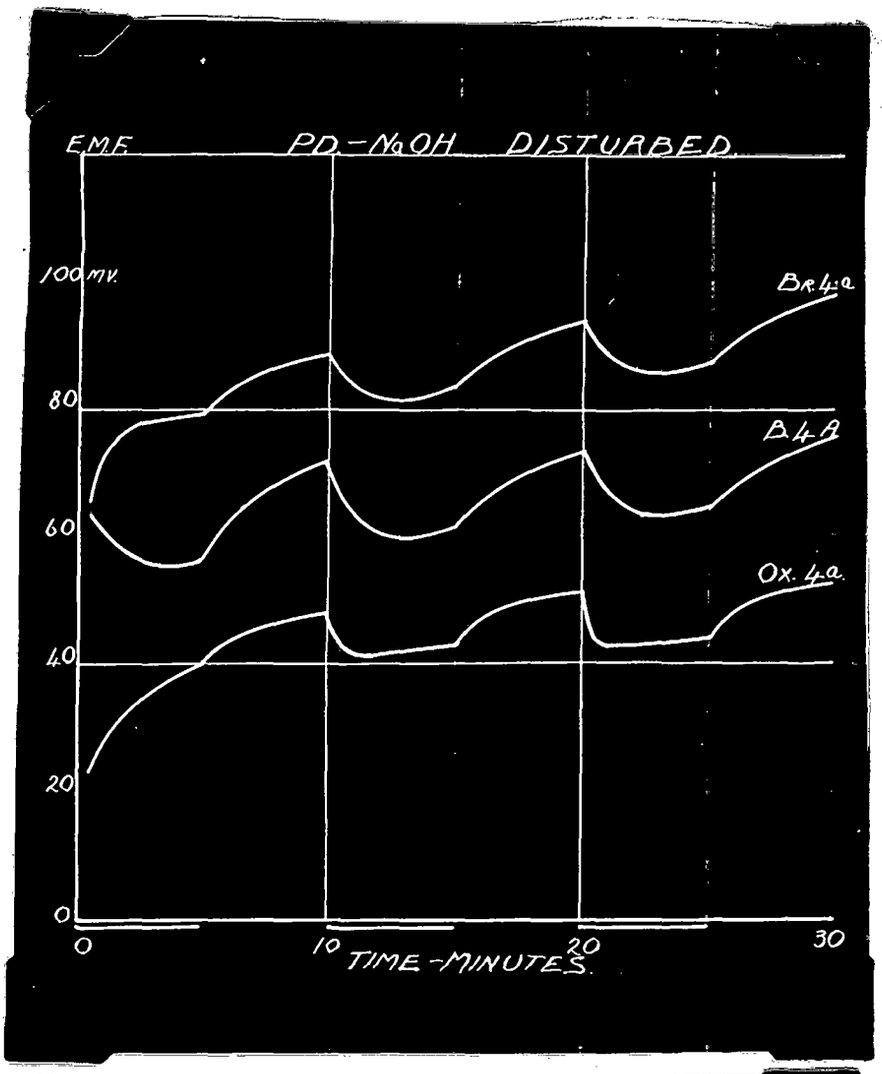

E.M.F.
PD. - KCL DISTURBED.
Br.2a.
B3b.
240 MV.
220
200
180
160
Ox 4a.
0
10
20
30
TIME - MINUTES.

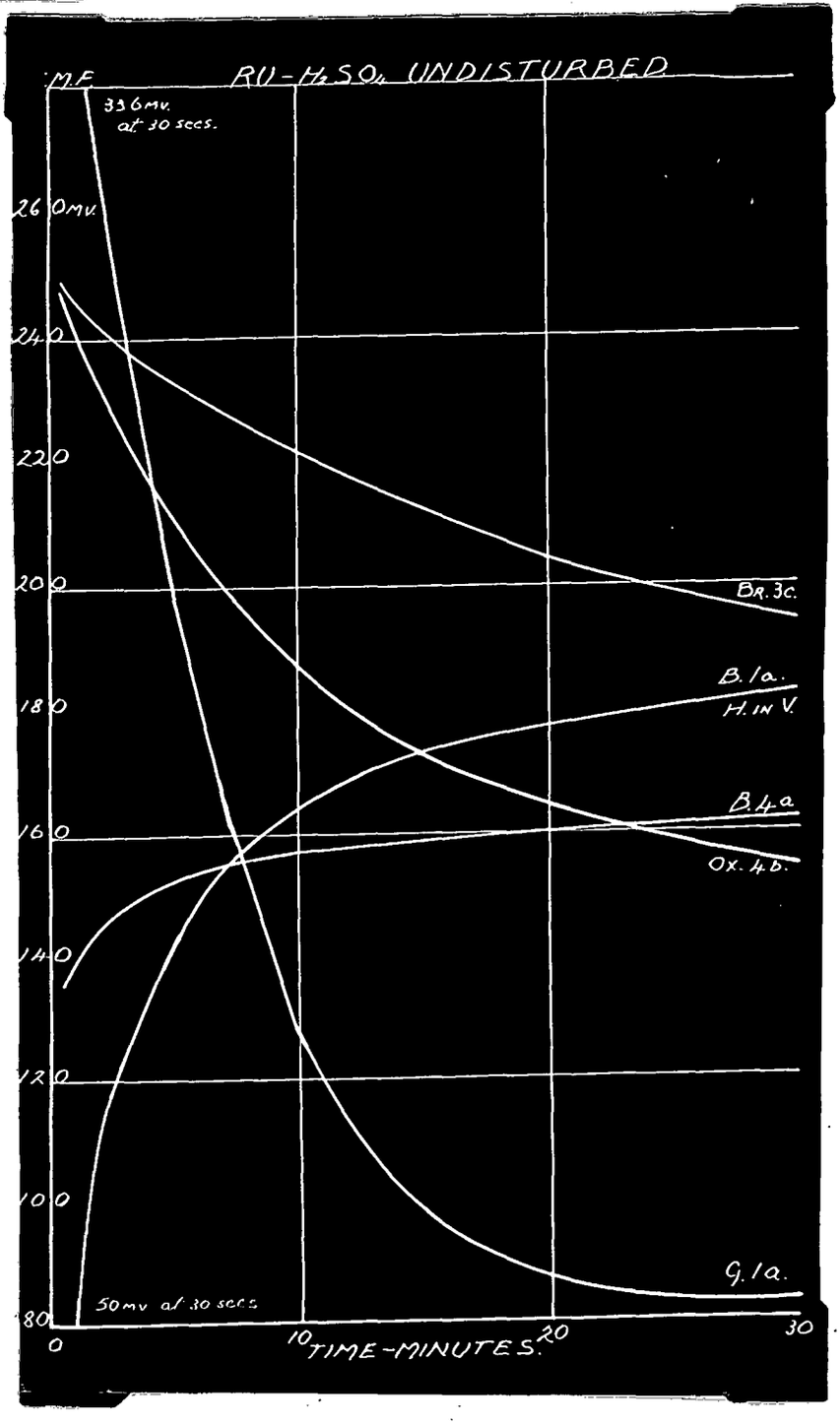

E.M.F.
PD - NaOH UNDISTURBED.
Br.2a.
B1A.
Ox. 1a.
B. 2 H in V.
80 MV.
60
40
20
0
0
10
20
30
TIME - MINUTES.

Disturbed electrolyte: In most cases the first period of bubbling shows a negative E.M.F. and in the case of oxidised Pd the negative E.M.F. continues during the second and third periods. In the case of bright and black Pd, however, the E.M.F. is positive - only low values but quite definitely positive. For black electrodes the average was +4 mv. and for bright +1.5 mv. The oxidised electrodes average -19 mv. It is extraordinary to find such a difference with the same metal in the same solution. The oxide coating is evidently not preventing mechanical disturbance of the electrolyte immediately round the electrode in this case, as was suggested for some cases of oxidised Pd. in sulphuric acid. Reproducibility is best for the bright electrodes, approx. 20 mv. - the black and oxidised electrodes give 30 - 40 mv. The general trend of the curves is slightly in a positive direction for black and bright Pd, but in the negative direction for the oxidised electrodes.

In NaOH:

Undisturbed Electrolyte: Constancy is very good for all forms of metal and the curves are regular with a positive drift in the case of bright and oxidised electrodes. In the case of black electrodes the drift is in both positive and negative directions, even with the same electrode during the 30 min. use. The magnitude of the drift, however, is very small. Reproducibility is poor for black and bright electrodes, 40 - 60 mv., but good for the oxidised electrodes, 10 mv. Heating a black electrode in vacuo had very much less effect on the initial potential in this electrolyte - it lowered it by approx. 80 mv., and after 30 mins. it was only 50 mv. lower than the usual final potential of black electrodes. Considering that the reproducibility for black electrodes in this solution is 40 - 60 mv., the discrepancy after 30 mins. is not very appreciable.


EMF
PD - NaOH DISTURBED
100 MV.
80
60
40
20
0
Br. 4a
B. 4A
Ox. 4a.
0
10
20
30
TIME - MINUTES.


EMF
RU - H2SO4 UNDISTURBED
33.6 MV. at 30 secs.
260 MV.
240
220
200
180
160
140
120
100
80
50 mv at 30 secs
Br. 3c.
B. 1a.
H. IN V.
B. 4a
Ox. 4b.
G. 1a.
0
10
20
30
TIME - MINUTES.

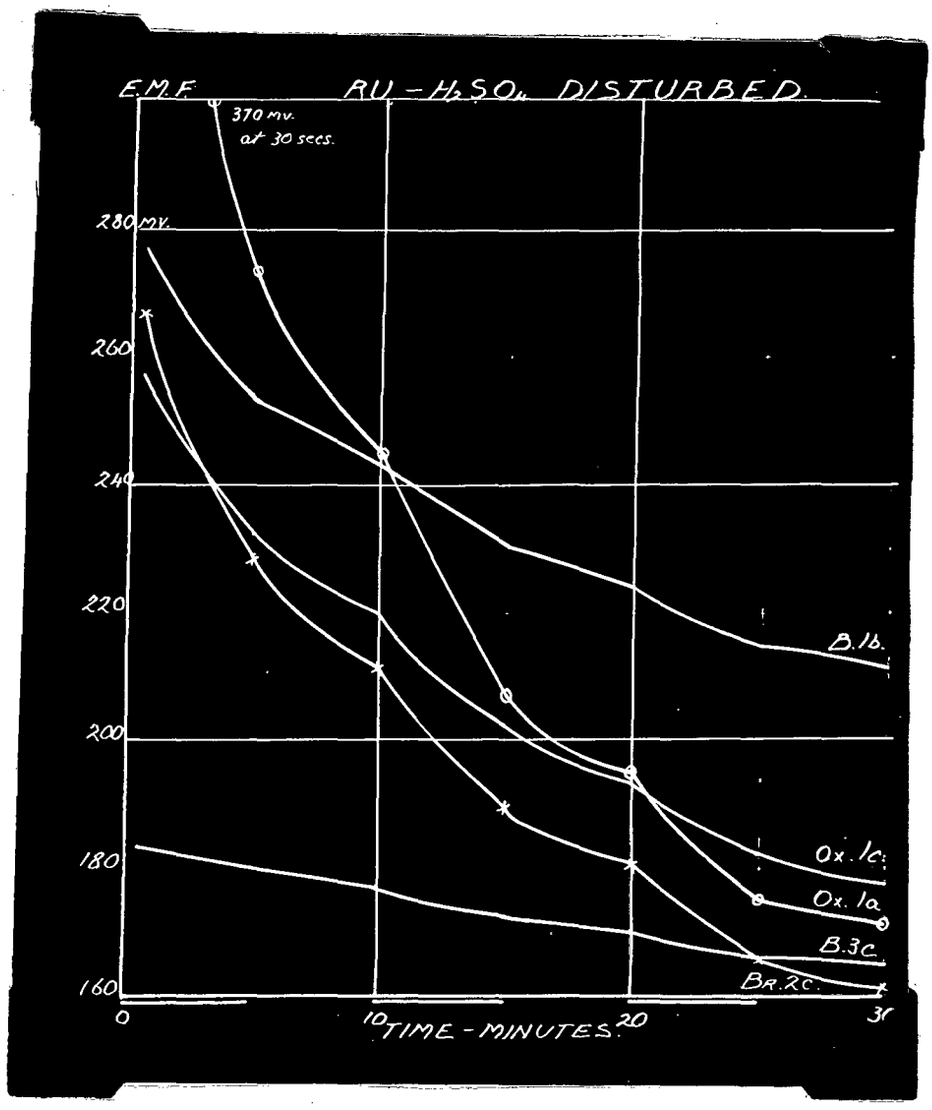
Disturbed electrolyte: The general trend of all the curves is in the more noble direction. The first period of bubbling for the black electrodes is regular, but for bright and oxidised electrodes the e.m.f. is positive during the first period. Average e.m.f's are:- -7 mv. for bright, -6 mv. for oxidised and -11 mv. for black electrodes. Fresh electrodes usually give highest e.m.f. and the values seem to decrease with time for black electrodes, but to increase with time for bright or oxidised electrodes. Reproducibility is about the same as for oxygen saturated electrolyte.

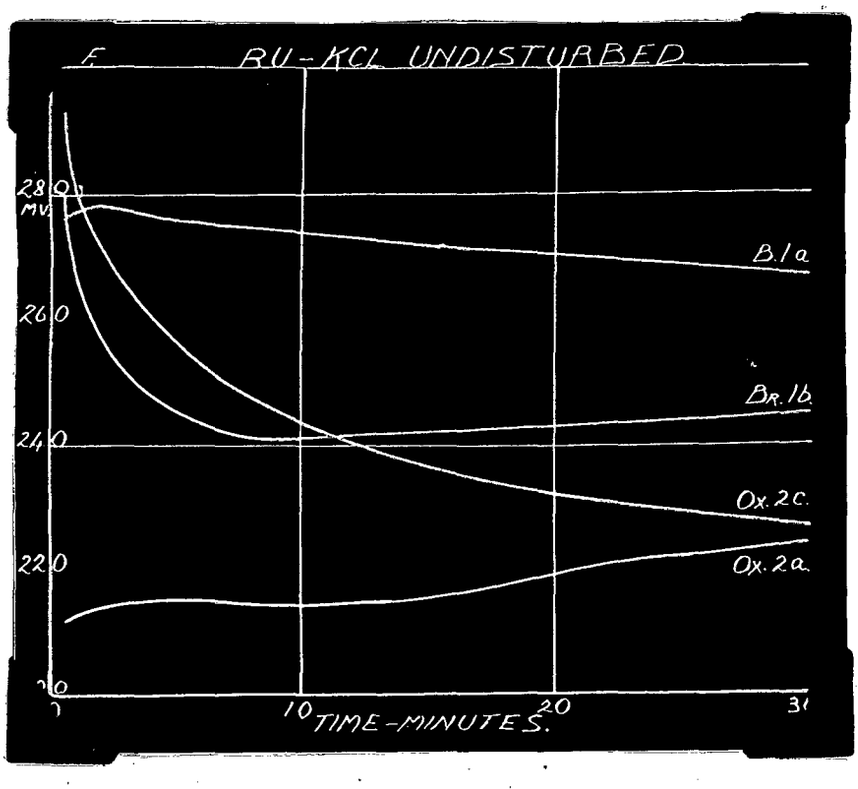
RUTHENIUM.

The three forms of Ru used were:- bright, oxidised and black. The black electrodes were heated in vacuo as they oxidised when heated in air. The oxidised Ru electrodes are a golden colour with still a considerable degree of polish on the surface. In a few cases, by very careful heating, an electrode was greyed without any obvious oxidation. Exposure to air for 5 - 6 hours after electro-deposition of Ru was usually sufficient to eliminate the effect of dissolved hydrogen on the electrode potential. These electrodes are still fresh and their history is referred to with the letter "a" in the graphs. The appearance of the metal is unchanged after use as an oxygen electrode.

In H_2SO_4:

Undisturbed Electrolyte: Reproducibility for all forms of metal is poor - approx. 40 mv. - and so is the constancy exc pt in the case of black electrodes, which have an average constancy of 2 mv. The few grey electrodes have a particularly poor constancy and are still falling rapidly after 30 mins. These grey electrodes start at the highest potential and finally reach the lowest potential of all the forms of Ru used, before becoming more or less constant.


E.M.F.
RU - H_2SO_4 DISTURBED.
370 mv. at 30 secs.
280 MV.
260
240
220
200
180
160
B.1b.
Ox. 1c.
Ox. 1a.
B.3c.
Br. 2c.
0
10
TIME - MINUTES.
20
30

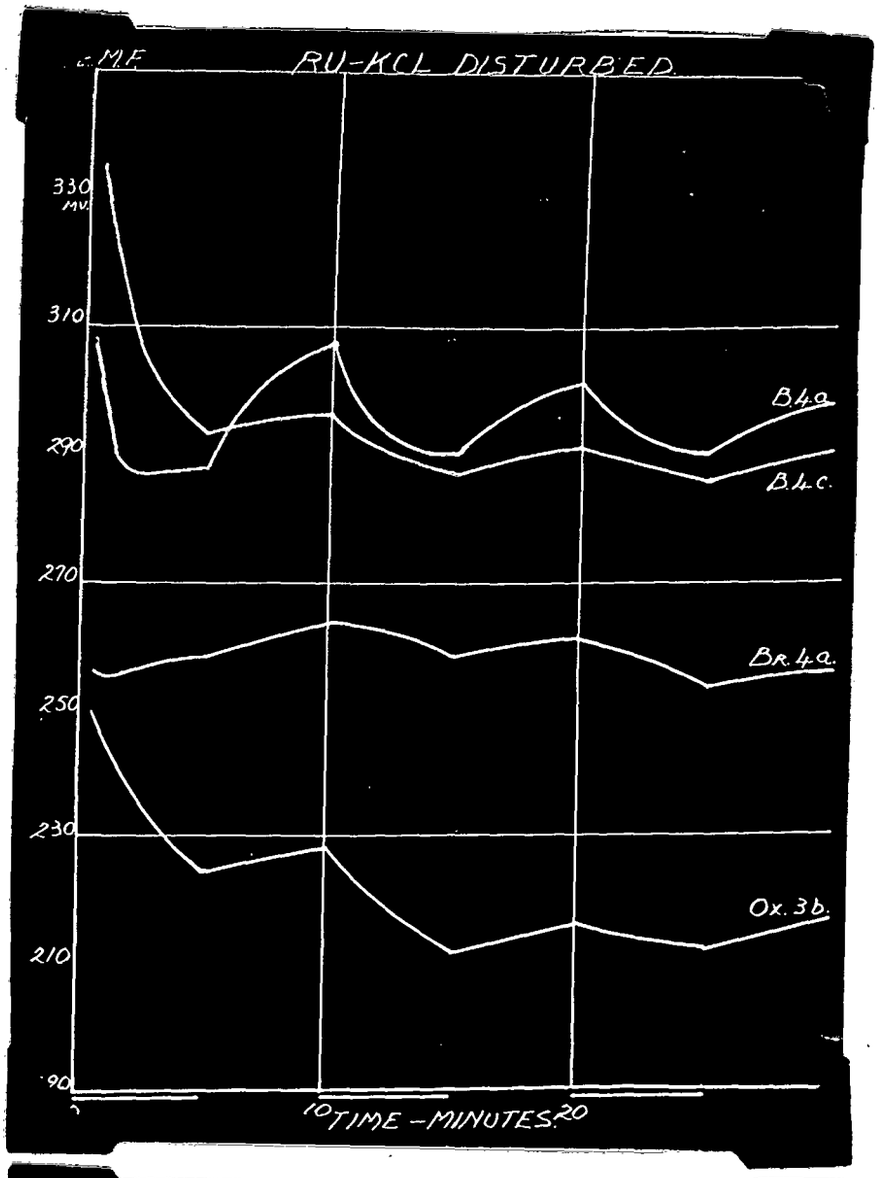

E
RU - KCl UNDISTURBED
280 MV.
260
240
220
200
B.1a
Br. 1b.
Ox. 2c.
Ox. 2a.
0
10
TIME - MINUTES.
20
30

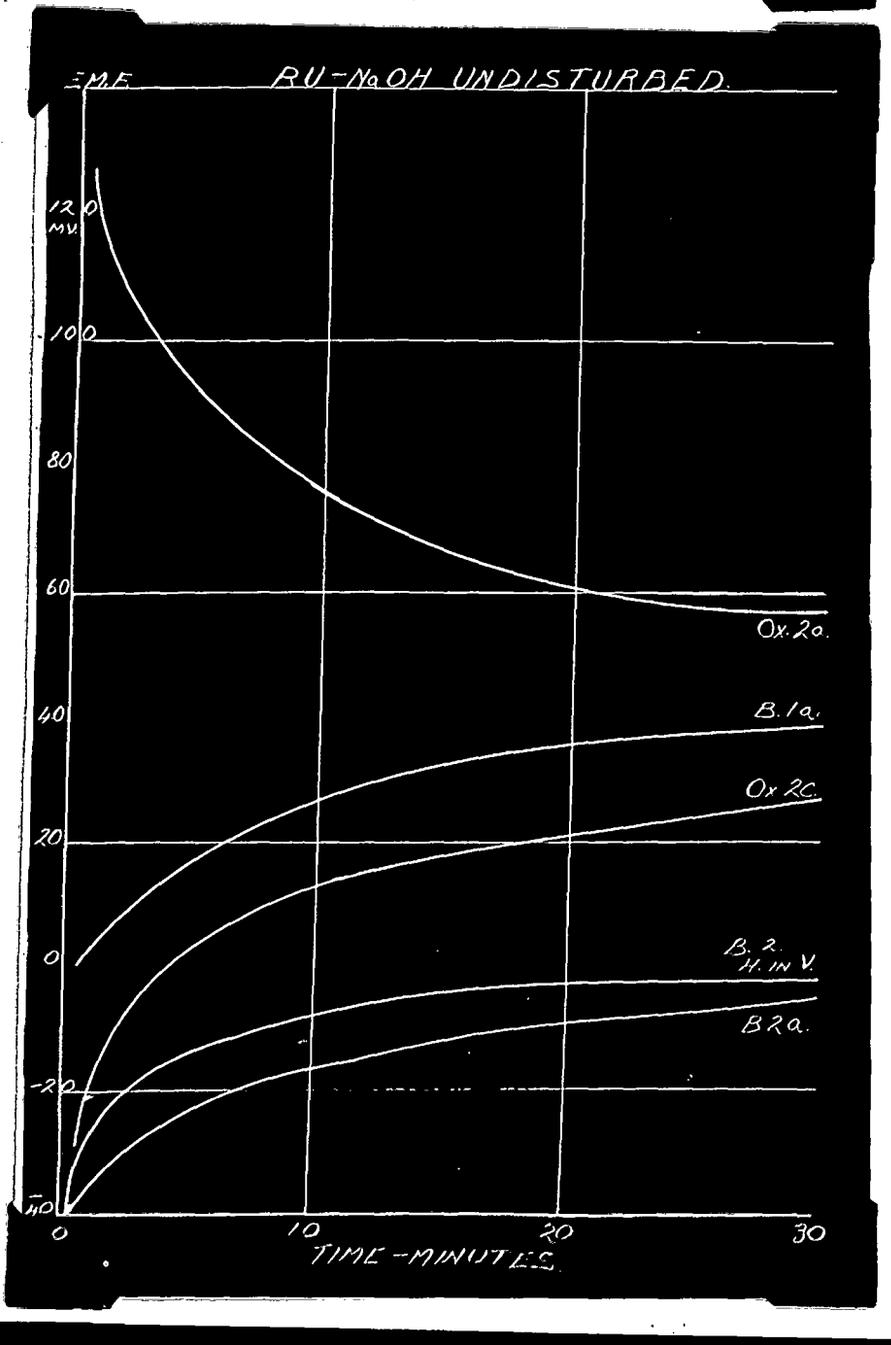
The potential of the bright, oxidised and grey electrodes drifts away from the theoretical oxygen potential, whilst that of the black may drift slightly in either direction. Freshly made electrodes usually give lower potentials than the ones which have been used previously. Black electrodes, heated in vacuo, give initial potentials approx. 100 mv. below those given by the ordinary black electrodes. By the end of 30 mins., however, they have risen to the corresponding potential given by the air-treated black electrodes. The potential of grey electrodes after 30 mins. in the oxygen saturated solution have fallen to approx. the same potential as that given initially by a black electrode heated in vacuo. The oxidised electrodes give a potential 30 - 70 mv. lower than the bright.

Disturbed Electrolyte: The E.M.F.. curves here consist almost of a series of straight lines. The first period of bubbling is always quite regular. The general trend of all the curves is very definitely in the negative direction. The negative trend is least in the case of black electrodes. The potentials of freshly made bright and oxidised electrodes fall more quickly than those of electrodes with other histories. Here oxidised electrodes give almost the same values as bright electrodes. E.M.F. decreases with time in all cases; the average values are:- bright and oxidised -15 mv., black -5 mv. These, of course, are not the maximum values since the potential falls steadily throughout the 5 min. periods of bubbling without approaching any minimum. The reproducibility is very poor, 90 mv., for black electrodes but improves for bright and oxidised electrodes.

In KCl:

Undisturbed Electrolyte: Reproducibility for oxidised and bright electrodes is poor, 40 - 60 mv., but for black electrodes is good at 15 mv. Potential drift, for all forms, may be in either a positive or negative direction. Constancy


E.M.F
RU-KCL DISTURBED.
330 MV.
310
290
270
250
230
210
190
B.4a.
B.4c.
Br.4a.
Ox.3b.
10
TIME-MINUTES.
20

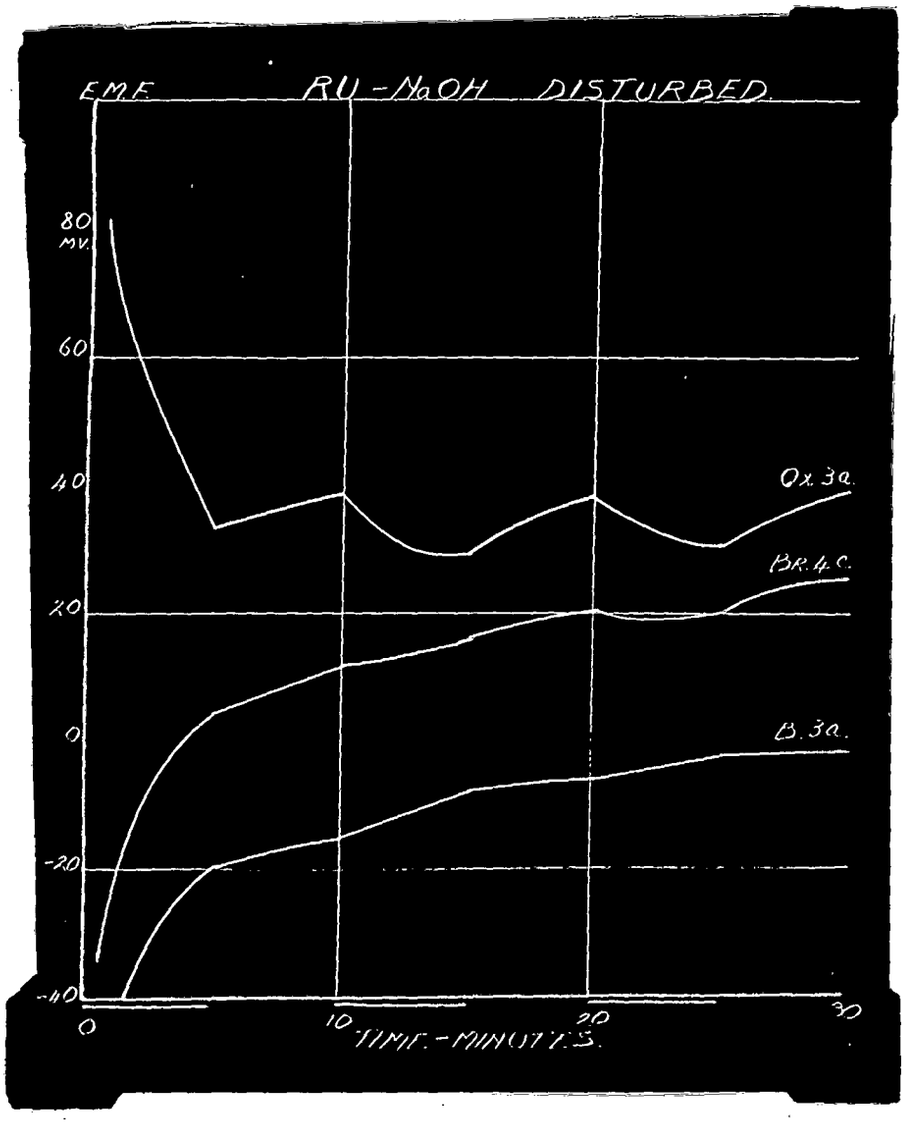

E.M.F
RU-NaOH UNDISTURBED.
120 MV.
100
80
60
40
20
0
-20
-40
Ox.2a.
B.1a.
Ox 2c.
B.2. H. IN V.
B2a.
0
10
20
30
TIME-MINUTES.

is good for black electrodes, 1 - 2 mv., but varies considerably with bright and oxidised electrodes, averaging 3 - 4 mv. Oxidised electrodes are 30 - 60 mv. lower than bright ones. On heating a black electrode in vacuo it showed an initial potential of .05 volts compared with the usual initial potential of .28 volts for black electrodes. The potential rises rapidly, however, to the potential of the air-treated black electrodes.

Disturbed Electrolyte: The general trend of all the curves is in a negative direction, but it is not as decided as is the case for Ru in sulphuric acid. Average M.E.P. values are, for black and bright electrodes, -9 mv., and for oxidised -15 mv. The first period of bubbling is usually regular but in a few cases is positive. In the case of one oxidised electrode the positive M.E.P. continued through the second and third periods although it became smaller. This same electrode, on being used again, having stood for 23 hours under distilled water, gave a perfectly ordinary curve with the usual negative M.E.P. Freshly made electrodes usually give highest values of M.E.P. Reproducibility is approx. 15 mv. for oxidised electrodes and for black and bright 40-50 mv. Oxidised electrodes give oxygen potentials 30 mv. lower than bright electrodes. M.E.P. decreases with time.

In NaOH:

Undisturbed Electrolyte: Potential drift in the case of oxidised electrodes is sometimes positive and sometimes negative, whereas with black and bright electrodes it is nearly always positive. Constancy is approx. the same for all forms (4 mv.) and reproducibility is poor in all cases, black electrodes being the best with a reproducibility of 40 mv. Oxidised and bright electrodes give almost the same oxygen potential within the limits of reproducibility.


EMF
RU-NaOH DISTURBED.
80
MV.
60
40
20
0
-20
-40
Ox. 3a.
BR. 4c.
B. 3a.
0
10
20
30
TIME-MINUTES.

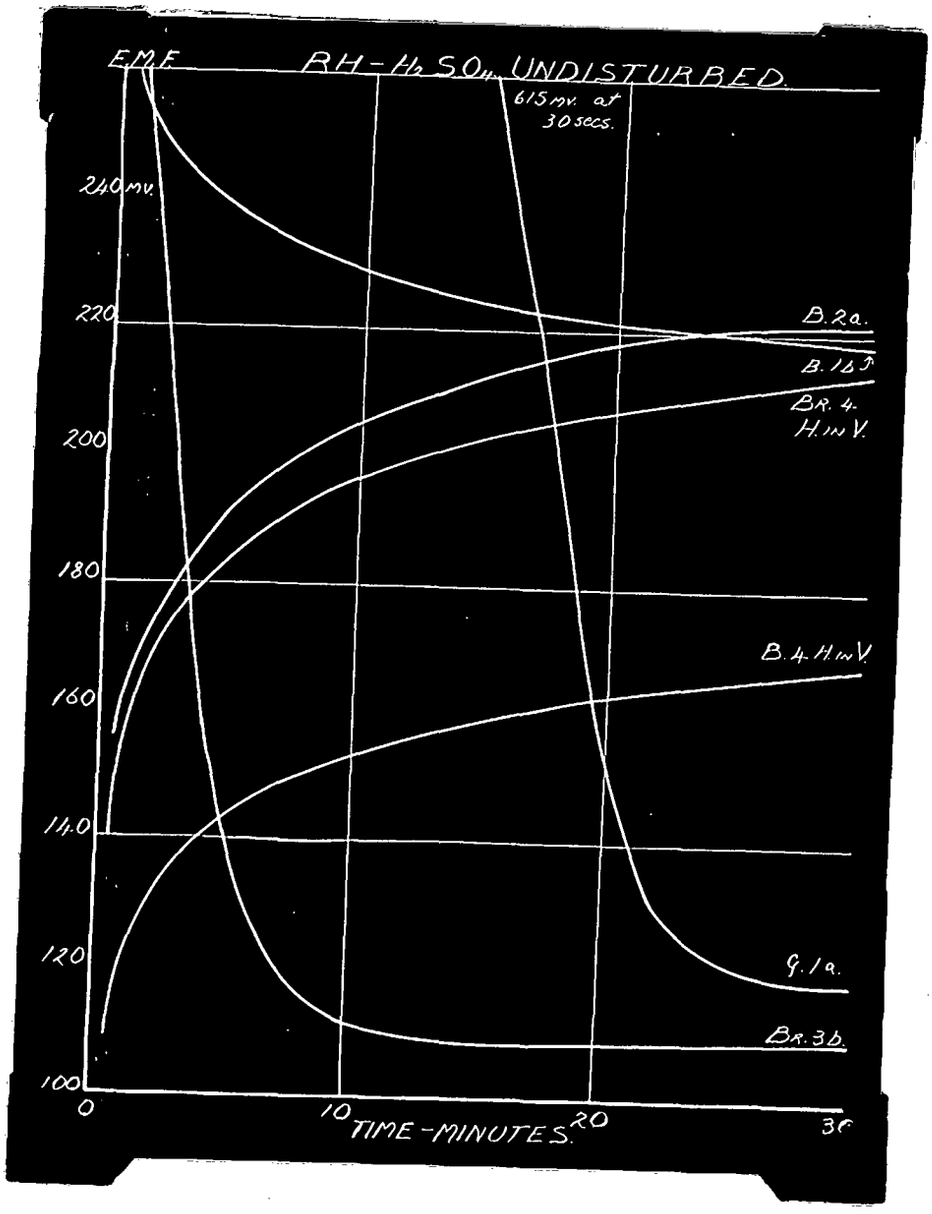
A black electrode after heating and cooling in vacuo and using immediately gave a curve identical in all respects with the usual black electrode curve.

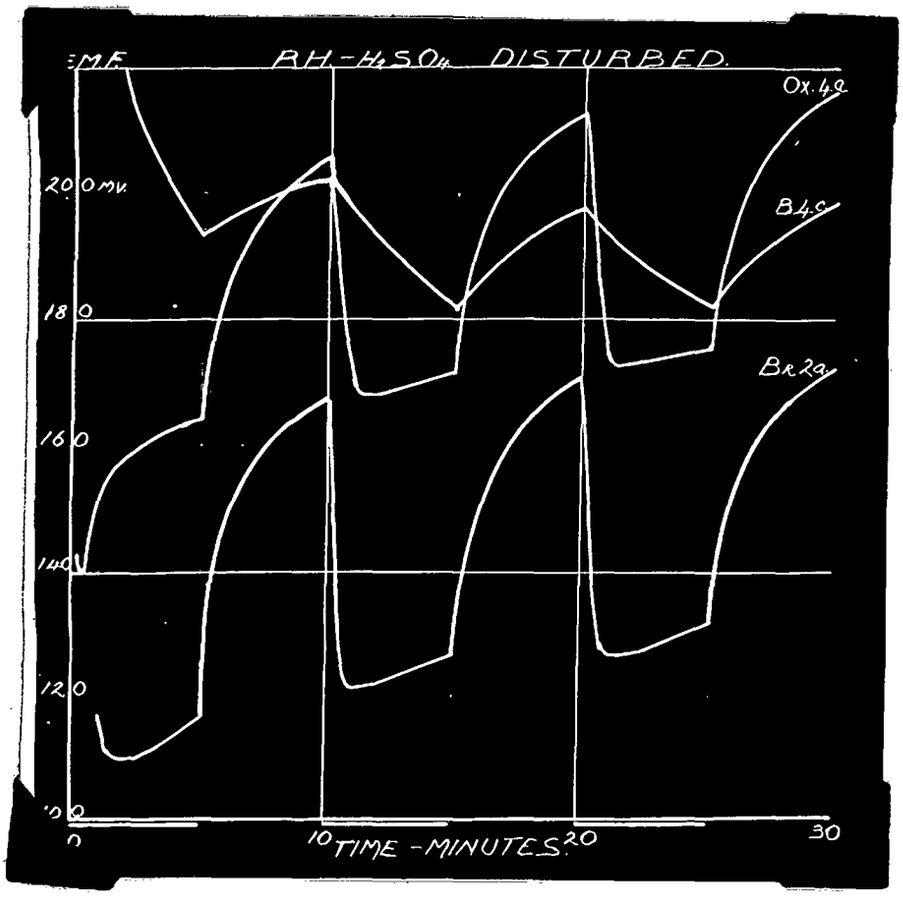
Disturbed Electrolyte: The black electrode E.E.F. curves are almost identical in shape with the curves of black electrodes in oxygen saturated electrolyte - bubbling has very little effect on the potential and the positive value of E.E.F. decreases rapidly with time just as black electrodes in quiescent electrolyte become constant with time. Freshly made oxidised and bright electrodes usually show a negative E.E.F. during all periods of bubbling, but electrodes with other histories usually begin with a positive E.E.F. which always becomes negative by the third period of bubbling. E.E.F., in all cases, changes rapidly with time. Reproducibility is 30 - 40 mv. for all three types of metal. Bright and oxidised electrodes give a E.E.F. of -4 to -5 mv. and black of +4mv.

RHODIUM

This metal was used in the bright, oxidised, black and grey forms, since the electrode could be turned grey at a temperature at which no visible oxidation took place.

It was not always obvious whether visible oxide coatings had been built up or not, since in some cases very light bluish patches appeared after heating, which may or may not have been oxidised - the bright and oxidised electrodes behave very similarly, however, and when only one form is illustrated, the other may be taken to be of the same type. Usually the oxidised Rh electrodes are a grey-blue colour and retain a considerable amount of the polish of bright electrodes. Some bright electrodes, on heating to redness in the bunsen flame, refuse to oxidise visibly, but assume a matt finish, which slightly dulls the usually highly polished surface given by ordinary bright electrodes.


EMF
RH-H2SO4 UNDISTURBED.
615 mv. at 30 secs.
240 mv.
220
200
180
160
140
120
100
0
10
20
30
TIME-MINUTES.
B.2a.
B.1b
BR. 4. H in V.
B.4 H in V.
9.1a.
BR.3b.


EMF
RH-H2SO4 DISTURBED.
Ox.4a
B4c
BR2a
200 mv
180
160
140
120
100
0
10
20
30
TIME-MINUTES.

This change in the finish of the electrode surface may indicate a change in the crystal structure of the metal, but apparently it does not greatly affect the oxygen electrode's properties.

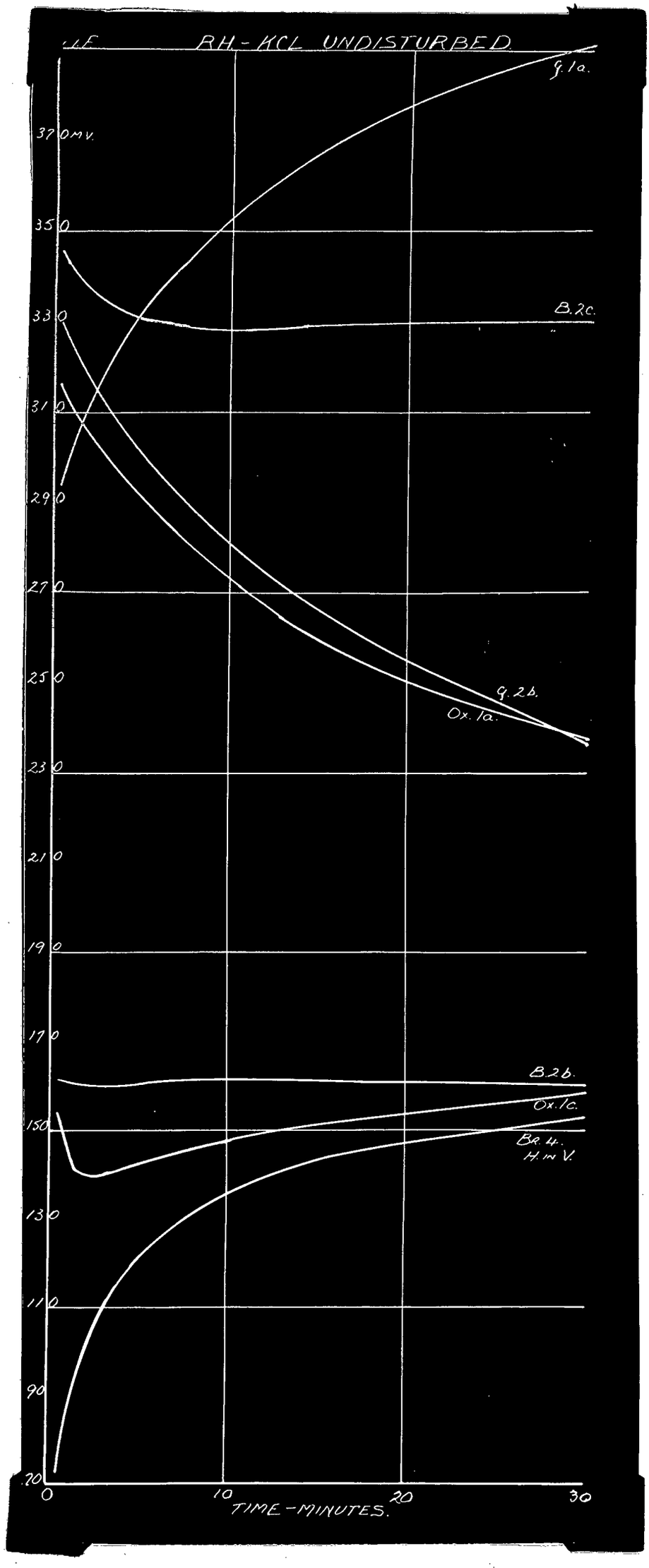
The electro-deposited metal in most cases showed no disposition to register the hydrogen potential, even when used immediately after electrodeposition and washing. The grey electrodes are definitely a lighter colour than the black, but they do not go as light a grey as ~~rt~~ black do. All the electrodes were apparently unchanged in external appearance after use.

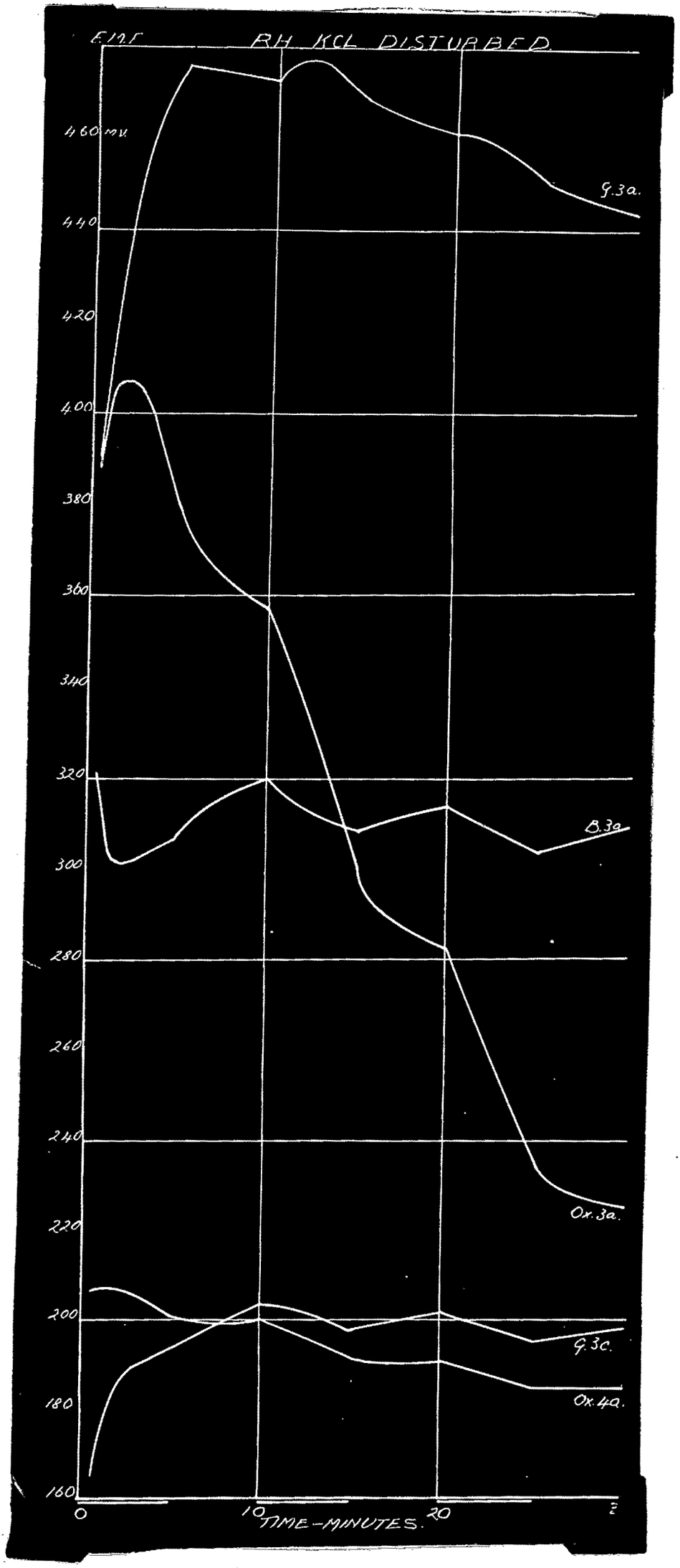
In H_2SO_4:

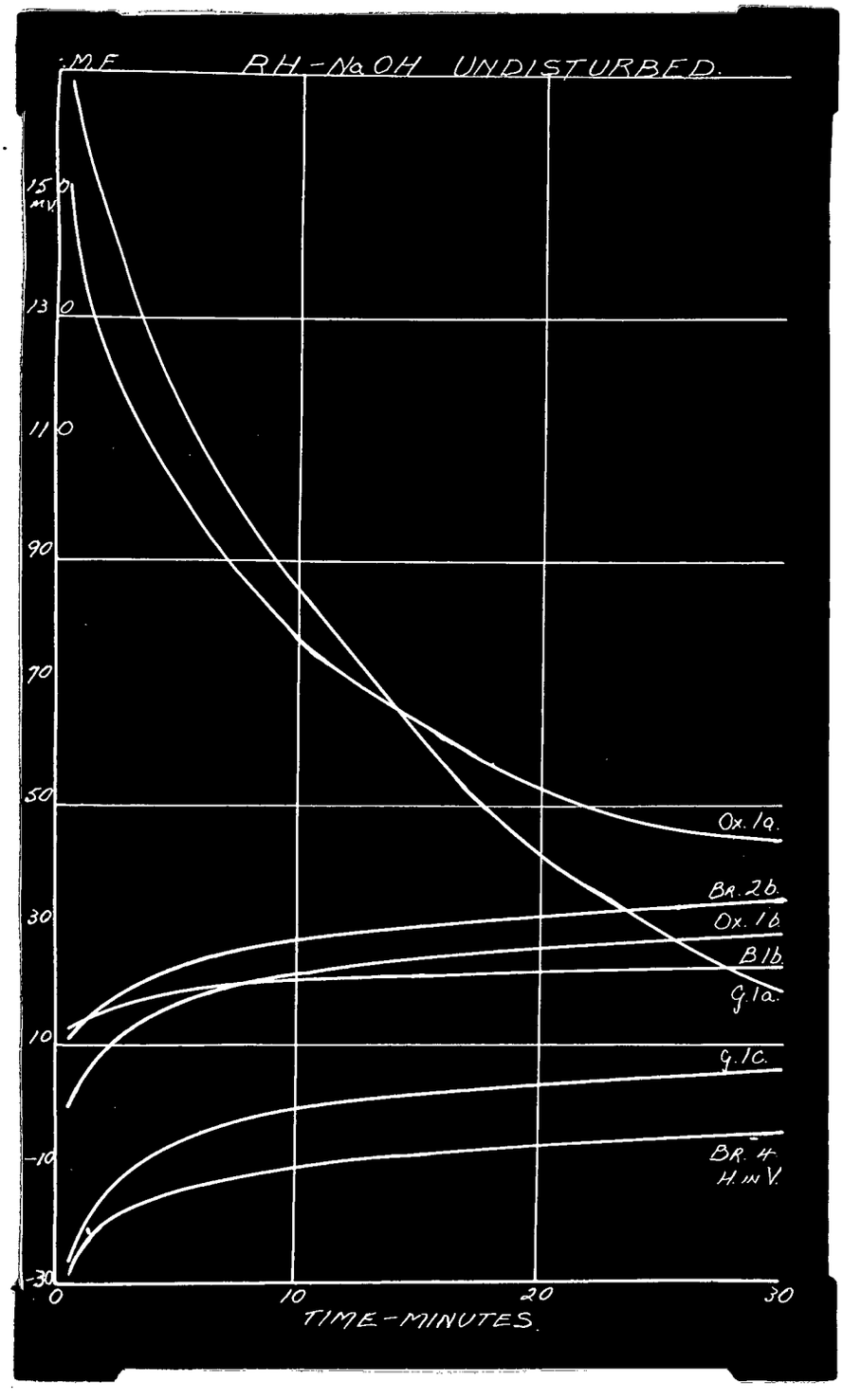
Undisturbed Electrolyte: Bright and grey Rh in this solution give a completely new type of curve. Very high, but transient, initial values are given, sometimes exceeding 1.23 volts measured against a hydrogen electrode in the same solution, i.e. exceeding the theoretical oxygen potential. The potential falls very rapidly, however, and after about twenty minutes reaches a value of approx. .8 volts for the O_2-H_2 cell, at which value the potential remains constant (constancy 1 - 2 mv.). The slight potential drift after the electrode has settled down is usually in a positive direction. The high initial values differ widely; freshly heated electrodes giving the highest values - for grey Rh 1.30 volts for the O_2-H_2 cell and for bright Rh 1.28 volts - whilst after keeping under distilled water the initial potential is only 100 - 200 mv. above the final constant value. The final values are all, however, much the same - reproducibility is 30 mv., including the grey and bright electrodes together. The black electrodes on the other hand give quite the usual type of curve, with potential drift either positive or negative and sometimes changing in direction during the 30 mins. Constancy is not quite as good as for the bright and grey electrodes, and reproducibility is 40 mv.

These black electrodes are usually about 100 mv. higher than the bright and grey ones. A bright Rh electrode, heated in vacuo, gave an initial potential about the same as the final potential of the bright and grey electrodes, i.e. .8 volts referred to a hydrogen electrode in the same electrolyte, but rises eventually to the potential of the air-treated black electrodes, i.e. 100 mv. higher. A black Rh electrode, heated in vacuo, behaves similarly but the potential in this case takes longer to rise. One bright Rh electrode was heated and cooled in an atmosphere of oxygen. Its' potential after 30 secs. in the solution was 1.24 volts for the O_2-Hg cell, but the rate of fall was much slower than with Rh electrodes heated and cooled in air. After 30 mins. the potential was still 1.1 volts. It seems that the oxides formed in an oxygen atmosphere are more stable than those formed in air, or else that a greater quantity of oxide is formed in oxygen and therefore takes longer to be decomposed.

Disturbed Electrolyte: Bright, oxidised and grey metal all give an E.E.P. curve similar to that of black Pt in sulphuric acid, although the first periods of bubbling may be irregular - grey Rh gives a very high initial potential, but it drops within the first period of bubbling to the regular potential of bright and grey E.E.P curves. Reproducibility is poor throughout. The usual trend of the curves is in a positive, more noble direction, although some black Rh curves show a slight negative trend. The values of the E.E.P. are: for bright Rh -46 mv., for oxidised Rh -40 mv., for grey Rh -25 mv., and for black Rh -15 mv. The highest potentials are always given by fresh electrodes. Sometimes M.E.P. decreases with time, sometimes it increases - there is no general rule.


RH.-KCL UNDISTURBED.
Q.1a.
B.2c.
Q.2b.
Ox.1a.
B.2b.
Ox.1c.
Br.4.
370 MV.
350
330
310
290
270
250
230
210
190
170
150
130
110
90
70
0
10
20
30
TIME-MINUTES.


E.M.F.
RH KCL DISTURBED
460 MV.
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
G.3a.
B.3a
Ox.3a.
G.3c.
Ox.4a.
0
10
20
TIME-MINUTES.


RH-NaOH UNDISTURBED.
150 MV.
130
110
90
70
50
30
10
-10
-30
0
10
20
30
TIME-MINUTES.
Ox. 1a.
Br. 2b.
Ox. 1b.
B 1b.
G. 1a.
G. 1c.
Br. 4.
H. in V.

In KCl:

Undisturbed Electrolyte: The curves here are very irregular, potential drift varying greatly both in magnitude and direction. Reproducibility is exceptionally poor, except for the black electrodes (30 mv.). Constancy is also poor, black electrodes being again the best with a value of approx. 3 mv. In the case of oxidised and grey metal, fresh electrodes give the highest potential, but there is no general rule for the other forms. A bright Rh electrode, heated in vacuo, gave a curve similar to the air-treated bright electrodes and at the same potential. No particularly high potentials are given by Rh in this electrolyte, the highest being the value of 1.09 volts for the O_2-H_2 cell given by a grey electrode. It is extremely puzzling to find that the freshly heated grey electrodes, in this case, start at a moderately low potential and rise to their highest value after about 30 mins., which is quite unlike their behaviour in sulphuric acid or sodium hydroxide.

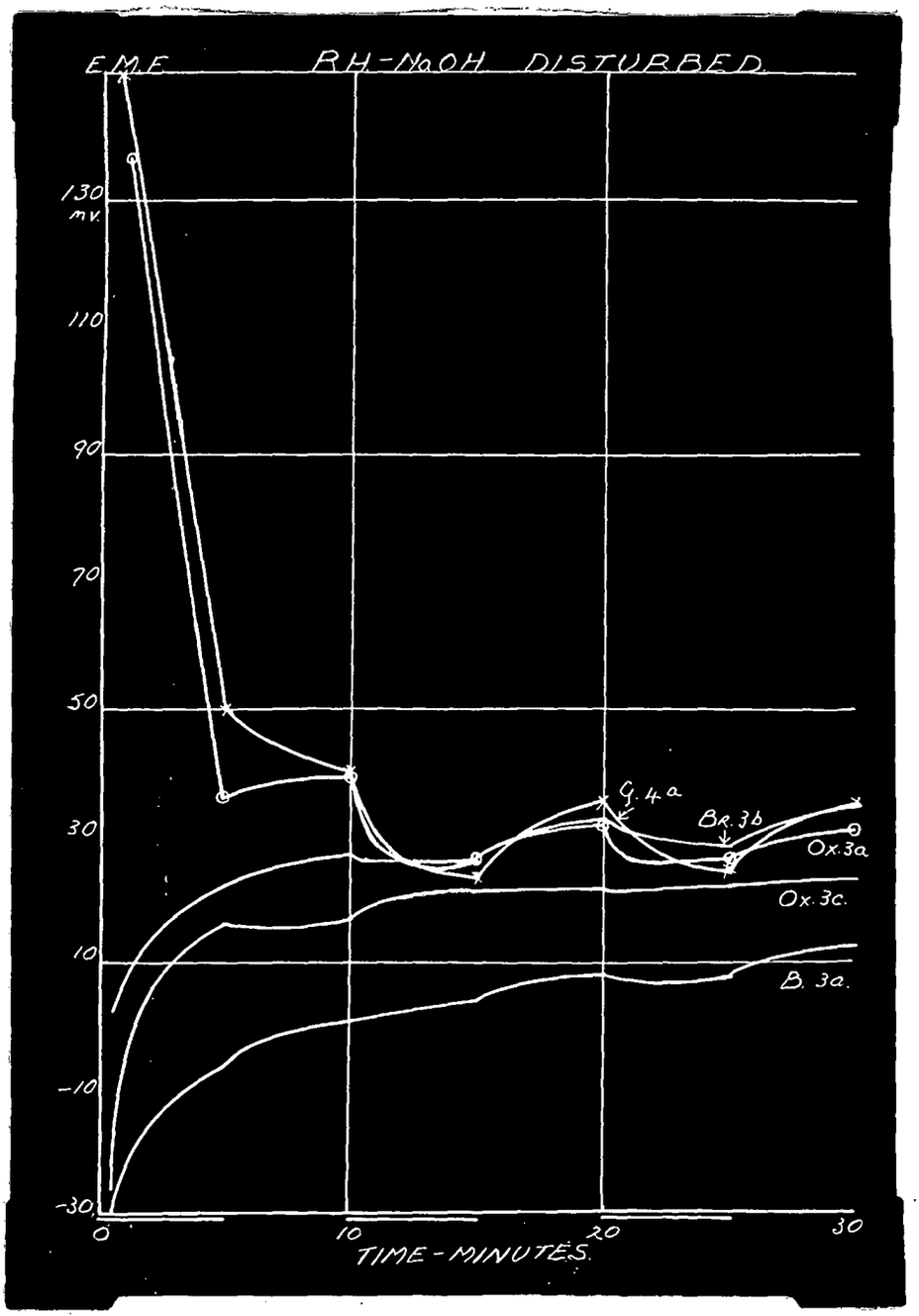
Disturbed electrolyte: Again freshly heated grey or oxidised electrodes give a considerably higher potential than any other electrodes. A peculiar point is that, whereas in sulphuric acid the highest potential is given immediately on immersion in the electrolyte, here the initial potential is often quite low, but rises rapidly during the first five or ten minutes to a maximum, and then declines steadily again. This causes very irregular E.M.F. values. The highest maximum (1.19 volts, for the O_2-H_2 cell) was reached by a grey electrode, eight minutes after immersion. Grey electrodes, which have been kept in air or under distilled water, however, give a potential well below that given by black electrodes, which lie midway between the high and low grey electrodes, i.e. between the freshly heated grey electrodes and the grey electrodes with other histories.

Reproducibility is again exceptionally poor except for the black metal. M.E.P. is very irregular in sign and magnitude for all forms of metal except the black, which gives a regular M.E.P. with a negative sign . In the case of oxidised and grey electrodes the first period of bubbling almost always gives positive M.E.P. values, but this changes, sometimes immediately, sometimes much later, into a negative M.E.P. The curve then consists of almost straight line sections. The average M.E.P's are:- Oxidised electrodes -21 mv., black -7 mv., grey -4 mv.

In NaOH:

Undisturbed electrolyte: With freshly heated oxidised or grey electrodes potential drift is very rapid in the negative direction, but for all the bright, black and the oxidised or grey electrodes, which have been kept in air or under distilled water, the drift is much less and in a positive direction. Constancy is good at 1 - 2 mv. in the latter cases. Reproducibility is fair at approx. 40 mv. in all cases. Very high initial potentials , resembling those in sulphuric acid, are given by oxidised and grey Rh in this electrolyte. The highest potential attained was the value of 1.28 volts for the O_2-H_2 cell given by freshly oxidised electrode. A bright Rh electrode, heated invacuo, gave sensibly the same potential as the air-treated bright Rh electrodes. Reproducibility is fair.

Disturbed Electrolyte: M.E.P. is low in all the forms of the metal; occasionally a small positive value is given. Average values are:- Bright Rh -6 mv., oxidised Rh -4 mv., black Rh -1 mv., grey Rh -11 mv. Oxidised electrodes which have been kept in air give the lowest M.E.P. Reproducibility, at 20 mv., is better than the undisturbed electrolyte value. The general trend of the curves is in a positive direction. The first period of bubbling,


E.M.F
RH-NaOH DISTURBED
130 mv.
110
90
70
50
30
10
-10
-30
0
10
20
30
TIME-MINUTES.
G. 4a
Br. 3b
Ox. 3a
Ox. 3c.
B. 3a.

however, in the case of fresh oxidised or grey electrodes, exhibites a negative trend. The highest value for the O_2-H_2 cell was given by a freshly heated grey electrode immediately on immersion in the electrolyte (1.12 volts). The curves of bright Rh in both undisturbed and disturbed electrolyte are almost identical in all respects with those given by bright Ru in this same electrolyte.

A remarkable thing about Rh in this solution is that all forms of the metal give approximately .97 volts for the O_2-H_2 cell, after 30 mins. in the electrolyte.

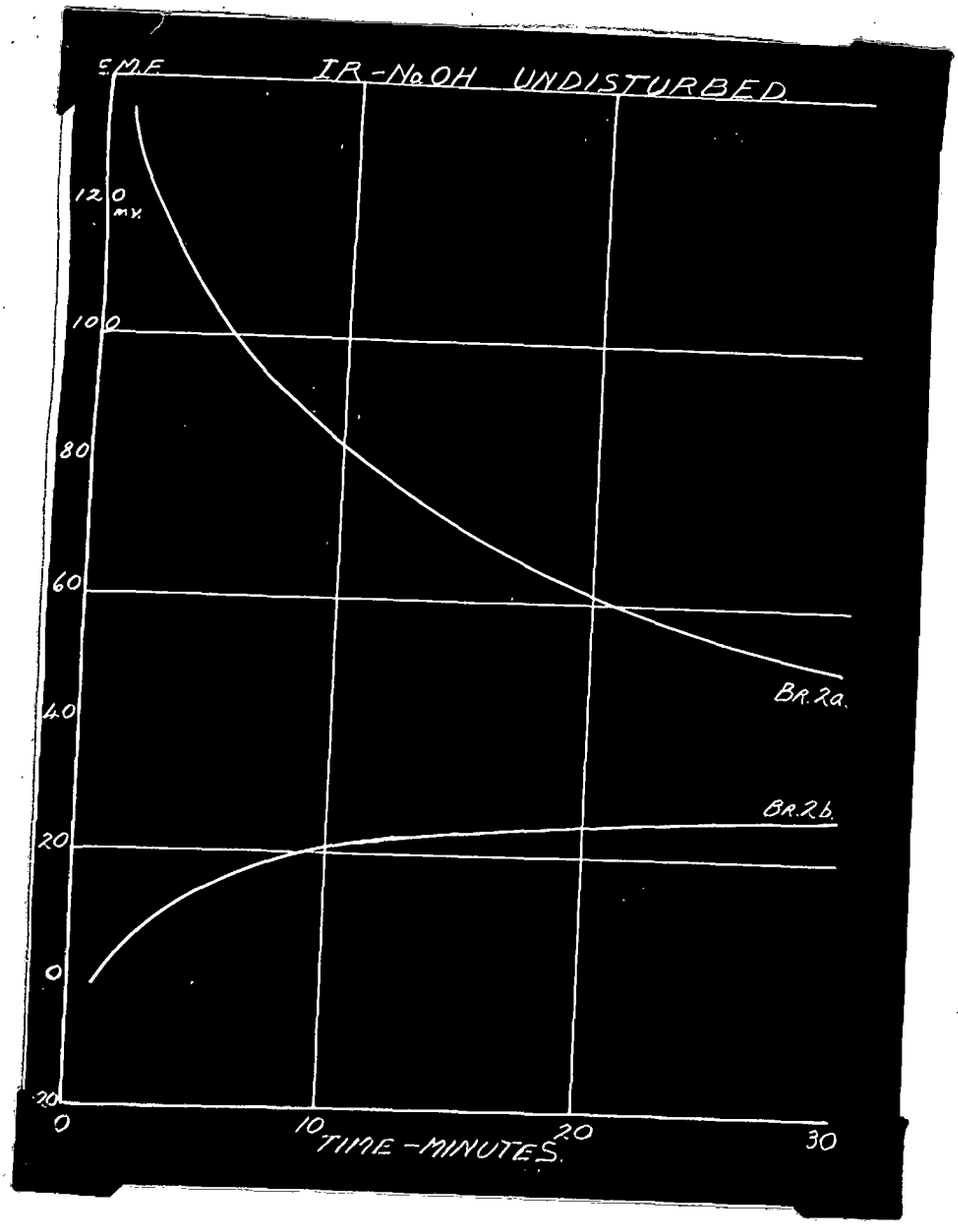
It is interesting to note, in connection with all those values exceeding the generally accepted theoretical potential of the O_2-H_2 cell, that Soderholm and Benedicks[109] have suggested that the true value is 1.48 volts. This is as far beyond the values reported here, as 1.23 volts was beyond the previous highest values.

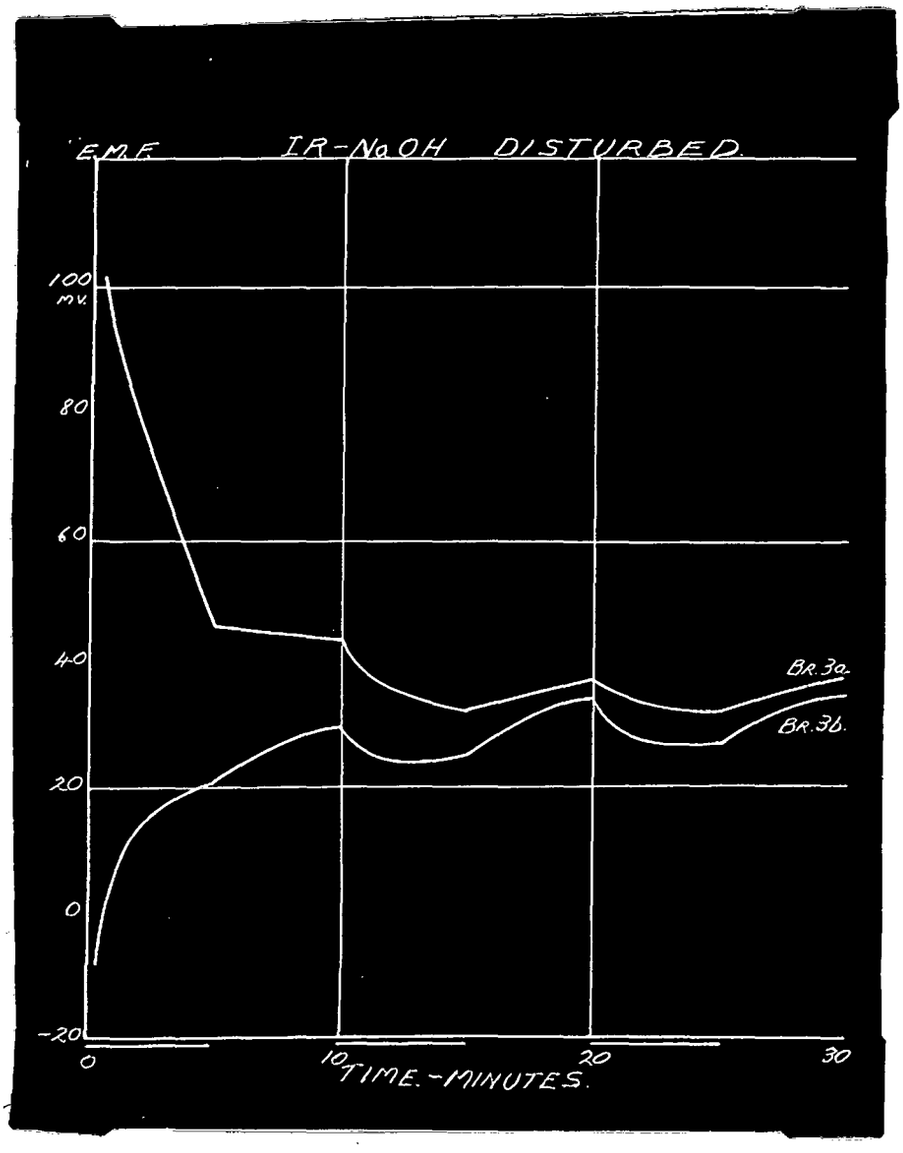
IRIDIUM

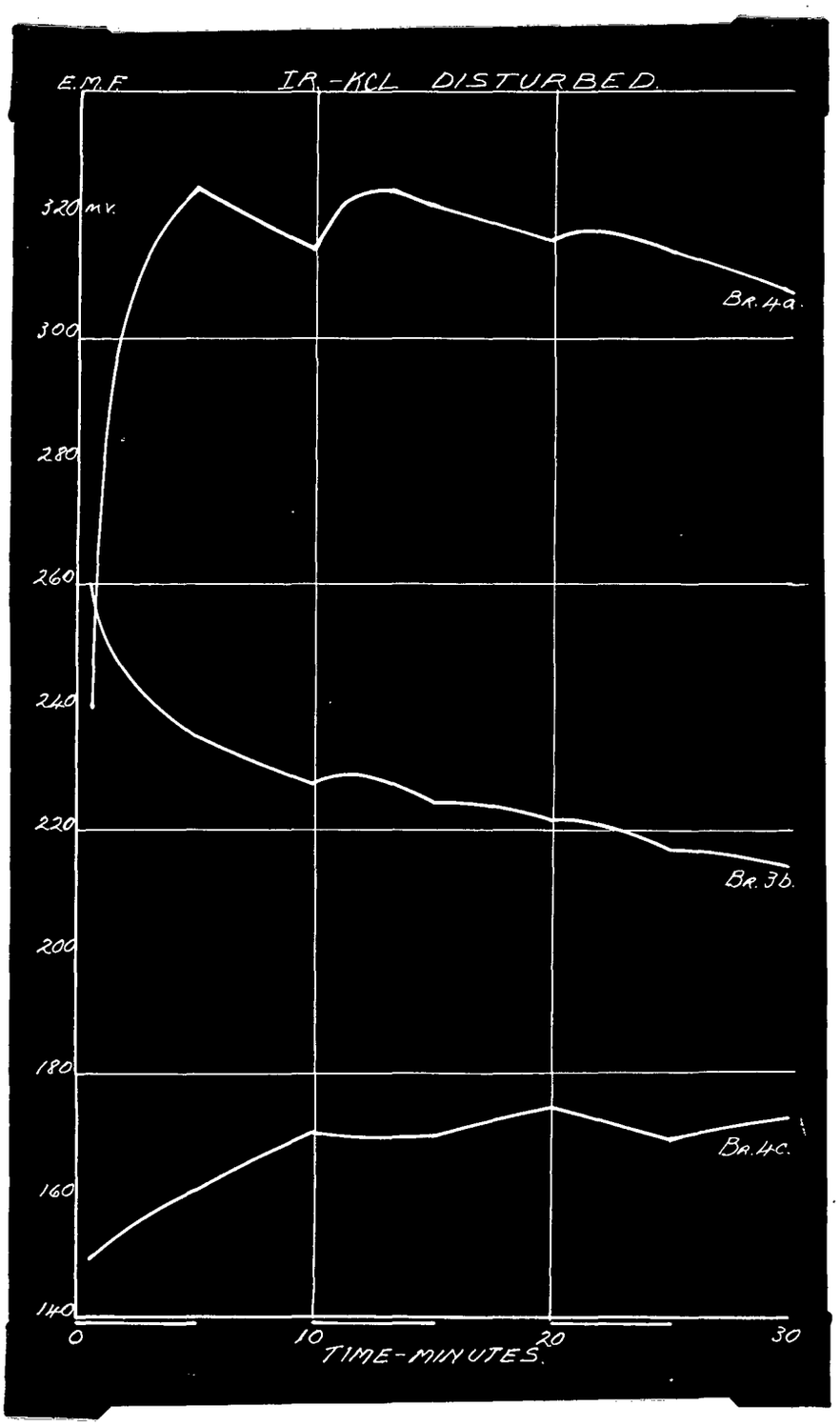
This metal was usually used only in the bright form as it could not be visibly oxidised even at red heat, and as no satisfactory black deposits were obtainable. The appearance of the metal remained unchanged after use.

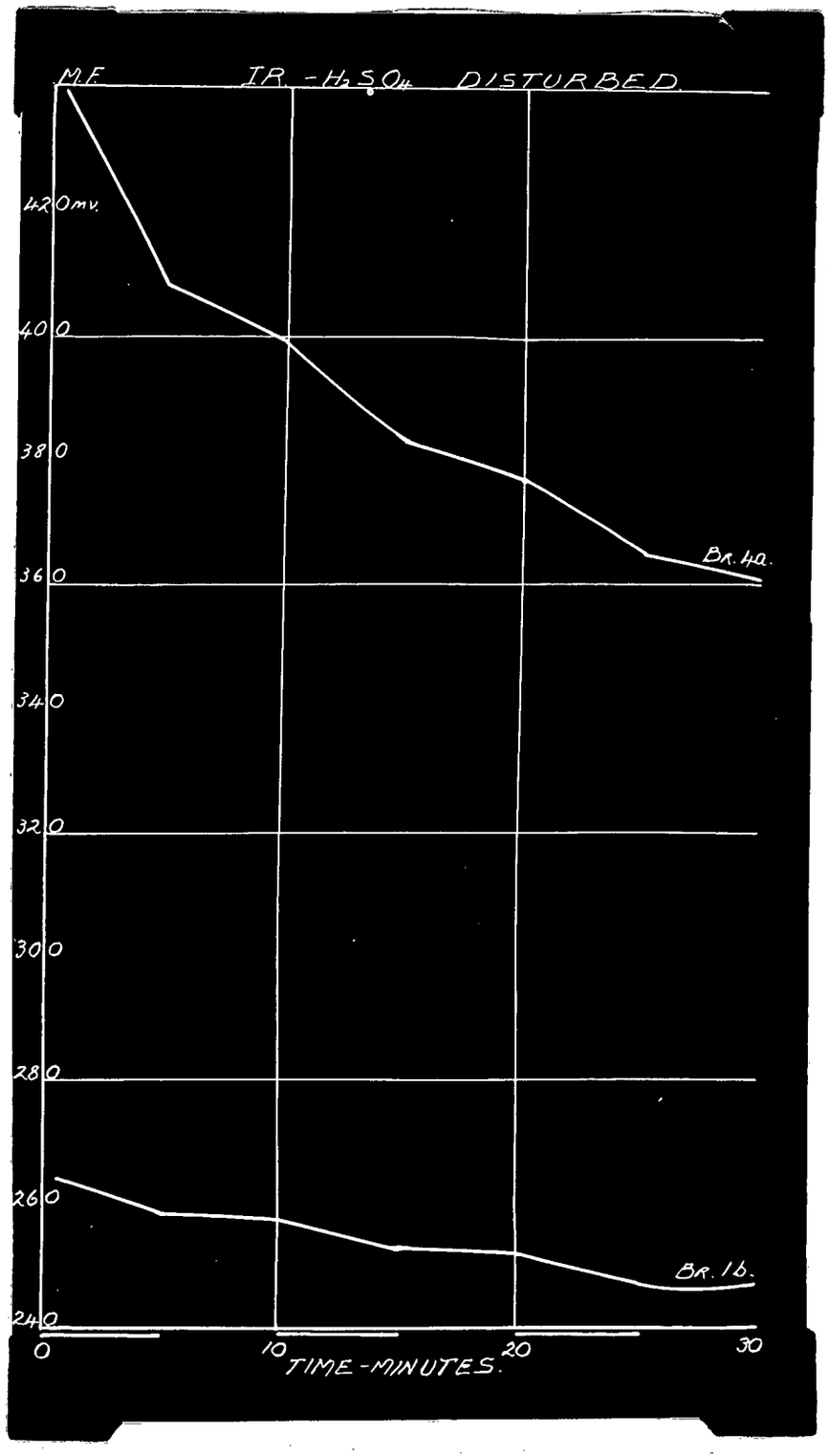
In H_2SO_4;

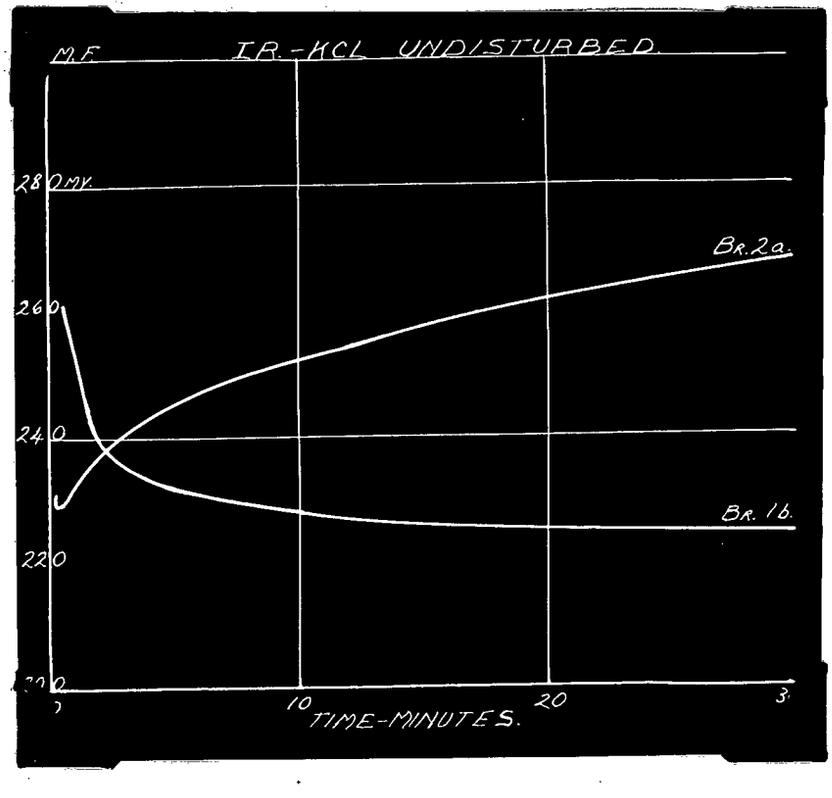
Undisturbed Electrolyte: Here, as in the case of Rh, very high initial values for the O_2-H_2 cell were given by freshly heated electrodes, the highest recorded being exactly 1.23 volts. As a rule, however, the potential does not fall rapidly to a constant valve as in the case of Rh, but falls more or less regularly throughout the 30 mins. Reproducibility is exceptionally poor. A bright electrode heated in vacuo gave an initial potential, approximately 180 m.v. lower than the average but the potential rose during the 30 mins. almost to the potential of the corresponding air-treated electrodes. Using the very unsatisfactory "black" Ir deposits of Foerster[61] and


E.M.F
IR-NaOH UNDISTURBED
120 m.v.
100
80
60
40
20
0
-20
0
10
20
30
TIME-MINUTES.
BR. 2a.
BR. 2b.


E.M.F
IR-NaOH DISTURBED.
100 m.v.
80
60
40
20
0
-20
0
10
20
30
TIME.-MINUTES.
BR. 3a.
BR. 3b.


E.M.F.
IR-KCL DISTURBED.
320 mv.
300
280
260
240
220
200
180
160
140
BR. 4a.
BR. 3b.
BR. 4c.
0
10
20
30
TIME-MINUTES.


M.F.
IR. - H_2SO_4 DISTURBED.
420 mv.
400
380
360
340
320
300
280
260
240
Br. 4a.
Br. 1b.
0
10
20
30
TIME-MINUTES.


M.F.
IR. - KCl UNDISTURBED.
280 mv.
260
240
220
Br. 2a.
Br. 1b.
10
20
TIME-MINUTES.

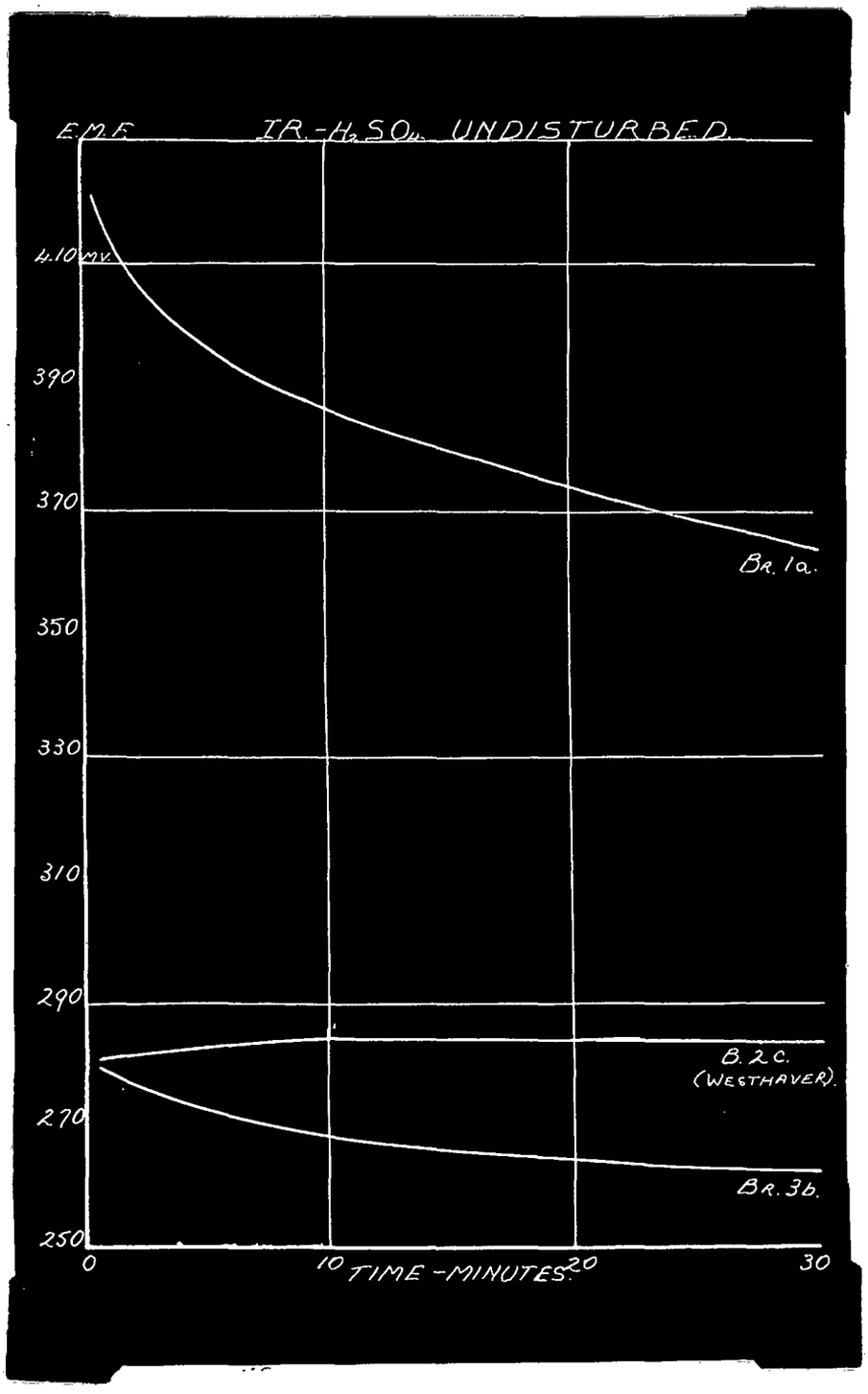
Westhaver[59], initial values for the O2-H2 cell ranging from 1.38 volts to .76 volts were obtained. Foerster's "black" gave the highest values, Westhaver's never exceeded 1.19 volts. Despite the very high values reached the potential did not fall rapidly but remained constant, within a few millivolts. in most cases, throughout the 30 mins. On attempting to grey the electrodes a fairly high initial potential was observed, but this fell rapidly throughout the 30 mins. to the low value of approximately .85 volts for the O2-Hg cell. This is very much like the behaviour of bright Ir although in the latter case the fall of potential is not as rapid.

One black electrode made by Westhaver's method was heated in vacuo, and gave a low potential, (.82 volts for the O_2-H_2cell), at first, which rose steadily, reaching .94 volts after 95 mins. in the solution. This is the usual value for bright ir electrodes. In view of the fact that no satisfactory deposits could be obtained, only bright Ir was used in the other electrolytes. It seems very probable from the above observations that the "black" electrodes are registering the single potential of some compound of Ir.

Disturbed electrolyte: The typeof curve given by bright Ir is similar to that of bright Ru in H_2SO_4. The E.M.F. averages -11 mv., and decreases with time. The curves are mostly very regular, but reproducibility is very poor. The freshly heated electrodes give the highest potentials. - one started at 1.21 volts referred to a hydrogen electrode in the same electrolyte. The trend of all of the curves is in a negative direction.

In HCl:

Undisturbed electrolyte: Potential drift occurs in both directions, and the curves are rather irregular. Reproducibility is very poor at 100 mv., and constancy approximately 3 mv. No very high values for the O_2-H_2


E.M.F.
IR.-H2SO4. UNDISTURBED.
4.10 MV.
390
370
350
330
310
290
270
250
Br. 1a.
B. 2c.
(WESTHAVER).
Br. 3b.
0
10
20
30
TIME - MINUTES.

cell were recorded in the undisturbed electrolyte. An electrode heated in vacuo gave an initial potential of approximately 180 mv. below the usual initial potential, and after 30 mins. in the electrolyte the potential had risen to within 80 mv. of the usual final potential.

Disturbed Electrolyte: Here high values for the O_2-H_2 cell are attained - up to 1.11 volts - after about 5 mins. immersion in the electrolyte. The type of curve is similar to that of Gray & Wh in KCl, giving, at first, positive values for the E.M.F. which gradually change to negative. Freshly heated electrodes give the highest potential. The first period of bubbling, for electrodes other than freshly heated ones, is often irregular sometimes giving a positive, and sometimes a negative E.M.F. Reproducibility over all the electrodes taken together is very poor (200 mv.), but for freshly heated ones only is 40 mv., and for the rest taken separately it is also 40 mv., i.e. the fresh electrodes are quite separate from the others - at a potential over 100 mv. more noble. The average E.M.F. is -5 mv. This value is averaged from the final periods of bubbling only, since E.M.F. changes rapidly during the first two periods of bubbling.

In NaOH:

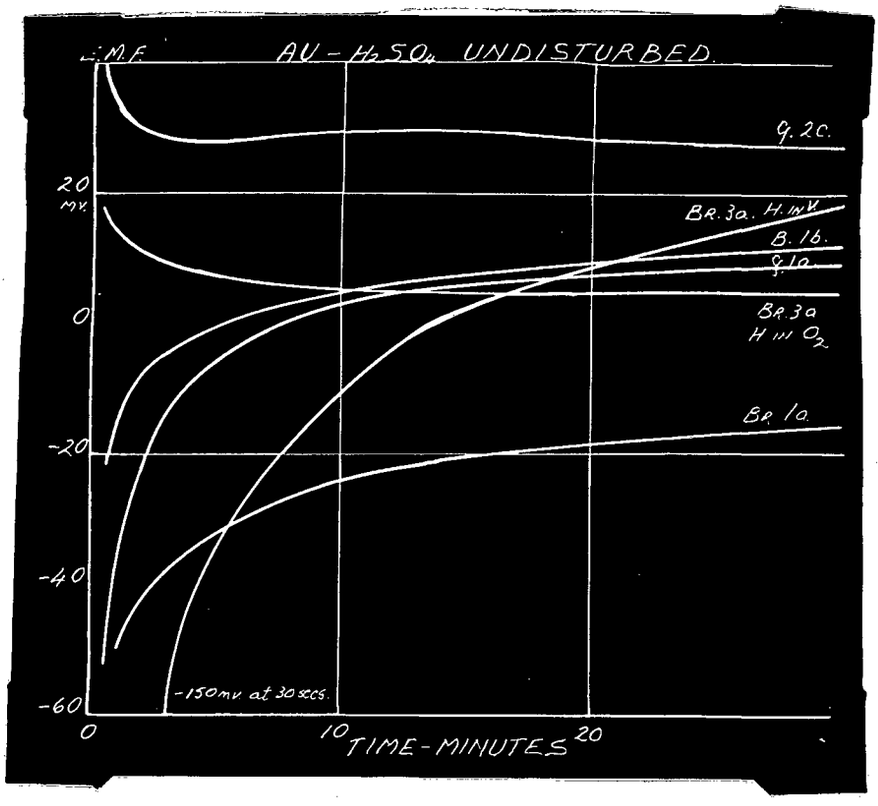
Undisturbed Electrolyte: Potential drift may occur in either a positive or negative direction, depending on the history of the electrode. Freshly heated electrodes start at a high potential (above 1.0 volts for O_2-H_2 cell) and drop smoothly. Electrodes with other histories start with lower potentials (approximately .93 volts for the O_2-H_2 cell), and rise to about the same final potential as the fresh electrodes. Reproducibility, however, is only about 40 mv. An electrode heated in vacuo followed the second type of curve, but was about 30 mv. lower. The constancy of fresh electrodes is poor at 11 mv., but

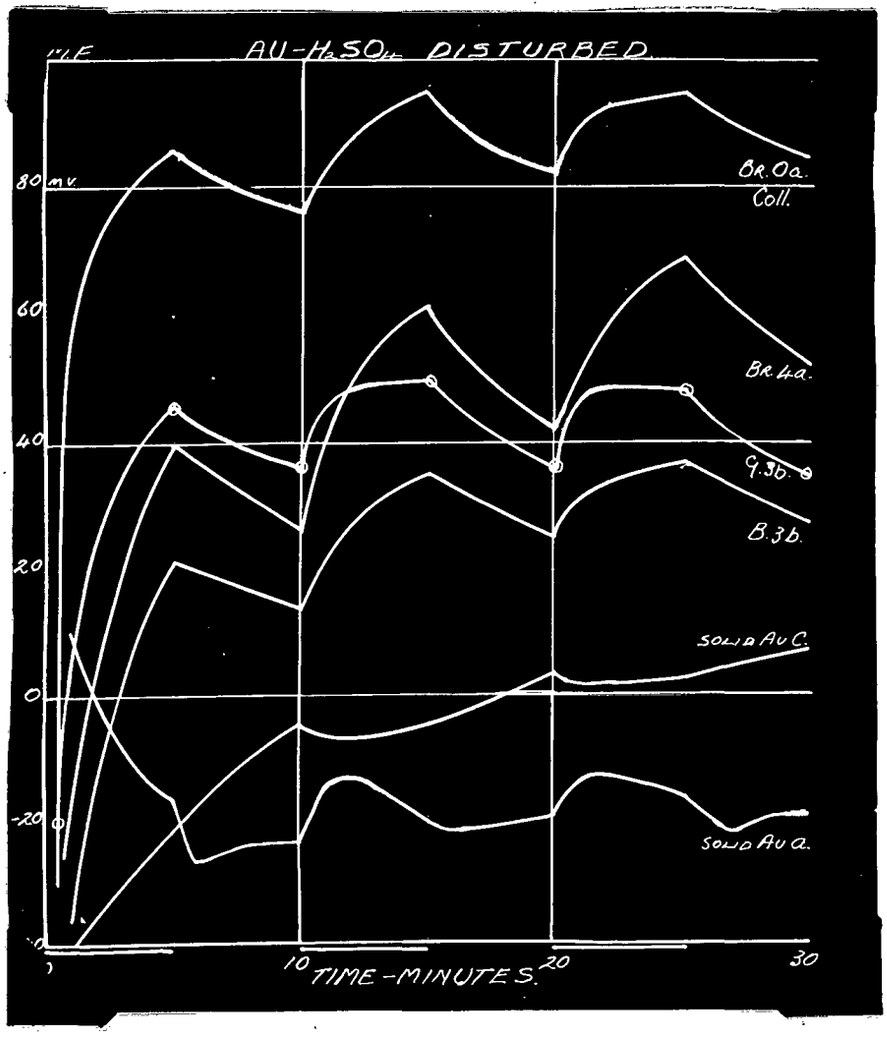
cell were recorded in the undisturbed electrolyte. An electrode heated in vacuo gave an initial potential of approximately 180 mv. below the usual initial potential, and after 30 mins. in the electrolyte the potential had risen to within 80 mv. of the usual final potential.

Disturbed Electrolyte: Here high values for the O_2-H_2 cell are attained - up to 1,11 volts - after about 5 mins. immersion in the electrolyte. The type of curve is similar to that of Gray-Hh in KCl, giving, at first, positive values for the e.m.f. which gradually change to negative. Freshly heated electrodes give the highest potential. The first period of bubbling, for electrodes other than freshly heated ones, is often irregular sometimes giving a positive, and sometimes a negative e.m.f. Reproducibility over all the electrodes taken together is very poor (200 mv.), but for freshly heated ones only is 40 mv., and for the rest taken separately it is also 40 mv., i.e. the fresh electrodes are quite separate from the others - at a potential over 100 mv. more noble. The average e.m.f. is -5 mv. This value is averaged from the final periods of bubbling only, since e.m.f. changes rapidly during the first two periods of bubbling.

In NaOH:

Undisturbed Electrolyte: Potential drift may occur in either a positive or negative direction, depending on the history of the electrode. Freshly heated electrodes start at a high potential (above 1.0 volts for O_2-H_2 cell) and drop smoothly. Electrodes with other histories start with lower potentials (approximately .93 volts for the O_2-H_2 cell), and rise to about the same final potential as the fresh electrodes. Reproducibility, however, is only about 40 mv. An electrode heated in vacuo followed the second type of curve, but was about 30 mv. lower. The constancy of fresh electrodes is poor at 11 mv., but


AU - H2SO4 UNDISTURBED.
M.F.
20 MV.
0
-20
-40
-60
0
10
20
TIME - MINUTES
Q. 2C.
BR. 3a. H. in V.
B. 1b.
Q. 1a.
BR. 3a H in O2.
BR. 1a.
-150 mv. at 30 secs.


AU-H2SO4 DISTURBED.
M.F.
80 MV.
60
40
20
0
-20
0
10
20
30
TIME-MINUTES.
BR. 0a. Coll.
BR. 4a.
Q. 3b.
B. 3b.
SOLID Au C.
SOLID Au a.

but the others are better at ±5 mv. The highest value for the O2-H2 cell, 1.1 volts, was given by a fresh electrode immediately on immersion in the electrolyte.

Disturbed electrolyte: The curves here are, in all respects, similar to those given by bright Au and bright Ru in NaOH and are at the same potential. Reproducibility is fairly good at 20 mv.. The general trend of the curves is slightly upwards towards the theoretical oxygen potential. The average e.m.f. is -6 mv.

GOLD.

The forms of metal used were the bright, rough electro-deposited or "R form", and the heat treated or "A form", corresponding to the usual grey electrodes. The electro-deposited form is of an earthy brown colour, which goes much lighter on heating, becoming a golden orange colour which, however, is deeper than the light gold of the bright electrodes. Where the coating of bright Au is thin, the film can be viewed by transmitted light, and the colour is seen under these conditions to be purplish.

There is no visible oxidation of the bright form when heated in air. The bright Au electrodes, esplated from alcoholic $AuCl_3$, are dull but may be brightened by polishing with an agate burnisher without apparently affecting the oxygen electrode properties. There is no visible change in the metal surface during use as an oxygen electrode.

In H_2SO_4:

Undisturbed Electrolyte: The curves for bright Au are rather irregular in this electrolyte, and the direction of the potential drift may change more than once during the 30 mins. the electrode is in the solution. Constancy is therefore variable. A bright electrode heated and cooled in oxygen gave a much steadier and

but thqothers are better at 2-3 mv. The highest value for the O_2-H_2 cell, 1.1 volts, was given by a fresh electrode immediately on immersion in the electrolyte.

Disturbed electrolyte: The curves here are, in all respects, similar to those given by bright Rh and bright Ru in NaOH and are at the samepotential. Reproducibility is fairly good at 20 mv.. The general trend of the curves is slightly upwards towards the theoretical oxygen potential. The average m.e.f. is -6 mv.

GOLD.

The forms of metal used were the bright, rough electro-deposited or "R form", and the heat treated or "H form", corresponding to the usual grey electrodes. The electro-deposited form is of an earthy brown colour, which goes much lighter on heating, becoming a golden orange colour which, however, is deeper than the light gold of the bright electrodes. Where the coating of bright Au is thin, the film can be viewed by transmitted light, and the colour is seen under these conditions to be purplish.

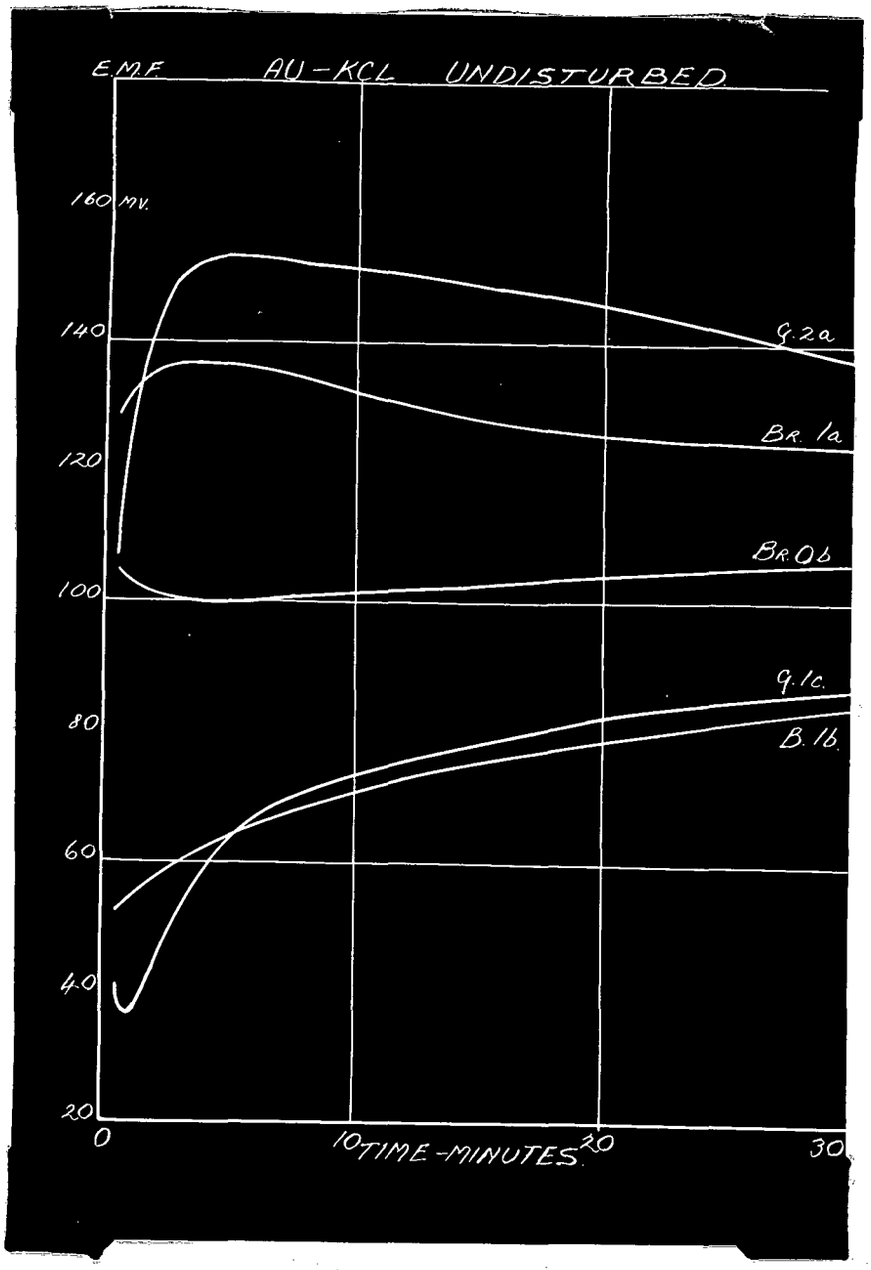
There is no visible oxidation of the bright form when heated in air. The bright Au electrodes, asplated from alcoholic $AuCl_3$, are dull but may be brightened by polishing with an agate burnisher without apparently affecting the oxygen electrode properties. There is no visible change in the metal surface during use as an oxygen electrode.

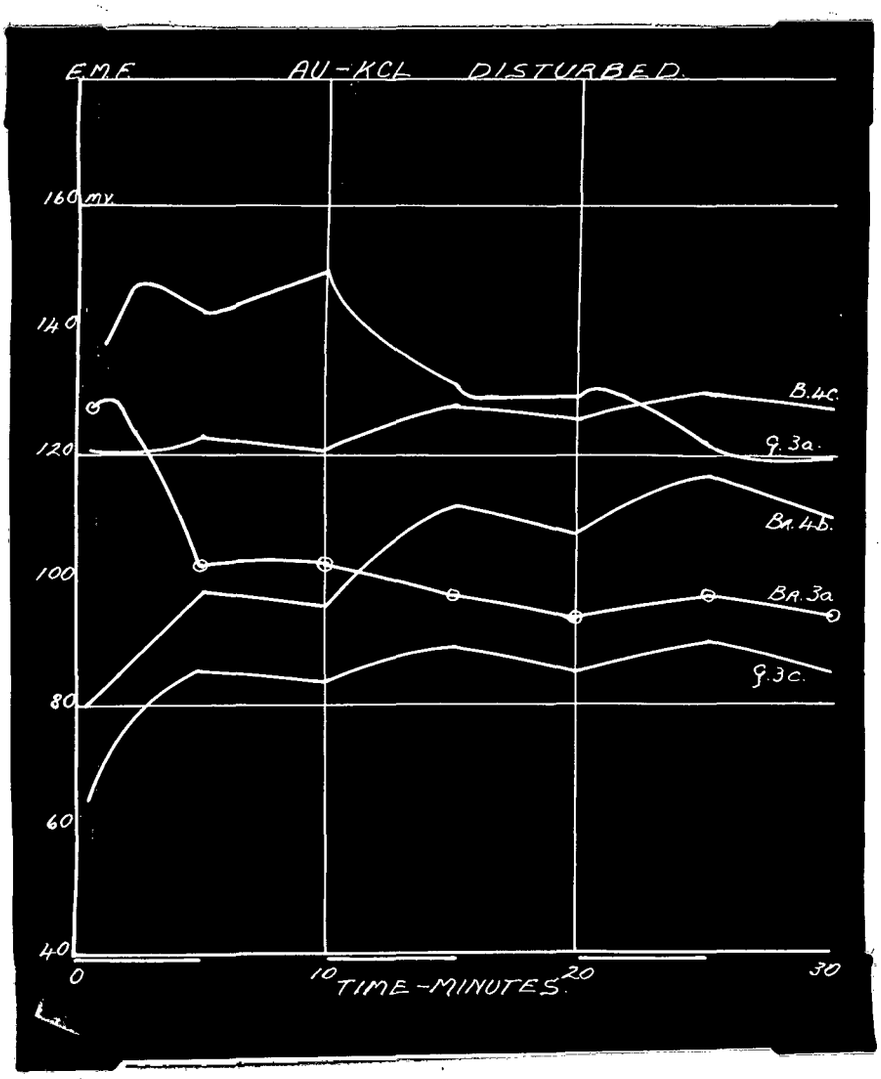
In H_2SO_4:

Undisturbed Electrolyte: The curves for bright Au are rather irregular in thiselectrolyte, and the direction of the potential drift may change more than once during the 30 mins. the electrode is in the solution. Constancy is therefore variable. A bright electrode heated and cooled in oxygen gave a much steadier and

and more regular curve but at the same potential. The bright, R and H forms of Au all give approximately the same potential, but the value is low, usually being approximately .7 volts referred to a H electrode in the same electrolyte. Reproducibility is poor in all cases. The general trend of the curves is in the more noble direction. The constancy of the R and H forms is good at 1-2 mv. Electrodes which have been freshly electroplated give exceptionally high values of the order of 1.29 volts for the O2-H2 cell. This appears to be due to some of the electrolysing solution remaining in the pores of the coating even after thorough washing. This very high potential falls rapidly, and may be destroyed by keeping the electrode under distilled H_2O for approximately 24 hours before use. The usual low potentials of bright Au and of the H form are then given. An electrode, which had been left to reach the usual low values given by Au, was dipped in the electroplating solution, 5% $HAuCl_4$, and then tried as an oxygen electrode. It gave the exceptionally high values mentioned above immediately on immersion, thus showing that the high potential was probably due to incomplete washing of the electroplated electrodes. A bright Au electrode, heated in vacuo, gave an initial potential 100 mv. lower than the ordinary bright Au electrodes but, after 30 mins, it had risen up to the usual potential of bright Au in H_2SO_4.

Disturbed Electrolyte: Au is quite exceptional in this electrolyte in giving consistently high positive values of E.M.F. in all forms of the metal. The disturbed electrolyte curves lie approximately 60 mv. higher than those in undisturbed electrolyte for bright electrodes. The R and H forms, however, lie at much the same potential, whether E.M.F. is in action or not. Continuous bubbling for the full 30 mins. gave, in the case of a bright


E.M.F AU-KCL UNDISTURBED
160 MV.
140
120
100
80
60
40
20
0
10 TIME-MINUTES 20
30
Q. 2a
BR. 1a
BR. 0b
Q. 1c.
B. 1b.


E.M.F AU-KCL DISTURBED.
160 mv.
140
120
100
80
60
40
0
10 TIME-MINUTES 20
30
B. 4c.
Q. 3a.
Br. 4b.
Br. 3a
Q. 3c.

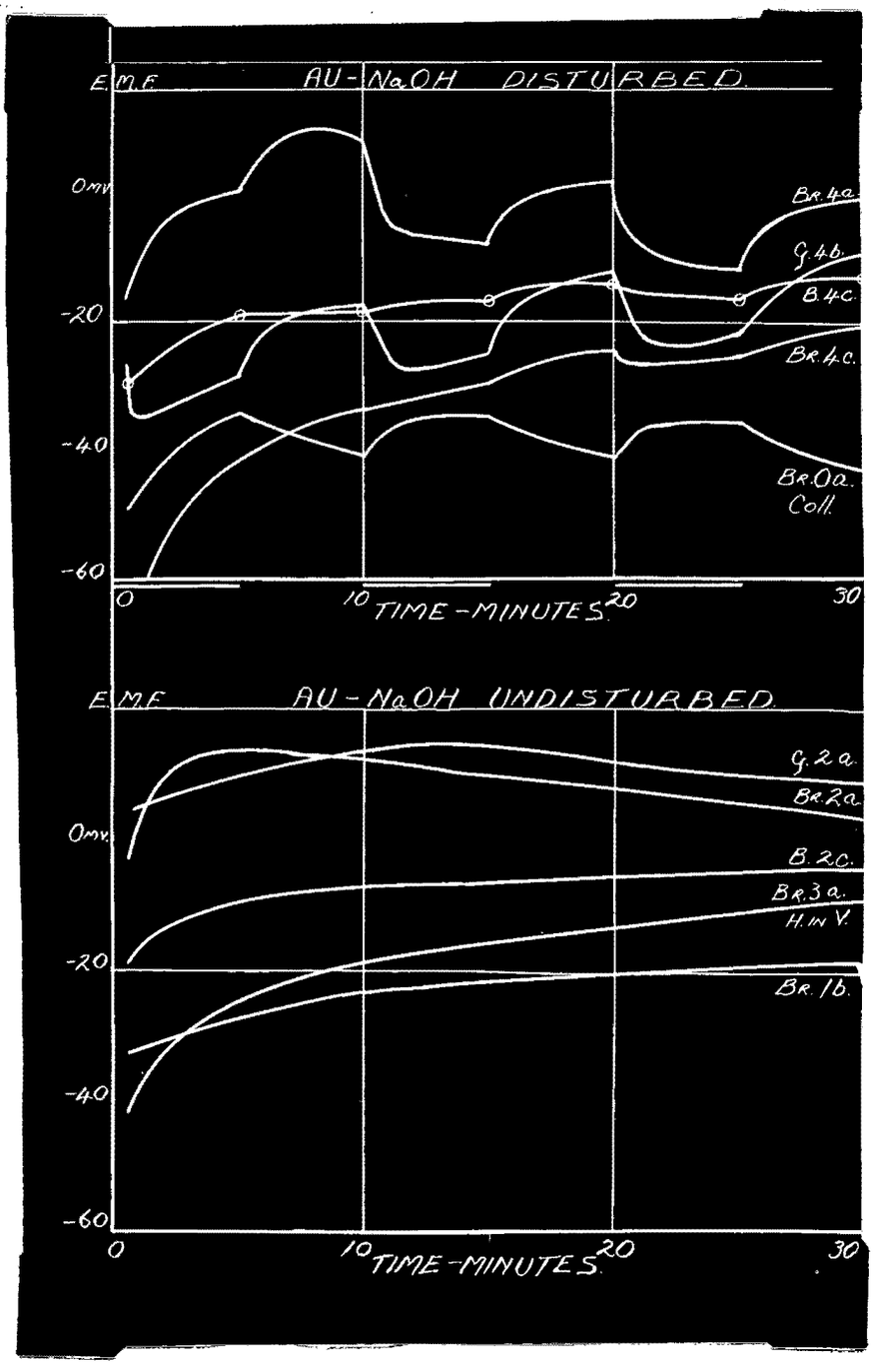
electrode, approximately the same potential as intermittent bubbling. M.E.F. usually decreases with time. The average values are: bright Au + 23 mv., R form + 13 mv., and H form + 20 mv. The general trend of the curves is in the more noble direction, but there are a considerable number with the opposite trend. The reproducibility of the bright electrodes is still poor but that of the R and H forms is 30 mv.

The first period of bubbling is usually regular, giving a positive M.E.F. A few bright electrodes were collodionised and it was found that there was no remarkable effect on the M.E.F., as in the case of Pt. With Pt in H_2SO_4 collodionising the electrode altered the M.E.F. radically from -50 mv. to +2 mv., but with Au the M.E.F. was only slightly reduced - from +23 mv. to +15 mv. A solid Au plate electrode, which had been standing in air for at least twelve months, was used and gave a low negative M.E.F. of -2 to -3 mv. (curve, solid Au c.) This electrode was then heated, cooled and used immediately, and then gave an M.E.F. of the order of +10 mv., i.e. with the usual positive sign (curve, solid Au c.).

In KCl:

Undisturbed Electrolyte: Both constancy and reproducibility are poor for all forms of Au in this electrolyte. Potential drift is irregular and may vary in direction several times during the 30 mins. In all cases freshly made electrodes give the highest potential. The H form and bright Au give, in general, a higher potential than the R form. A bright Au electrode, heated in vacuo, started off 190 mv. below the usual initial potential, and after 30 mins. it was still about 120 mv. below the average final potential of ordinary bright Au electrodes.

Disturbed Electrolyte: The average M.E.F's are: bright Au +3 mv., R form +7 mv., H form varying from -8 to +5mv. The values usually decrease with time. The


E.M.F.
AU-NaOH DISTURBED
0mv.
-20
-40
-60
Br.4a.
G.4b.
B.4c.
Br.4c.
Br.0a. Coll.
0
10
20
30
TIME-MINUTES.
E.M.F.
AU-NaOH UNDISTURBED
0mv.
-20
-40
-60
G.2a.
Br.2a.
B.2c.
Br.3a.
H. in V.
Br.1b.
0
10
20
30
TIME-MINUTES.

curves are very irregular. Both positive and negative M.E.P's are given in the bright and H forms, but the R form always gives a positive M.E.P. In most cases, with the bright and H forms, the M.E.P. has settled down to a positive value by the final period of bubbling. Reproducibility is fair at 30-40 mv. The general trend of the curves is in a more noble direction, but there are exceptions to this rule.

In NaOH:

Undisturbed Electrolyte: Reproducibility for all forms of metal is approximately 40 mv. but for the R and H forms, after keeping in air or under distilled water, it improves to 10 mv. Constancy is usually approximately 2 mv. but for the R and H forms, other than freshly made, it is very good at 0-1 mv. Freshly made electrodes always give the highest potentials. One such bright Au electrode gave an initial potential of 1.04 volts for the O_2-H_2 cell which is very good for a Au electrode. Potential drift may be in a more noble or less noble direction, and often changes direction during use. A bright Au electrode heated in vacuo gave a curve similar in shape to, and at the same potential as the ordinary/air treated bright electrodes. One bright Au electrode was heated in air and then cooled in an atmosphere of hydrogen. It gave a curve similar in all respects to a freshly heated electrode, which had been cooled in air.

Disturbed Electrolyte : Most of the electrodes start with a positive M.E.P., but this changes rapidly to a negative value in all cases except a few R form electrodes. M.E.P. usually decreases with time. The average values of M.E.P. are : bright Au -8 mv., R form from -5 to +5 mv., and the H form -10 mv. Reproducibility for the R and H forms is good at 20 mv., but poor for bright electrodes at 40 - 50 mv. Freshly made electrodes all have a negative trend away from the theoretical oxygen potential, but the

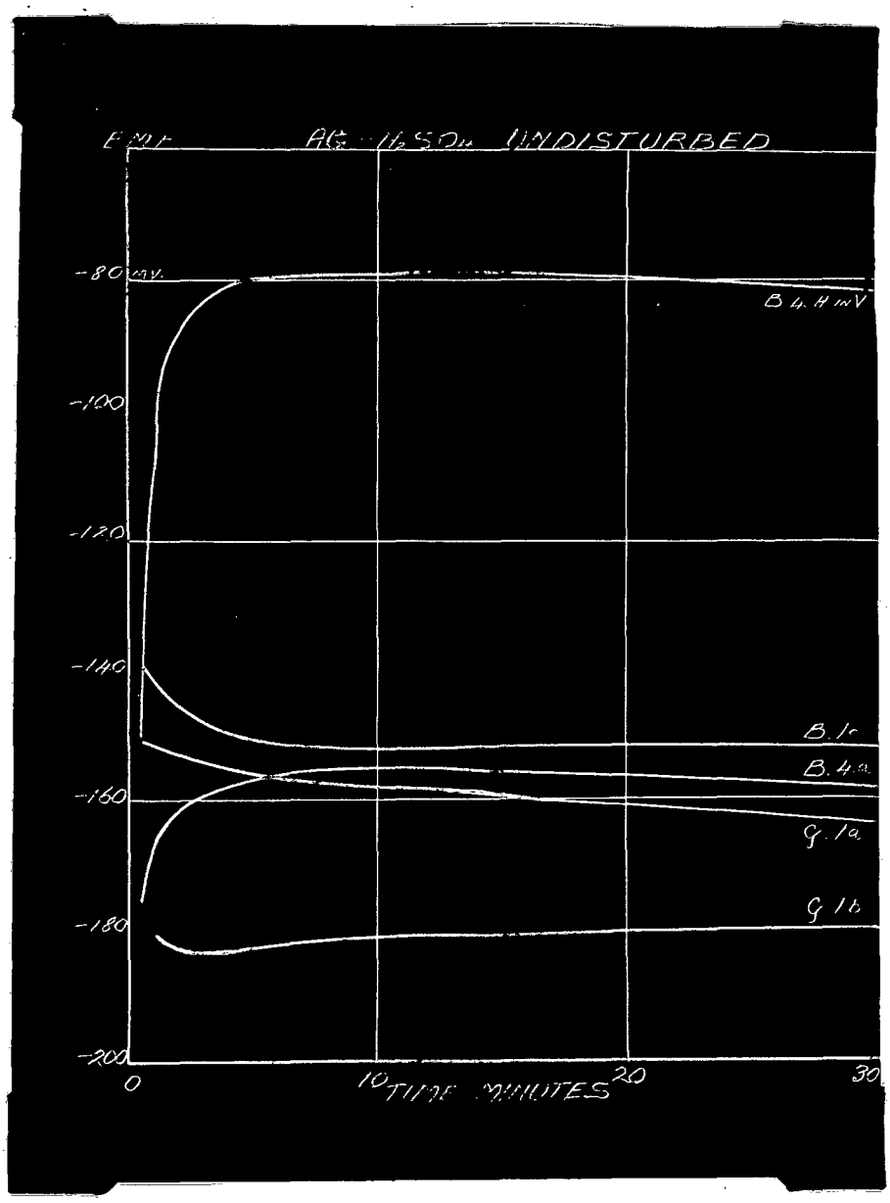
potentials of electrodes with other histories tend to rise with time. A bright Au electrode was collodionised, and this treatment immediately altered the e.m.f. from -8 mv. to +6 mv.

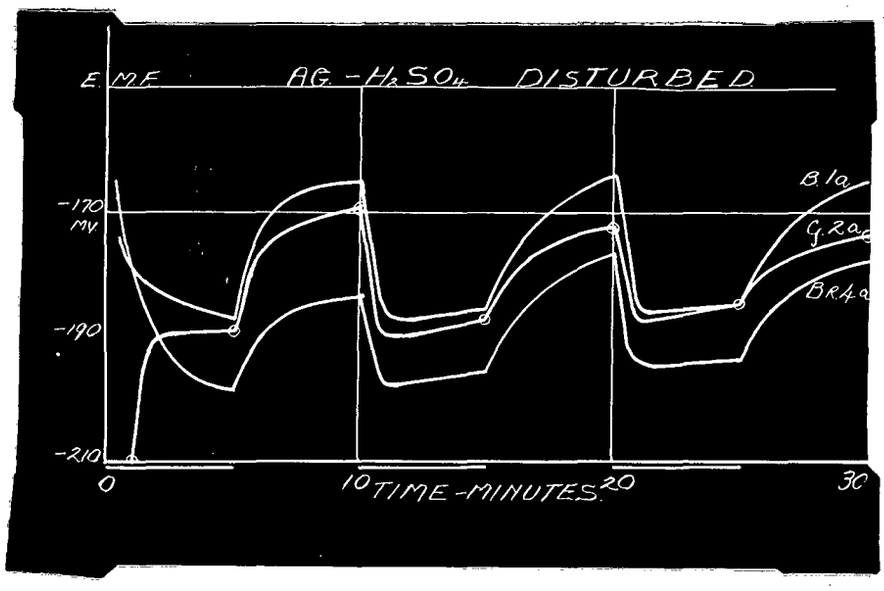
SILVER.

This metal was used as bright Ag, electro-deposited Ag or "R form", and this R form heat treated - the "H form". The electro-deposited Ag is a dead white colour as deposited from a cyanide plating bath, and on heating this it brightens up slightly. Care must be taken during the heating of both bright and R form electrodes, as, if the Ag is heated to too high a temperature, patches of the metal turn a dirty greyish white, and apparently become non-conducting. On heating the R form the Ag skin seems to expand and not contract to the same extent on cooling thus forming wrinkles. Ag as plated on glass according to Nesbery [101], i.e. from an alcoholic solution of ammonio - silver oxide, is rather dull but may be brightened, as with Au, by polishing with an agate burnisher. This apparently does not affect the oxygen electrode properties. The thin films of Ag, when viewed by transmitted light, are a brown colour. The electro-deposited form could be usually used immediately after deposition and washing without any untoward effects on the potential. The metal was unchanged in external appearance after use as an oxygen electrode.

In H_2SO_4:

Undisturbed electrolyte: Bright Ag electrodes in this electrolyte give curves which are not reproducible at all. The potential drifts and jumps in all directions, at all times, for no apparent reasons. It is scarcely possible to find two curves of the same shape amongst all the experiments on bright Ag in undisturbed H_2SO_4,


E.M.F.
Ag - H_2SO_4 UNDISTURBED
-80 MV.
-100
-120
-140
-160
-180
-200
B.4. H INV
B.1c
B.4a
G.1a
G.1b
0
10 TIME MINUTES 20
30

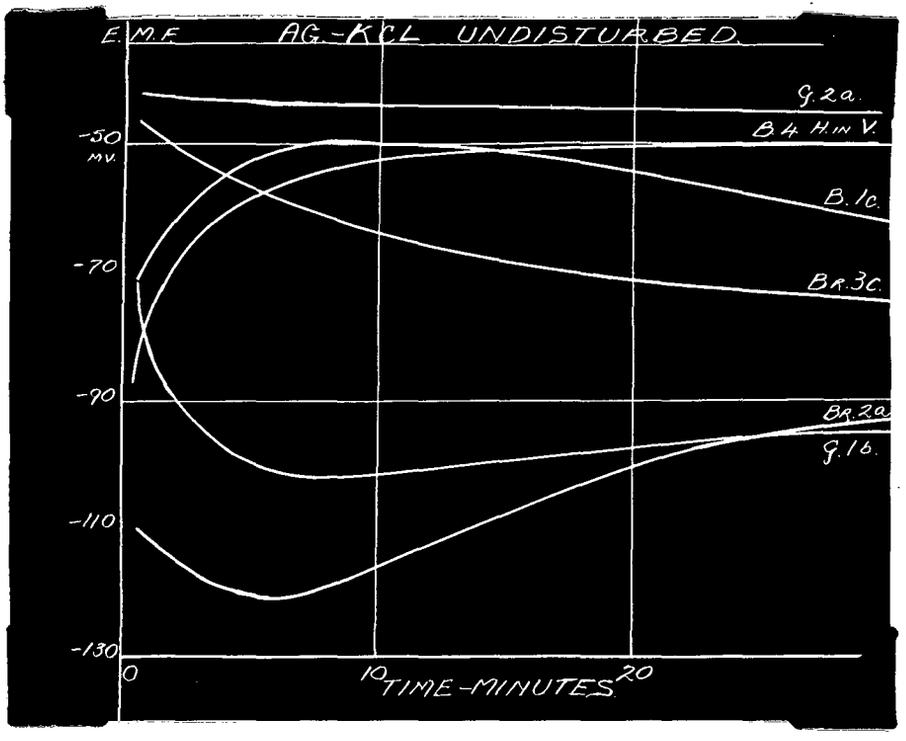

E.M.F.
Ag - H_2SO_4 DISTURBED
-170 MV.
-190
-210
B.1a
G.2a
BR4a
0
10 TIME-MINUTES 20
30

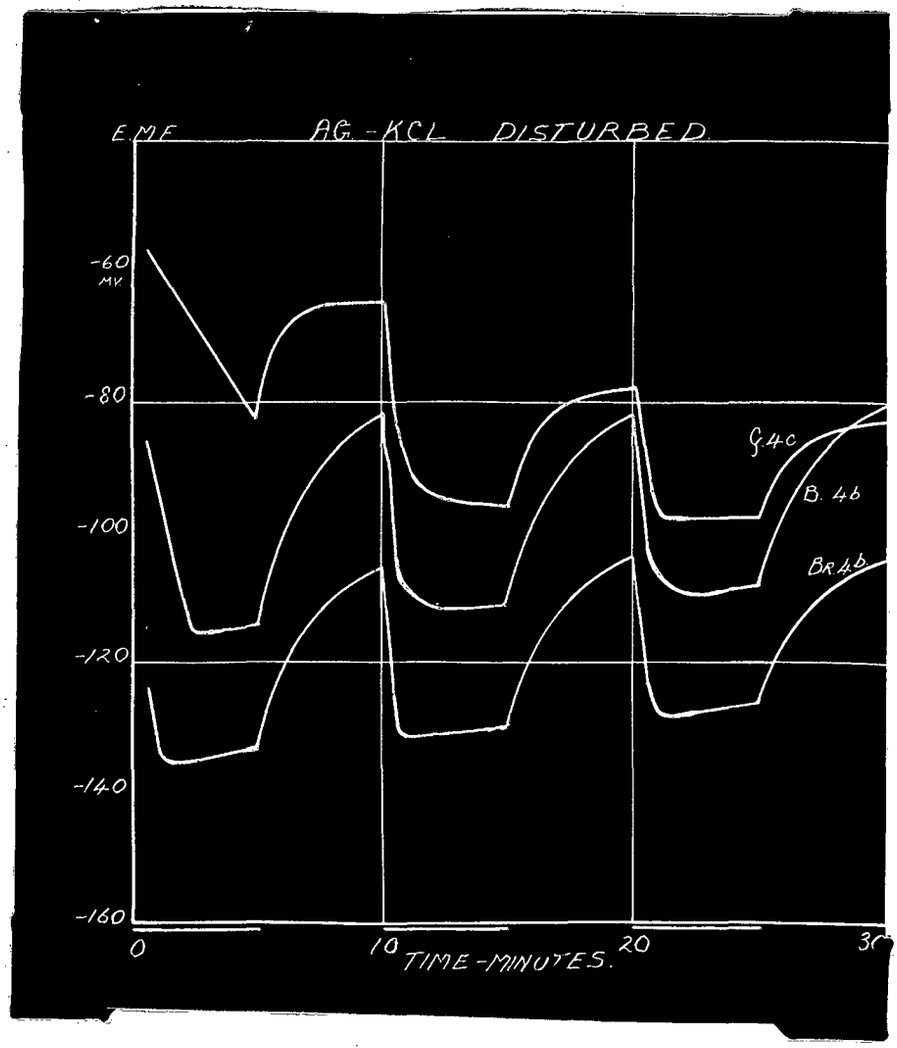
and consequently no graph is shown for this case. This erratic behaviour may possibly be connected with the fact that Ag is known to dissolve in hot concentrated H_2SO_4.

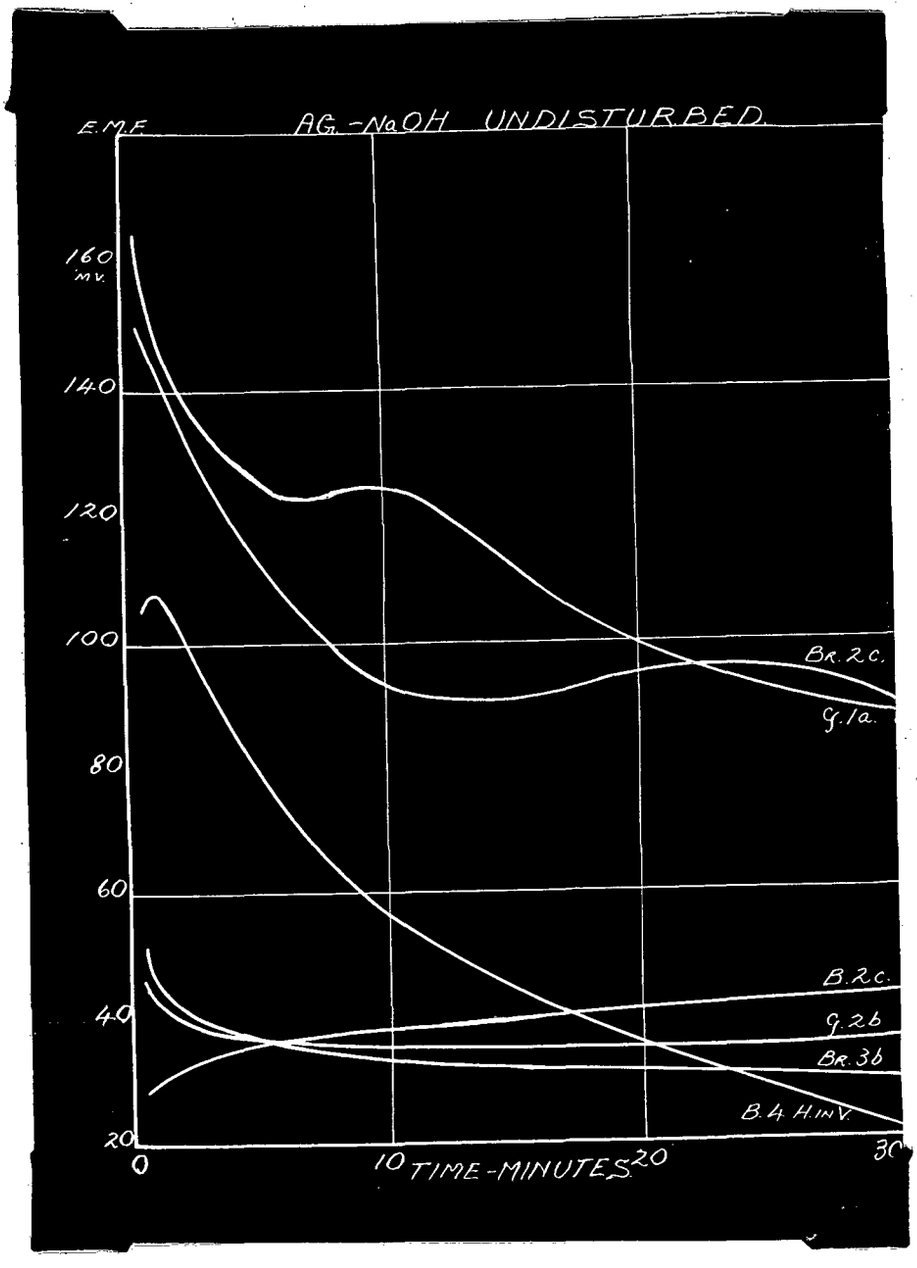
The sudden changes in potential are not caused by slight movement of the electrolyte relative to the electrode since the E.M.F. for bright Ag in H_2SO_4 is only -19 mv., whereas the potential sometimes changes 50-100 mv. in either a positive or negative direction within a few minutes.

The R and H forms, however, are perfectly regular with excellent constancy (0-1 mv.) and a reproducibility of approximately 50 mv. Potential drift for the R and H forms may be in either a positive or negative direction. The R form electrodes usually give slightly higher potentials than the H form, and for both types freshly made electrodes, in general, give the highest potential. In this electrolyte Ag is conspicuous as giving the lowest values for the O_2-H_2 cell of any found throughout the entire investigation. Some bright Ag electrodes finished up with a potential of .38 volts for the O_2-H_2 cell. The R and H forms are slightly better, averaging .54 volts for the O_2-H_2 cell. A R form silver electrode, heated in vacuo, started at the usual initial potential, but rose to a value at least 40 mv. higher than the highest attained by any other R form electrode.

Disturbed electrolyte: Here bright Ag is perfectly normal and gives E.M.F. curves identical in shape and at the same potential as those given by the R and H forms. The reproducibility taking all three forms together is good at 20 mv. Bright electrodes taken alone give a reproducibility of approximately 15 mv., which is a remarkable change from the behaviour of bright Ag in saturated electrolyte. The curves are all very regular in shape, although in a few cases the first period of bubbling is irregular, showing a positive E.M.F.


E.M.F AG.-KCL UNDISTURBED.
G.2a.
B.4 H.IN V.
B.1c.
BR.3c.
BR.2a
G.1b.
-50 MV.
-70
-90
-110
-130
0
10
20
TIME-MINUTES


E.M.F
AG.-KCL DISTURBED.
-60 MV.
-80
-100
-120
-140
-160
G.4c
B.4b
BR.4b
0
10
20
30
TIME-MINUTES.


E.M.F
AG.-NaOH UNDISTURBED.
160 MV.
140
120
100
80
60
40
20
BR.2c.
G.1a.
B.2c.
G.2b
BR.3b
B.4 H.INV.
0
10
20
30
TIME-MINUTES.

Average values of M.E.F. are: bright Ag -19 mv., R form -15 mv., and H form -14 mv. Time has very little effect on the M.E.F. The trend of the curves is very slight and may be either positive or negative. Since bubbling of oxygen seems to improve the reproducibility of bright Ag to such a marked extent, two bright Ag electrodes were tried with continuous bubbling of oxygen for a full 30 mins. The curves given were perfectly regular and fairly reproducible, being well within 10 mv. of each other after 30 mins. in the electrolyte. The constancy was good at 1-2 mv. The position of the curves was at the same potential as that given by the average R and H forms of metal electrodes. It seems that in some way bubbling of oxygen renders the bright Ag passive, and it stops dissolving. What is very difficult to explain, however, is how the R form has become passive without any bubbling of oxygen. There is far less likelyhood of an oxide film being present on a cathodically deposited metal than on a bright Ag electrode, which has been heated in air. Consequently it hardly seems that the passivity could be explained by assuming that the bubbling of oxygen caused the formation of an oxide film over the bright Ag electrodes.

In KCl:

Undisturbed Electrolyte: In this electrolyte bright Ag behaves normally again, giving similar curves to those given by the R and H forms. The average value for the potential of the O_2-H_2 cell is still very low, approximately .6 volts. Potential drift varies considerably, and may be in either a positive or negative direction. Electrodes often show a drift in both directions during the thirty minutes in the solution. Reproducibility for the R and H forms is poor at 60-80 mv., but for bright electrodes is 30 mv. Constancy for bright electrodes is 3 mv., for R form 7 mv. and the H form 1 mv. Freshly deposited R form

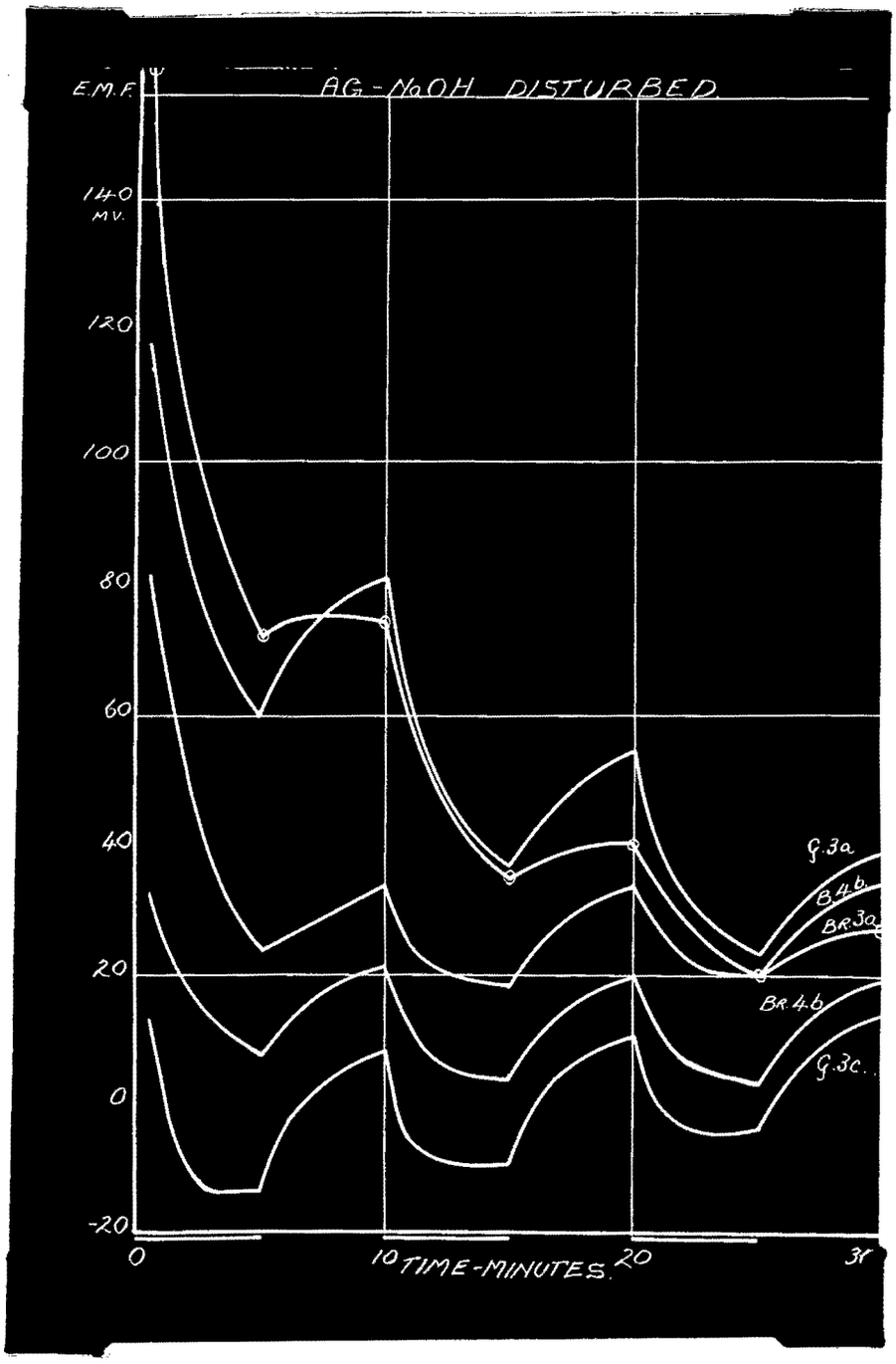
electrodes usually give the lowest potential of all. The R form electrode heated and cooled in vacuo gave the same results as an air-treated R form electrode.

After heating an R form electrode in order to obtain the A form, the Ag skin wrinkled up on cooling and came away from the glass at the top. Using this electrode, after electroplating a fresh deposit of Ag on the H form, it was found to give exceptionally low results. This was traced to the presence of a small quantity of plating bath solution, which had remained between the glass and the wrinkles in the Ag skin at the top of the metallic film. An ordinary electrode dipped into the plating bath and used without washing, gave similar exceptionally low values.

Disturbed electrolyte: The M.E.P3s in this electrolyte are approximately -20 mv. for all forms of metal. The values tend to decrease with time. Reproducibility is not very good - 30 mv. for bright or R form electrodes and 50 mv. for the H form electrodes. The trend of the curves may be either positive or negative. The first periods of bubbling are here regular, i.e. they give negative M.E.P's.

In NaOH:

Undisturbed electrolyte: The values given by Ag for the O_2-H_2 cell are excellent for this electrolyte, compared with the corresponding values in KCL and H_2SO_4 where they seldom exceed .6 volts. In NaOH the highest value recorded was 1.13 volts, given by a fresh H form electrode immediately on immersion. The average value for the O_2-H_2 cell lies in the neighbourhood of .97 volts. Reproducibility is poor except forthe R form (30 mv.). The poor reproducibility in the other cases is due to some of the graphs being very irregular. These irregular curves occur sometimes with freshly made electrodes, and sometimes with electrodes with other histories - there appears to be no connection between


AG-NaOH DISTURBED
E.M.F.
140 MV.
120
100
80
60
40
20
0
-20
0
10 TIME-MINUTES.
20
3r
G.3a.
B.4b.
BR.3a.
BR.4b.
G.3c.

previous history and irregularity.(Cf. curves G1a.,G2b.,and curves Br.2c., Br.3b.)

The magnitude of potential drift varies continuously; the direction of drift may change more than once during the 30 mins. The constancy for these irregular graphs is very poor, but for the others is fair at 1-2 mv. Freshly heated H form electrodes give the highest oxygen potential. An R form electrode was heated and cooled in vacuo, and gave a curve similar to a fresh, H form electrode, although not starting at so high a potential. This is the only case among the electrodes heated in vacuo, where the initial potential is fairly high, and the potential falls with time; usually the initial potential is low and the potential rises with time. Actually, even in this case, the potential did rise to a maximum after about one minute in the electrolyte, after which it fell steadily.

Disturbed Electrolyte : The general trend here is away from the theoretical oxygen potential, although this trend becomes much less if the electrode is kept in air or under distilled water. A few R and H form electrodes show a positive trend. The bright and H forms average -20 mv. E.M.F. and the R form -15 mv. In general the E.M.F. decreases with time. Reproducibility is 30 mv. for the R and H forms, but very poor for the bright electrodes. The first period of bubbling is usually quite regular. The highest potential attained was 1.14 volts, by a freshly heated bright electrode.

OSMIUM

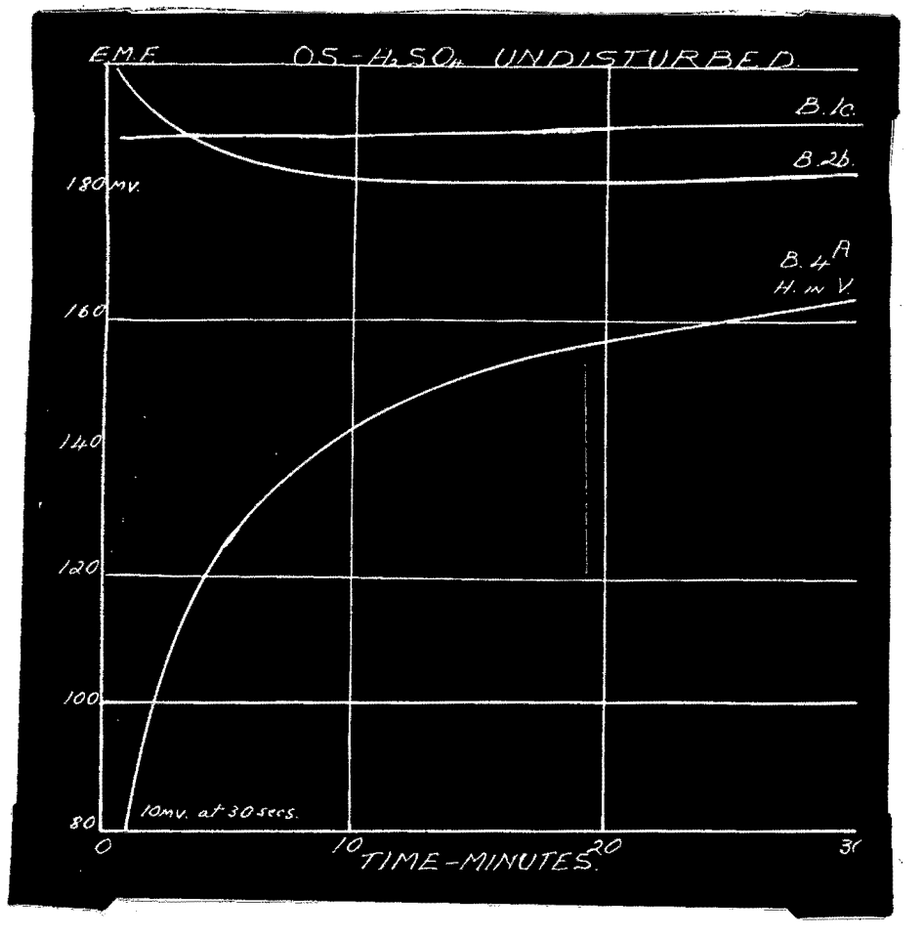
Since OsO_4 is so easily volatilised this metal could not be plated on glass by decomposition of it's salts by heat. A coating of black Os was therefore deposited on a base of bright Pt on glass. In a few cases other metallic bases on glass were tried, notably Rh and Ag. Os black, of course, could not be heated in air in order to grey it, and it was

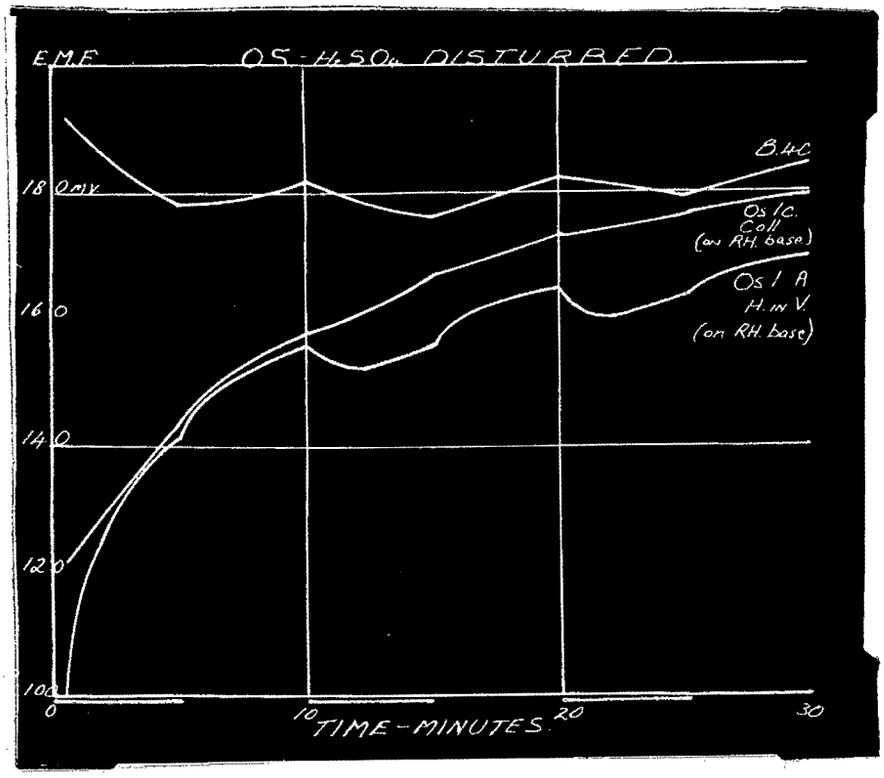
therefore be tested and cooled in vacuo. The electrolytically deposited metal is liable to retain hydrogen very persistently, and the black electrodes must usually be kept in air or oxygen for 48 hours after making, before they can be satisfactorily used as oxygen electrodes. Such electrodes, kept in air for 48 hours before use, are referred to with the letter "A" in the graphs. The black, which is well known as having a tremendous capacity for dissolving hydrogen, has only to be kept in air or oxygen for 24 hours after use, in order to eliminate this hydrogen. It seems, then, that either os black has a still greater capacity for dissolving hydrogen, or else it is far more sensitive to small traces of hydrogen, which might remain.

The black metal is not as rough in appearance as at or rd black, but has a slight sheen on the surface. It is quite easily rubbed off with the fingers, however, just as at or rd black are. Some of the black electrodes have a shiny, silvery appearance when immersed in the electrolyte, as if they have not been wetted properly, and as if there were a thin film of air between the metal and the solution. The potentials, however, are quite normal.

In H_2SO_4:

Undisturbed electrolyte: The constancy of the os electrode in this electrolyte is excellent, usually being considerably less than 1 mv. Reproducibility is good at 1 mv., but may be improved to the excellent figure of 0 mv., if the electrodes are kept in an oxygen atmosphere. The general trend of the curves is usually in a slightly negative direction. The other base metals were used in addition to os, on which to deposit the os black. These were bright Pt and bright Ag. The os electrode on the Pt base gave results identical with those given by an os electrode on a Pt base. When using Ag as the base, however, very low potentials were recorded. Bright Ag in H_2SO_4 gives

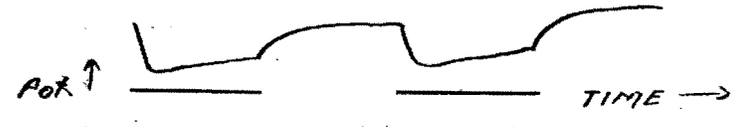

E.M.F
Os - H_2SO_4 UNDISTURBED.
B.1c.
B.2b.
180 MV.
B.4 A
H. in V.
160
140
120
100
80
10mv. at 30 secs.
0
10
20
30
TIME-MINUTES.


E.M.F
Os - H_2SO_4 DISTURBED.
B.4C.
180 MV.
Os 1C.
Coll
(on RH. base)
Os 1 A
H. in V.
(on RH. base)
160
140
120
100
0
10
20
30
TIME-MINUTES.

.5 volts referred to a hydrogen electrode in the same electrolyte, and Os, deposited on a Pt base, about .89 volts but Os on a Ag base gave approximately .65 volts. So that in the case of Ag, at any rate, the base metal has a very definite effect on the potential. Os electrodes heated in vacuo give, initially, potentials about 160 mv. lower than is usual, but this initial value rises rapidly on after 30 mins. approaches within 20 or 30 mv. of the corresponding potential given by air-treated electrodes. After keeping in air or under distilled water for 24 hours, the electrodes are quite normal.

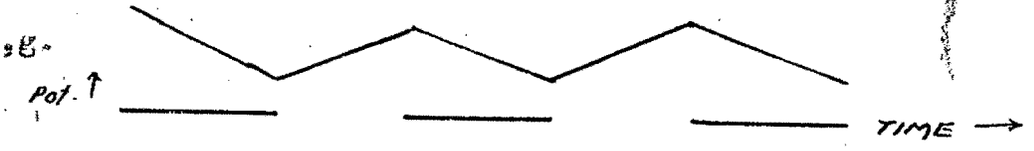
Disturbed Electrolyte : Reproducibility in this electrolyte is approximately 15 mv. The curves are regular throughout all three periods of bubbling. The values of the E.M.F. are very low, averaging -3 mv., which value tends to decrease with time. The general trend of the curves is slightly in the more noble direction. Some electrodes were collodionised and used. These started at a lower potential than the others (60-70 mv. lower), and rose fairly regularly, without showing much change with bubbling, to the usual final values given by uncoated electrodes. The E.M.F. was therefore positive for these collodionised electrodes. One electrode, which had been heated in vacuo, was used and showed a negative E.M.F. of -4 to -5 mv., but the curve was different from the air-treated E.M.F. curves. The curve of the electrode heated in vacuo showed a minimum value after about one minute's bubbling, when the potential started to rise again, although bubbling was still continued.

e.g.

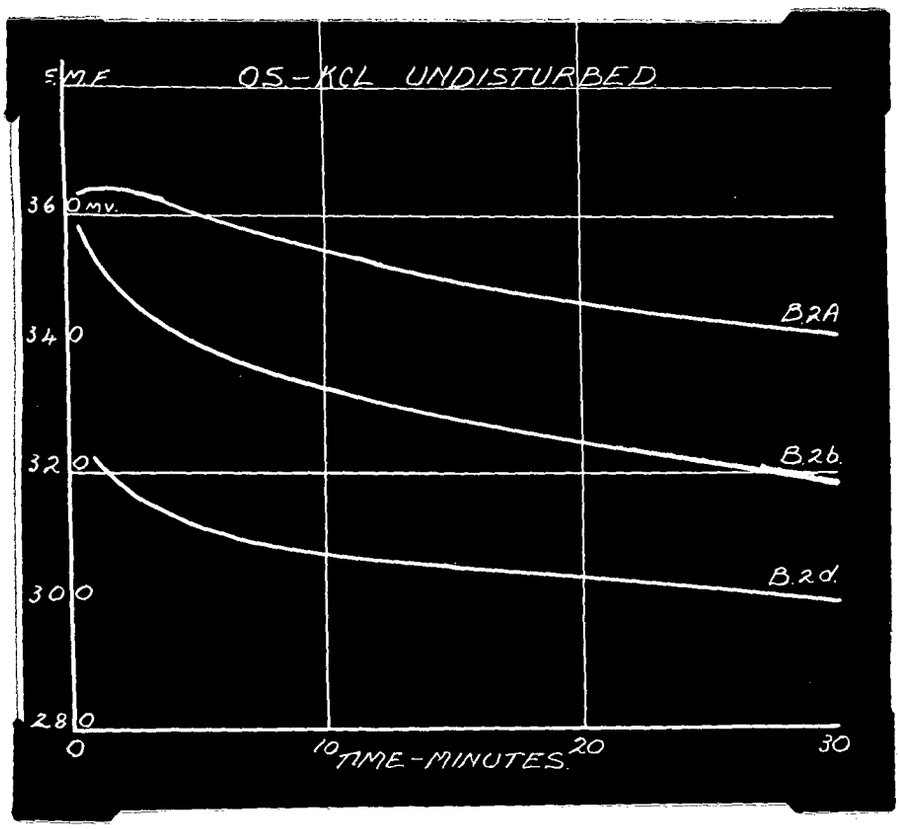


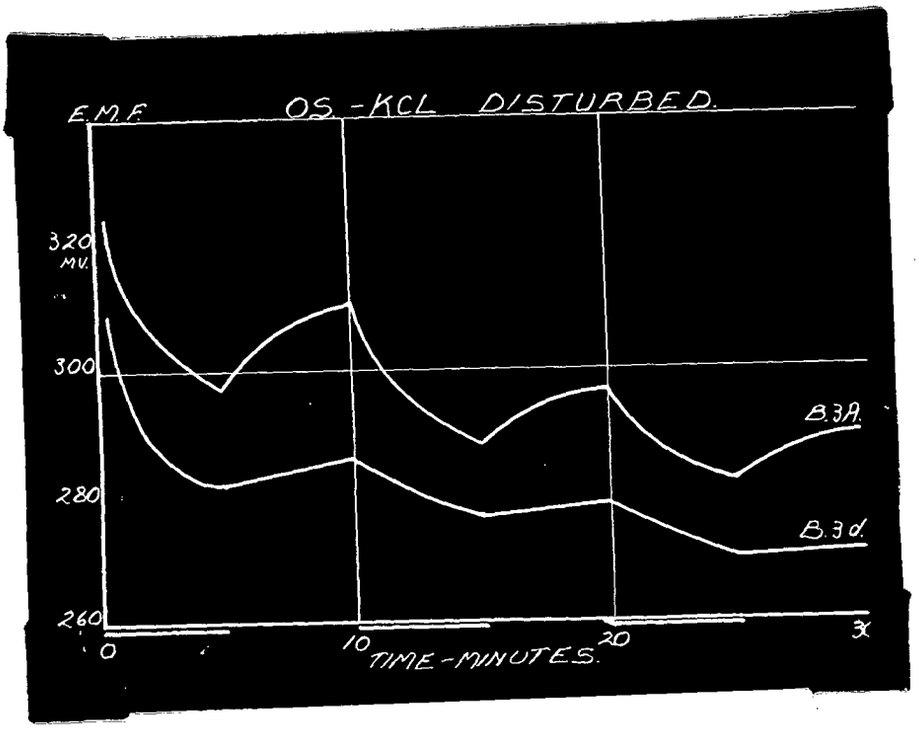
The usual type of E.M.F. curve given by the air-treated Os electrodes in H_2SO_4 consists almost of straight line sections

e.g.



In KCl :


E.M.F
0.5.-KCL UNDISTURBED.
360 MV.
340
320
300
280
B.2A
B.2b.
B.2d.
0
10
TIME-MINUTES.
20
30


E.M.F.
0.5.-KCL DISTURBED.
320 MV.
300
280
260
B.3A.
B.3d.
0
10
TIME-MINUTES.
20
30

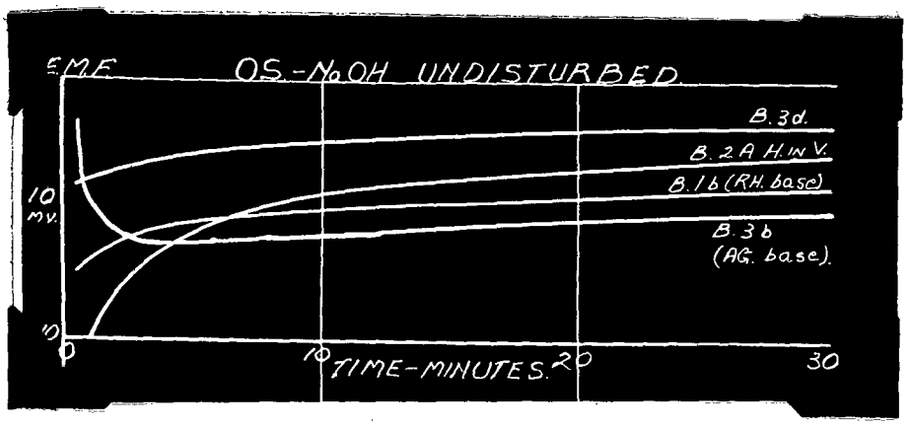
In KCl:

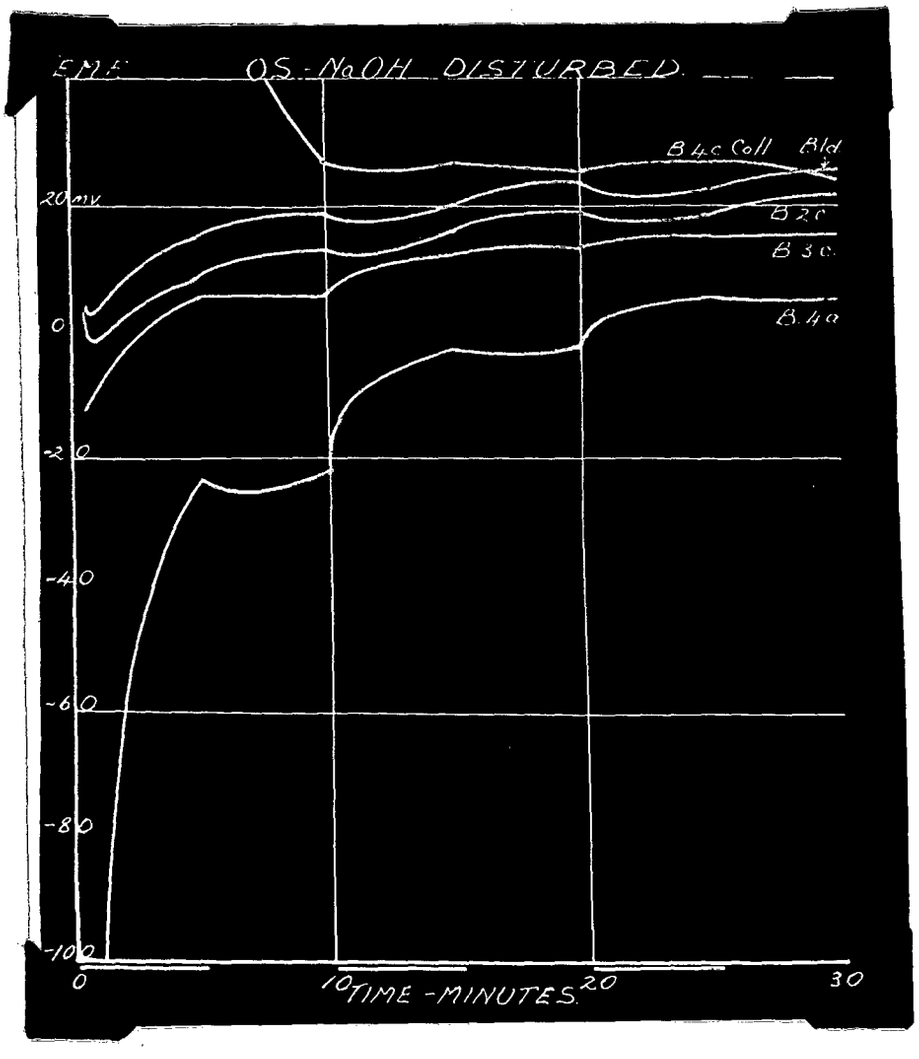
Undisturbed Electrolyte: In KCl both the constancy and reproducibility are considerably less satisfactory than in H_2SO_4. The constancy is approximately 5 mv. and the reproducibility 60-70 mv. Keeping in an oxygen atmosphere does not inprove the constancy but lowers the potential approximately 30 mv. If the electrodes, which have been kept in oxygen, are taken alone, they give a reproducibility of 25 mv., but including all the different histories the reproducibility is 60-70 mv.

The curves in this electrolyte are grouped together according to the previous history of the electrodes. In the figure the groups are represented by single graphs. Thus the group at the highest potential consists of freshly bleched electrodes, and the group at the lowest, of electrodes kept in an oxygen atmosphere. A similar, but much more definite grouping according to the previous history of the electrodes was found with Os in disturbed NaOH. In the case of NaOH, however, the electrodes kept in an oxygen atmosphere give the highest potentials, and fresh electrodes the lowest.

The general trend of the curves is in a less noble direction. An electrode treated in vacuo commenced at a potential 320 mv. lower than the usual, and after 30 mins., the potential was still 230 mv. lower than the usual final values.

Disturbed Electrolyte: The general trend of the curves is definitely in a less noble direction. The M.E.P. is considerably higher than in H_2SO_4, averaging -11 mv. Reproducibility is approximately 20 mv. M.E.P. decreases slightly with time. Freshly made electrodes give the highest M.E.P. values. Keeping in oxygen reduced the M.E.P. to much the same extent as keeping in air, and also reduced the oxygen potential


EMF
0.5-NaOH UNDISTURBED
B.3d.
B.2A H.in V.
B.1b (RH. base)
B.3b
(AG. base).
10
mv.
0
10
TIME-MINUTES.
20
30


EMF
0.5-NaOH DISTURBED
B.4c Coll
B.1d
20 mv.
B.2c
B.3c
B.4a
0
-20
-40
-60
-80
-100
0
10
TIME-MINUTES.
20
30

by 10-20 mv.

In NaOH:

Undisturbed Electrolyte: In this electrolyte Os behaves very much as it did in H_2SO_4. Constancy is very good at 1 mv. and reproducibility at approximately 15 mv. The general trend of the curves is in a positive direction. In NaOH the Os electrode on a Ag base gave a curve similar to the usual curve, but at a potential 10 mv. lower than usual. Of course, bright Ag in NaOH gave curves at much the same potential as bright Pt electrodes, so one would expect very little difference between an Os electrode on a Pt or Ag base in this particular electrolyte.

An Os electrode on a Pt base, on heating in vacuo, gave curves at the same potential as, and similar in shape to those given by ordinary air-treated electrodes. Freshly blacked electrodes gave very low initial values, but rose rapidly to the usual steady potential of approximately 0.0 volts referred to the N HgO electrode, i.e. it seems that even 48 hours standing in air or oxygen is not sufficient completely to eliminate the occluded hydrogen, if the electrode is used in NaOH.

Disturbed electrolyte: The M.E.P. for freshly made Os electrodes is highest, even reaching +10 mv., but after continued use the M.E.P. drops and eventually become negative, giving values of approximately -2 mv. The average M.E.P. for all cases is +3 mv. In all cases the first period of bubbling gives a positive M.E.P. The M.E.P. usually decreases with time. Reproducibility is good. The general trend of the curves is in a positive direction. The curves in this case are grouped together according to previous history in a way more marked than in any other case.

The group showning the highest potential is one of

several electrodes, which have been used a number of times and finally kept in an oxygen atmosphere before these readings were taken. The curves never differ from one another by more than 1 or 2 mv. throughout the 30 mins. At a potential of about 5 mv. less noble is a second group of electrodes, which have been used several time, but kept in air only, while not in use. Five mv. lower still is a third group, which consists of electrodes which have been used once only, kept in air or under distilled water and used again giving these curves. Freshly made electrodes make up the final group a further 10-15 mv. lower, and here the curves do not follow one another quite as closely as in the previous groups. In the figure, the groups are represented by single graphs. A similar grouping is shown by Os in undisturbed NaOH, but it is not nearly as clearly defined as in the case of undisturbed electrolyte.

One Os electrode was coated with collodion, and it started at a potential of 1.19 volts referred to a hydrogen electrode in the same electrolyte. This value fell rapidly, within 10 mins., to the usual potential of about .06 volts. The M.E.P., which should have been approximately -2 mv., since the electrode had been used several times previously, was finally, however, + 1 mv.

This metal, Os, gives the most constant and reproducible results of all the metals in NaOH and H_2SO_4, together with a very low M.E.P. and reasonably high oxygen potentials. By careful standardisation of procedure this electrode could possibly be developed into a very useful instrument for direct pH measurements in alkaline or acid solution. If the Pt base could be eliminated, it would possibly be found that Os alone would behave even better as far as constancy and reproducibility are concerned. In neutral solution Pd

black gives results as constant and reproducible as Os does in the other electrolytes, and could possibly be similarly developed.

DISCUSSION AND GENERALISATION OF EXPERIMENTAL RESULTS :

Most workers, who have turned their attention to the problem of the oxygen electrode, have confined their experiments to Pt, and, on a limited set of observations, have boldly stated that such and such a form of metal is best to use, or that the electrode is more reproducible in this or that electrolyte. As a result, different workers have come to different, and sometimes completely incompatible, conclusions. During the present investigation close on 15,000 readings were taken, and the greater the volume of experimental results the less did it seem possible that any accurate, comprehensive generalisations could be made, so little regularity was shown by the data obtained. Taking limited portions of the data only, certain generalisations seemed fairly obvious but, as more data was accumulated, it became evident that these generalisations were, in most cases, not nearly general enough to deserve the name. Consequently, when generalisations are made from limited data, they may very easily lead to conclusions which further experimental work would prove to be of only very limited application. In consequence of the large number of experimental results here obtained it is considered that any generalisations made will carry more weight than those obtained with less extensive data.

A number of graphs have been arranged as an appendix These are curves averaged from the experimental ones in each electrolyte, and then calculated to refer to the hydrogen electrode in the same electrolyte. Thus the E.M.F. values are those of the O_2-H_2 cell, and

the values given by the different forms of metal in the different electrolytes may be difectly compared. Except in cases where separate curves are given for the oxidised and grey metal, the bright curves are averaged from all the bright and oxidised experimental curves, and the black from all the black and grey result. This, of course, only refers to metals which have been respectively oxidised or greyed. No "H.in V." or "Cell" curves are included.

Curves Obtained in Undisturbed Electrolyte: These curves may be, very roughly, devided into two classes: (a) Curves that fall and tend to become steady with time, and (b) Curves that rise and tend to become steady with time. Some, of course, do not become steady, but in most cases a steady potential is approached after 30 mins. The drift which still remains may be either in a positive or negative direction. During the first few minutes, immediately after immersion in the electrolyte, a change in the direction of the potential drift is often found. In neutral soultion, however, this change of direction instead of taking place within a few minutes seems to be spread out over a much longer period - sometimes changing slowly throughout the 30 mins. This later change of direction is hardly ever found in NaOH or H_2SO_4 if we omit the metals Au and Ag. In many cases no initial or later change in direction of potential drift is found, and this may be due to the change taking place too rapidly to be shown up by readings taken at the timeintervals which have been used. Only in a few cases, especially Ag, grey Pt and Au in H_2SO_4, is a double change in the direction of the potential drift found, i.e. a curve which, say, falls, then rises and finally falls again.

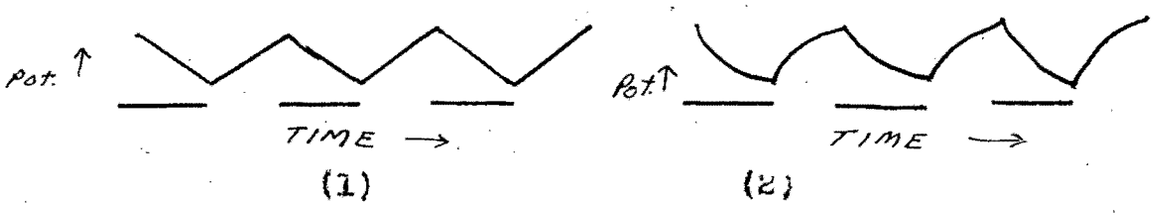
An attempt was made to classify the metals according to whether they fell in group (a) or (b), but there was

no regularity evident. Bright, oxidised and grey forms of metal show no decided preference, about 50% falling in each group. The black form of electrode, however, shows a slightly greater tendency to rise, i.e. 60% of the black form of metals fall in class (b). Of the rising curves, approximately 45% occur in NaOH, 34% in KCL and 20% in H_2SO_4. Of the falling curves approximately 43% occur in H_2SO_4, 30% in KCL and 27% in NaOH. Here there is nothing very definite to go on, and there seems to be no generalisation as to which type of previous history of the electrode provides the most class (a) or class (b) curves.

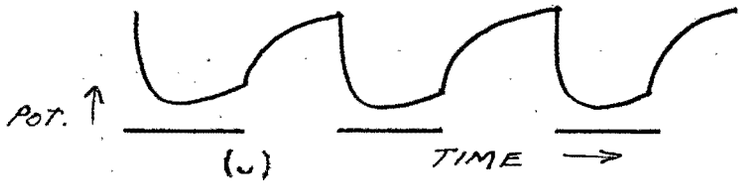
Curves Obtained in Disturbed Electrolyte. These may be divided, roughly, into the same two classes as the curves obtained in undisturbed electrolyte, i.e. (a) Curves that have a general trend in a positive direction, and (b) Curves that have a general trend in a negative direction. In this case there are slightly more definite indications as to which form of metal falls into which class. 71% of the black metals and 60% of the bright metals fall into class (a), but again oxidised and grey metals show no decided preference. Alkaline solution again promotes the rising type of curve, but more definitely in this case. Of the rising curves, 55% occur in NaOH, 27% occur in H_2SO_4 and 18% in KCL. Class (b) is specially evident in neutral solution: 66% of all class (b) curves occur in KCL, 25% in H_2SO_4, and 9% in NaOH. Thus again we find alkaline electrolyte tending to raise the potential towards the theoretical oxygen potential. The previous history of the electrodes seems to have no very definite effect in either direction.

Curves in disturbed electrolyte may, however, be

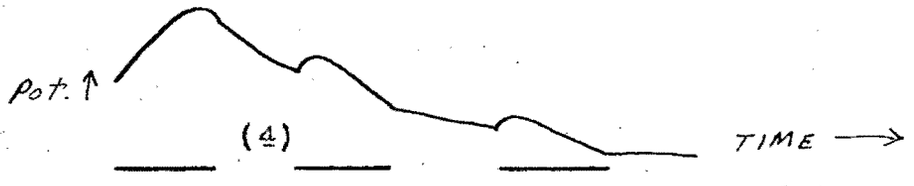
classified as well according to the type of curve given during the individual bubbling periods. The two main types are approximately as illustrated:



The general trend of the curve may, of course, be in either direction. The individual sections of the curve consist of, (1) almost straight lines, sometimes with a slight curve, and (2) definitely curved lines. The curved type often developes further, and the potential commences to rise while bubbling is still continued e.g.



But in general we have the two types (1) and (2) which will in future be referred to as the type (1) and type (2) of E.M.F. curve. In a few cases a different type of E.M.F. curve is found, e.g. Bright ir in KOH and Grey Fe in KOH,



but this usually developes rapidly into a type (1) curve. In many cases the initial periods of bubbling produce a type (1) curve but later it changes to type (2). It seems, then, that there is some relationship between all the four types of E.M.F. curve. Type (4) developes into type (1) with time; this development continues from type (1) to type (2), and finally from type (2) to type (3), which is the final and steady type. Judging from the few E.M.F. curves that have been published, either

Table 6.

Metal.	Average E.M.F. of the Metals in millivolts.		
	H_2SO_4	KCl	NaOH
Br. Pt.	-27	-14	-19
B. Pt.	-30	-13	-9
G. Pt.	-40	-12	-12
Br. Pd.	-10	+1.5	- 7
Ox. Pd.	-10	-19	- 6
B. Pd.	-24	+4	-11
Br. Ru.	-16	- 9	-4
Ox. Ru.	-18	-18	- 5
B. Ru.	- 5	- 8	+ 4
Br. Rh.	-46		- 6
Ox. Rh.	-40	-21	- 4
B. Rh.	-15	- 7	- 1
G. Rh.	-28	- 4	-11
Br. Ir.	-11	- 5	- 6
Br. Ag.	-19	-22	-19
B. Ag.	-15	-21	-15
G. Ag.	-12	-18	-20
Br. Au.	+23	+ 3	- 8
B. Au.	+13	+ 7	0 (+5 to -5)
G. Au.	+20	+ 1	-10
B. Cu.	- 3	-11	+ 2

Br. = Bright metal ; Ox. = Oxidised Metal ;

B. = Black or electro-deposited metal ;

G. = Grey or heat-treated black metal.

for metal or gas electrode M.E.F., it appears that type (1), at any rate, has never been observed before.

This type (1) M.E.F. curve is shown by each of the metals at some time or another, but it undoubtedly predominates in neutral solution - only Ag and Os show no type (1) curve in KCL. Black Os shows it, however, in H_2SO_4, bright Ag in NaOH and Ir and Ru in all three electrolytes. Very similar M.E.F. curves are given in H_2SO_4 by Ru, Ir and Os, in KCL by Ru, Pt, Pd, Rh, Ir and Au, and in NaOH by Ru, Ir and Ag. It is noticeable that the M.E.F. curves of Ir and Ru are very similar in all three electrolytes.

Numerical Values of M.E.F. :

In the table on the opposite page are given the average values of the M.E.F., in millivolts, of each form of each metal in all three electrolytes, ~~together with the highest and lowest values recorded in each case~~.

In discussing the numerical values of thevarious M.E.F.'s, these are calculated from the second and third periods of bubbling only or, in some cases,from the third period only, since, in many cases, the first and sometimes the second period of bubbling produces a M.E.F. of opposite sign and widely different in magnitude from that given when the electrode has settled down. Of course, in cases where the M.E.F. is of type (1), the maximum M.E.F. is never realised as the potential falls steadily throught the 5 min. period of bubbling.

In general M.E.F. appears to decrease with time, although every metal has some curves where M.E.F. increases with time. Most of these increases occur in alkaline solution. This generalisation is much improved if Au and Ag are left out, since these two metals have fewest increases with time, and these increases are spread out

evenly over all three solutions. The most increases of E.M.F. with time are found with Rh, Ir and Pt. The lowest E.M.F. values are given in alkaline or neutral solution. In $HClO_4$ the values are almost always the highest - the one exception is Ag. Tartar & Wellman[75] state that the change of potential with change of rate of flow of electrolyte is most marked in alkali - this appears to contradict the above statement that E.M.F. is usually lowest in alkaline electrolyte. The black or grey metal is usually the best for low E.M.F. values, the only outstanding exception being Pd, where the black metal gives a higher E.M.F. than the bright or oxidised forms in all electrolytes. Although E.M.F. is reduced, in most cases, by using the black form of the metal, it is quite definitely not eliminated as is the case with the E.M.F. of hydrogen electrodes[79]. The E.M.F. of the bright and oxidised forms is, as a rule, much the same.

E.M.F. is highest in 70% of the cases, when the electrode has been freshly made. After use and keeping in air, Oxygen or under distilled water the E.M.F. decreases in general.

Black Ru and black Os give extraordinarily similar E.M.F. curves in all three electrolytes and also give values for the E.M.F. which are among the lowest. These two metals have probably the greatest liking for oxygen of any of the Pt metals and this has, possibly, some bearing on their behaviour when the concentration of oxygen is suddenly increased, by bubbling the gas round the electrode. The following is a table of the average E.M.F's in all electrolytes:-

Table 4.

Metal.		Average H.E.P.
1.	Os	5.30 m.v.
2.	Ir	7.3 mv.
3.	Ru	9.0 mv.
4.	Au	9.3 mv.
5.	Pd	10.2 mv.
6.	Rh	16.4 mv.
7.	Ag	17.8 mv.
8.	Pt	21.1 mv.

In all cases some type (1) curves are found where the H.E.P. does not reach a maximum, but with Ir and Ru this occurs in all three electrolytes, whereas with other metals it only occurs in one electrolyte, usually KCl. As a result Ir and Au should probably be further down the list, if only the maximum H.E.P. were taken into consideration.

Müller and Konopicky[96], in dealing with metal electrode H.E.P., state that there is no change in potential when an electrode is rotated in an electrolyte, unless that metal is attacked by the electrolyte. This may account, in part, for the fact that the values for oxygen electrode H.E.P. are so low, since the Pt metals are among the most unattackable electrodes known. The H.E.P. for the black form of metal is, however, usually less than that for the bright form, whereas one would expect the finely divided black metal to be much more easily attacked, if any attack is taking place, than the other forms and consequently on the basis of Müller and Konopicky's statement, to have a larger H.E.P.

A few experiments were tried using electrodes coated with collodion. This collodion, when dry, provides a protective covering over the electrode, but the coat contains innumerable tiny pores, which enable the

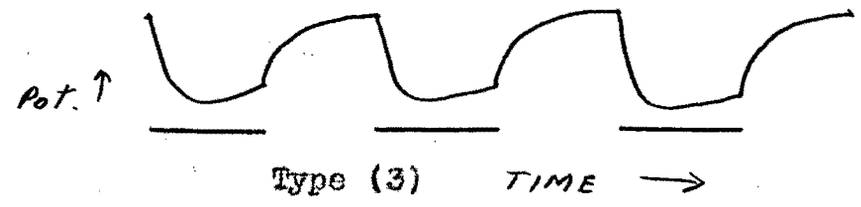
electrolyte to reach the electrode, but which prevent immediately round the electrode any mechanical disturbance of the solution, such as might be caused by bubbling gas or stirring the main body of electrolyte. However, the increased concentration of oxygen at the electrode brought about by bubbling, would still be available at the electrode surface by diffusion. On using these coated electrodes in quiescent electrolyte, they gave potentials just the same as, and just as easily as uncoated electrodes, thus showing that the electrolyte can easily penetrate the tiny pores in the collodion. When used in disturbed electrolyte, the M.E.F. was drastically changed in the few cases tried, although the final potentials were just the same as with uncoated electrodes. Of course, in order to make any definite statements regarding the effect of collodion coatings on the M.E.F., all the M.E.F. results would have to be repeated using collodion coated electrodes, on account of the marked irregularities found among the metals during this work. This it was not found possible to do, but several metals were picked out and tried in acid and alkaline solutions. Pt was chosen because it gave, with uncoated electrodes, such high negative values for the M.E.F. Bright Au was chosen because of the high positive values found for the M.E.F. in H_2SO_4, and because in NaOH an average value for the M.E.F. is given. Finally Cu was used because of the very low M.E.F. values given in H_2SO_4 and NaOH. Thus the effect of a collodion coating on a high positive, a high negative, an average and a low positive M.E.F. was examined. The following table gives the effect, on the M.E.F., of coating an electrode with collodion:-

Table 5.

Metal.	M.E.P. (Bare Metal)	M.E.P. (Collodionised Metal)
Black Pt	-50 mv. in H_2SO_4	+ 2 mv. in H_2SO_4
Grey Pt	-10 mv. in NaOH	+ 2 mv. in NaOH
Bright Au	+23 mv. in H_2SO_4	+ 15 mv. in H_2SO_4
Bright Au	- 8 mv. in NaOH	+ 6 mv. in NaOH
Black Os	- 3 mv. in H_2SO_4	+ 5 to + 10 mv. in H_2SO_4
Black Os	- 2 mv. in NaOH	+ 1 mv. in NaOH

In all the cases tried - and the M.E.P. with these metals, when uncoated, varies a lot - the M.E.P. is positive in sign, and usually of small numerical value. The total variation of M.E.P. with the collodionised metals is only 14 mv., whereas with the corresponding metal the variation is 73 mv.

With every metal at one time or another an M.E.P. curve of type (3) is given,



Type (3)

i.e. the potential, after commencing to fall, begins to rise while the bubbling is still continued. It seems that by covering the metal with collodion the first rapid drop of potential is eliminated, and the smaller positive movement shows through. This first rapid drop would then appear to be due mainly to mechanical disturbance and probably the secondary rise is due to increased concentration of oxygen round the electrode. In some cases, presumably, the first rapid drop completely obscures the second slight rise, i.e. when M.E.P. curves of a different form to type (3) are given.

Constancy and reproducibility:-

The constancy, of course, only refers to metals when used in undisturbed electrolyte, but the reproducibility includes the results in disturbed electrolyte. In general, the reproducibility of the metals is better in disturbed electrolyte, when M.S.R. is in action, than in undisturbed electrolyte. An extreme case of this is bright Ag in H_2SO_4. In undisturbed electrolyte there were no two similar curves, but in disturbed electrolyte reproducibility was excellent at 20 mv.

The generalisations for constancy and reproducibility are much the same throughout - there seems to be some connection between the two quantities. Both the best reproducibility and the best constancy are found in alkaline electrolyte, followed by KCl and H_2SO_4 in that order. This is contrary to the experience of Furman [15,16], Tartar and Wellman [75], and Tartar and Walker [76], all of whom found the oxygen electrode more constant in acid than in alkaline solution. Even considering Pt only, the metal to which these investigators restricted themselves, the experience obtained during this work is still contrary to the opinion expressed by the above three groups of workers. In this investigation the films of metal used were extremely thin - of the order of 10^{-4} cms. in thickness - whereas the above-mentioned workers used massive metal, and this may have something to do with the differences observed.

In all three electrolytes freshly made electrodes usually give the worst constancy and reproducibility, whilst after keeping in air, oxygen or under distilled water, both constancy and reproducibility improve.

Again the best form of metal to use for either a good constancy or a good reproducibility is generally the black or rough electro-deposited form. The exceptions for the

two cases are, however, different. For Ag and Au the best form to use in either case is the grey or H form, but bright Pt gives better constancy than black, and bright Ir gives the best reproducibility (since the black Ir deposits were so unsatisfactory from the point of view of reproducibility).

Burman[15,16] and Tarter and Walker[76] found a maximum potential drift for Pt of 30-60 mv. per hour in alkali, and 5-10 mv. per hour in acid solution. The following tables give the average constancy and reproducibility in all three electrolytes. If the constancy is multiplied by 6, the potential drift in mv. per hour is obtained, and the figure agrees fairly well with the above-mentioned figures. The drift, however, is not always towards a greater potential difference between the electrode and the electrolyte, i.e. in a positive direction, as stated by Tarter and Walker - it may be in a positive or negative direction, or even change from positive to negative or vice versa. Tarter and Hellman[75] found that there was no steady drift, when the electrolyte flowed past the electrode at a uniform speed, but a fluctuation in both directions.

Table 6.

Metal.	Average Constancy
1. Pd	1.8 mv. per 10 min.
2. Os	2.4 " " " "
3. Pt	2.6 " " " "
4. Au	3.7 " " " "
5. Rh	4.0 " " " "
6. Ru	4.3 " " " "
7. Ag	4.7 " " " "
8. Ir	8.0 " " " "

Table 7.

Metal.	Average Reproducibility
1. Os	8 mv.
2. Ru	19 mv.
3. Au	19 mv.
4. Pt	20 mv.
5. Pd	21 mv.
6. Rh	27 mv.
7. Ag	29 mv.
8. Ir	31 mv.

Table 6 (2).

Br. = Bright metal.
Ox. = Oxidised metal.
B. = Black or electro-deposited metal.
G. = Grey or heat treated black metal.

Average Initial and Final Potentials of Metals for O_2-H_2 cell in volts.

Metal.	H_2SO_4						KCl				NaOH	
	Undisturbed Electrolyte.		Undisturbed Electrolyte.		Disturbed Electrolyte.		Undisturbed Electrolyte.		Disturbed Electrolyte.		Undisturbed Electrolyte.	
	Initial Potential.	Final Pot.	Initial Pot.	Final Pot.	Initial Pot.	Final Pot.	Initial Pot.	Final Pot.	Initial Pot.	Final Pot.	Initial Pot.	Final Pot.
[illegible]t.	.82	.88	.93	.92	.93	.91	.95	.93	.955	.99	.98	1.00
[illegible]t.	.88	.85	.92	.96	[illegible]	.97	[illegible]	.98	.94	.92	[illegible]	1.00
[illegible]t.	.86	.82	.91	.89	.91	.89	[illegible]	.89	.92	.96	.95	.97
Br. C.	.89	.89	.91	.89	.93	.94	.95	.94	1.01	1.03	1.01	1.03
Ox. C.	.86	.85			.88	.88	.86	.90	.96	.99	.97	.99
[illegible] C.	.85	.87	.89	.90	.94	.94	.94	.94	[illegible]	1.01	1.01	1.01
Br. Ni.	.98	.85	.96	.89	.96	.94	.99	.96	.94	.97	.96	.98
Ox. Ni.	.98	.87	.93	.85	.92	.90	.91	.91	.97	.94	[illegible]	.98
[illegible] Ni.	.96	.89	.90	.89	.99	.97	.98	.96	[illegible]	[illegible]	[illegible]	[illegible]
Br. Sh.	.85	.89	1.05	[illegible]			.81	.85	.94	.975	[illegible]	.97
Ox. Sh.	.85	.89			.95	.89	[illegible]	.88	[illegible]	.97	1.04	.96
[illegible] Sh.	.90	[illegible]	.89	.91	1.02	[illegible]	1.05	1.02	[illegible]	.96	[illegible]	.96
G. Sh.	1.17	.91	1.13	.91	1.01	1.02	.97	1.00	1.01	.97	1.03	.97
Br. Ir.	1.04	.97	1.02	.96	.95	.95	.90	.91	.97	.975	1.01	.96
Ox. Ir.			1.08	1.09								
[illegible] Ir.			.96	.86								
Br. C.	.50	.51	.46	.47	.59	.59	.61	.60	1.05	.96	1.01	.97
Ox. C.	.52	.52	.55	.54	.61	.59	.59	.60	.92	.96	1.01	.97
[illegible] C.	.52	.51	.54	.52	.64	.61	.65	.61	1.00	.96	1.04	.99
Br. Ni.	.66	.71	.65	.68	.77	.79	.82	.81	.92	.94	.94	.93
Ox. Ni.	.68	.71	.67	.72	.75	.80	.77	.76	.90	.93	.92	.95
[illegible] Ni.	.66	.72	.66	.70	.75	.79	.79	.81	.92	.93	[illegible]	.94
[illegible] Co.	.88	.87	.89	.89	1.00	.97	1.02	1.00	.96	.96	.95	.95

These figures for the reproducibility are usually better than those mentioned in the experimental results, because here electrodes with different histories have been treated as dissimilar electrodes, i.e. their reproducibilities have been taken separately, whereas before an electrode was considered as similar to another, if it was of the same form of metal, no matter what their respective previous histories had been.

The average reproducibility for all the metals in H_2SO_4 is 27 mv., in KCL 20 mv. and in NaOH 14 mv. The average constancy for all the metals in H_2SO_4 is 4.4 mv., in KCL 3.7 mv. and NaOH 3.0 mv. Again NaOH comes out with the best figures. A very remarkable coincidence is here apparent. In the first case, there is a change of 1 mv. reproducibility per pH unit - i.e. from pH 14 to pH 7 there is a total change of reproducibility of 7 mv., and from pH 7 to pH 0 another change of 6 mv. Similarly, constancy apparently changes regularly by .1 mv. per pH unit from 3.0 mv. for strongly alkaline solution to 4.4 mv. in strongly acid solution. If it is nothing more, it is certainly a remarkable coincidence, and yet again constancy and reproducibility follow each other closely.

Values found for the O_2-H_2 Cell:-

The tables 8 and 9 on the opposite page give the average initial and final potentials attained by each of the forms of each metal in all three electrolytes, ~~together with the highest and lowest values recorded in each case~~. The values are those of the O_2-H_2 cell in volts.

The potentials in this section have all been calculated to refer to a hydrogen electrode in the same electrolyte, because the theoretical value of the O_2-H_2 cell is well known, 1.23 volts, and should be the same in all electrolytes, whereas the theoretical values of the potential versus the various reference electrodes are not

well known and are different for each solution. The potentials in all the electrolytes are then comparable, and it is easy to see how nearly the theoretical potential of the electrode has been approached.

The final potential given by these electrodes appears to be very little affected by bubbling. Treating the electrode with continuous bubbling for the full 30 minutes, or with alternate periods of bubbling and quiet, or with quiescent electrolyte for the full 30 mins. makes very little difference to the final potential, which is approximately the same with all three treatments.

Hoer[71] found that NaOH (.98 volts) was a better electrolyte for giving high potentials than H_2SO_4 (.82 volts) and in this investigation it has been found that, in general, both initial and final electrode potentials are highest in NaOH and KCl , with NaOH the better of the two. In the case of the initial potential given immediately on immersion in the electrolyte, there are a number of exceptions to this rule, but by the end of the 30 mins. NaOH is quite definitely the best solution for high oxygen potentials. Smale[56] also found the highest O_2-H_2 cell values to be given in alkaline electrolyte. The exceptions found among the initial potentials are possibly due, in most cases, to the fact that the electrodes, when used immediately after heating, are giving an oxidic potential, i.e. they are registering principally the single potential of an oxide formed on the metallic surface by heating in air.

Hoar has reported higher O_2-H_2 cell values for Pt black (1.06 volts) than for bright Pt (.98 volts), but there seems to be no general rule as to what form of electrode surface is the best to use for high potentials. In the case of Ru, Ir and Rh, however, it is very plain that the highest initial potentials are given by freshly

TABLE 10.

Metal	Initial potential immediately after heating and cooling in vacuo, in:-		
	$HgSO_4$	KCL	NaOH
Black Pt	L	Lv	Ls
Bright Rh	Ls	S	S
Black Pd	Lv	Lv	Ls-L
Black Ru	L	Lv	S
Black Os	L	Lv	S
Bright Ir	L-Lv	L-Lv	Ls
H form Ag	S	S	S
Bright Au	L	L-Lv	S

S = Same as corresponding potential of airtreated electrodes.

Ls = Approx. 50 mv. lower than " " " "

L = " 100 mv. " " " " " "

Lv = 250 mv. or more " " " " " "

heated electrodes, i.e. by the bright, oxidised or grey forms. The effect of heating the electrode, cooling it and using it immediately, is very pronounced in the case of Rh and Ir, where it produces very high initial potentials, but for the other metals, with a possible exception of Ag in NaOH, the heating has apparently very little effect on the electrode potential.

In both acid and neutral electrolyte freshly made electrodes give the higher final values, but in alkali there is nothing to choose between the different pre-treatments.

Ru, Rh (especially) and Ir give consistently high initial values in all three electrolytes, Pd, Ag and Au reach their highest values in NaOH, and Os and Pt in KCL. All the metals exceed 1.00 volts at some time or another, but only Rh and Ir exceed 1.20 volts. No metals give such consistently high final values (as 1.2 volts), but Pt and Pd (curves that become more noble with time), are the best in NaOH. Au is the least satisfactory metal, only once giving a potential above 1.00 volts for the O_2-H_2 cell. Ag and Au, except in NaOH where they give reasonably high potentials, give by far the lowest values for the O_2-H_2 cell. In H_2SO_4 Ag gives a value as low as .47 volts.

Some electrodes were heated and cooled in vacuo. The effect of this treatment on their initial potentials is given in the following table:- (See opposite)

This treatment of heating the electrodes to 400°C in vacuo not only enabled the metal to be heated out of contact with air, but also very probably decomposed any oxides that might have been formed on the electrode by previous treatment. It is extremely interesting to note how such decomposition has affected the potentials. In H_2SO_4 and KCL all the metals, with the exception of Rh and Ag, show initial potentials considerably lower than those

given initially by the air-treated forms, but in NaOH the heating in vacuo has little or no effect on the potential in all cases.

The curves given are all of the rising type, i.e. they start at a low potential and become more noble with time, with the exception of Ag in NaOH which gives a falling type of curve. The potential in many cases reaches the usual potential given by air-treated metal, within 30 mins., but in some cases, notably black Pt and Pd, the rise is much slower and the original air-treated potential is only given after a long period of use or standing in air - it may usually be attained immediately, however, by heating the metal in air, cooling and using.

Change of E...F. with pH:-

According to theory, the potential of the oxygen electrode should change the same amount per pH unit as the hydrogen electrode, i.e. .058 volts per pH unit. The electrode, to a certain extent, enters into equilibrium via the hydroxyl ions, with the hydrogen ions,/thus:-

$$O'' + H_2O \rightleftharpoons 2OH'$$

$$\text{Therefore} \quad \frac{[OH']^2}{[O'']} = k ,$$

$$\text{and since} \quad [H^+] \times [OH'] = K_W ,$$

$$[OH'] = \frac{K_W}{[H^+]}$$

and the above expression becomes,

$$\frac{K_W^2}{[H^+]^2 \times [O'']} = K$$

$$\text{or} \qquad [O''] = \frac{K_W^2}{K \cdot [H^+]^2}$$

The potential of the oxygen electrode is given by:-

$$E_{O_2} = \frac{RT}{nF}\log_e\frac{p}{p} = \frac{RT}{nF}\log_e\frac{C}{c}$$

$$= E' + \frac{.058}{2}\log\frac{1}{[O'']}$$

where E' = normal electrode potential of oxygen.

Substituting for $[O'']$, we get;-

$$E_{O_2} = E' + \frac{.058}{2}\log\frac{K.[H^+]^2}{Kw^2}$$

$$= E' + .029\ \log K - .058\ \log Kw + .058\ \log[H^+]$$

$$= E + .058\ \log[H^+]$$

$$= E - .058\ pH\ ,$$

i,e, the potential of the electrode will change theoretically by 58 mv. per pH unit.

In order to find how the potential was changing with pH, it was necessary to refer the E.M.F. readings in all electrolytes to the same standard electrode. The E.M.F. readings were, therefore, all calculated to refer to the normal hydrogen electrode in each case. The values, on which these calculations of the change of potential with pH were based, were the average final potentials given by each form of the metal in the particular electrolytes. In 16% of all the average final values the theoretical change is approximately attained. Between KCl and NaOH it was attained in 25% of the cases, between KCl and H_2SO_4 in 12%, and between NaOH and H_2SO_4 in 5%. Again KCl and NaOH give the more theoretical results. In a few cases the change found has been greater than the theoretical .058 v. per pH unit, and in these cases it is due to the metal giving low results in the one electrolyte, whilst the second electrolyte gives a more nearly theoretical potential.

The most outstanding metal in this section is undoubtedly Ir, which gives an almost theoretical change for all three electrolyte combinations, i.e.

i.e. KCl - NaOH

KCl - H_2SO_4

NaOH - H_2SO_4

Rh is also satisfactory, Au, Os and Pt less so, while Au, Ag and Pd are quite unsuitable as pH indicators. These last three metals never come within .05 volts of the theoretical change of E.M.F. with pH, which is approximately .4 volts between KCl and NaOH or H_2SO_4, and approximately .8 volts between NaOH and H_2SO_4.

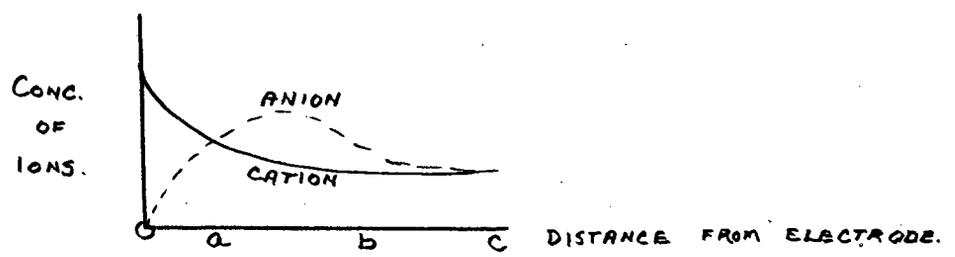
With the exception of Ir, where only bright metal was used, the black and grey forms of metal are by far the most reliable as pH indicators.

Theories Proposed To Account For The Irreversibility Of The Oxygen Electrode.

There appear to be three main theories to account for the irreversibility of the oxygen electrode - the H_2O_2 theory, the oxide theory, which is employed in different ways by different workers, and the adsorption potential theory. The H_2O_2 theory explains the irreversibility on the basis of the formation of H_2O_2 at the electrode, produced by the hydration of oxygen ions. This theory appears to have few advocates to-day, and most opinion is apparently in favour of the oxide theory. The decline in popularity of the H_2O_2 theory is probably due to the well known catalytic effect of Pt on the decomposition of H_2O_2, and the fact that it has not been conclusively proved that any H_2O_2 is actually found at the electrode.

The Adsorption Theory :- As Terter and Walker's[76] adsorption theory was not fully described in the introduction, an account of it's main points will be given here. These authors suggest, as did van der Leulen and Wilcoxon[19], that the Pt preferentially adsorbs ions from the solution thus creating

a potential difference between the electrode surface and the bulk of the solution. No electrical double layer of anions and cations is visualised, but a preferential adsorption of either the anion or the cation on the electrode, with a gradual change in concentration of both ions out into the solution, until eventually the concentrations become the same. The following figure, after one in the original paper, explains their idea.



As shown the electrode would be positively charged with respect to the solution; for a negatively charged electrode the anions would be adsorbed in preference to the cations. Potential drift is explained on the slow adjustment of the outer fringe, b to c, which, being a considerable distance from the electrode, would be bound by weaker forces.

E.M.F. is explained by the sweeping away of the outer fringe from a to c. The effect of oxygen and other gases on the potential of the electrode is attributed to the difference an adsorbed layer of oxygen molecules on the electrode would have on the adsorptive powers of the metal for the ions in the solution. This theory is very elastic; it could explain, quite easily, either a positive or a negative charge on an electrode, a positive or negative potential drift, or even an E.M.F. with either sign, simply by postulating a preferential ausorption of cations in some cases, and anions in others. This would be very welcome in an investigation such as this present one, where itÿs so very difficult to draw up any comprehensive generalisations. The theory, however, is unsatisfactory in that it leaves us still completely in the dark as to why certain electrodes adsorb certain ions more strongly than others. One difficulty is explained by postulating

something else just as unexplainable. In addition Tartar and LeLain[110] and Tartar and Co-workers[111] have modified the first ideas on the distance the adsorbed layer extends into the electrolyte.

Tartar and LeLain found that, by moving two Pt electrodes closer to each other in certain electrolytes, the potential could be changed, and explained this as being due to the re-arrangement of the ionic film which they considered to be .05 - .25 mm. thick round each electrode. In a later paper[111], however, they found that the results formerly obtained were due to faulty apparatus and state that "The authors concur in the opinion that bringing parallel plates together would not produce a re-alignment of the ionic layers which one could measure potentiometrically", consequently there is a doubt as to whether they themselves still support their original theory or not. These facts probably account for the lack of support found for this theory in the published literature.

The Oxide Theory of Hoar :- In dealing with the oxide theory, we have two main points of view, (a) that the potential of the electrode is actually due to the oxide film supposedly present on the surface of the metal - this oxide being the electromotively active material, and (b) that proposed by Hoar, that the oxide film, as such, would not affect the potential, except in so far as it slows up the attainment of equilibrium, being less catalytically active than a surface of bright metal. This theory demands that the oxide film be, not continuous, but porous, enabling the electrolyte to reach the base metal through the pores. In the cell thus formed an electric current is set up, the base metal being relatively anodic to the film surface, which removes, irreversibly, electromotively active material from the film surface, thus depressing the potential below the theoretical value.

As the current flows, the pores become choked up with

precipitated oxides or hydroxides of Pt. This precipitation in the pores increases the resistance and therefore cuts down the self-polarising current, which in turn reduces the rate of filling up of the pores. Consequently equilibrium at the theoretical potential will only be attained after a very long period of time; Hoar estimates it at 10,000,000 years, after which time the resistance of the pores will be so great that the oxide surface willbe able to "catalyse the reversible reaction at the reversible potential at a rate relatively rapid to the rate at which it allows electromotively active material to be removed by self-polarisation". This theory suggests, therefore, that the potential will slowly increase with time, although never, within reasonable time limits, reaching the theoretical oxygen potential.

This affords an excellent explanation of the slow positive potential drift found with some electrodes, but fails to explain why, as found in many cases in this investigation, the potential drift should be negative, and also why the potential drift, in many cases, changes in direction from positive to negative or vice versa. If we accept the theory of Hoar as it stands, it becomes impossible to explain the very high values reached by Ir and Rh, which sometimes exceed 1.23 volts for the $O_2 \rightarrow H_2$ cell, since Hoar deduces from his theory of the oxygen electrode that, under the present conditions, the theoretical potential can never be attained.

It is interesting to note that Evans, who is the foremost champion of the non-continuous oxide film as the main cause of corrosion [72-74], asserts that the thinner the film, the less likelihood is there of there being discontinuities, i.e. thin films, in general, provide the best protection from attack. If we apply this to the Pt metals, it is obvious that the oxide film must be extraordinarily complete, since it protects these metals from attack in a

most effective manner, Yet Moar's theory, which is evidently based on Evan's electrochemical theory of corrosion, demands a film permeable to the electrolyte .

The totally oxidic theory of the oxygen potential :- In dealing with the first view of the oxide theory, i.e. that the potential is of a totally oxidic nature, it should be borne in mind that, as yet, the evidence for or against the existence of an oxide film on the Pt metals is not conclusive, although there is too much evidence in favour of the existence of such a film to deny the probability of this being so. It is not necessary, however, to assume that these oxides are electromotively active - Moar assumes the presence of oxide films, but does not attribute the oxygen potential to them - neither is it necessary to assume that , if the oxides are responsible for a potential, they are wholly responsible for the oxygen potential, since there is nothing to prevent an oxygen ion potential, or even a H_2O_2 potential existing at the same time. The final oxygen potential may quite conceivably be a combination of these - a compromise potential.

The following is a short account of the evidence for and against the existence of oxide films on the Pt metals, Ag and Au. The earliest evidence for the presence of these oxides has already been cited in the introduction, where the the work of Bond, Ramsay and Shields [52,53], of Woehler [54] and of Luther and Brislee [55] was mentioned. Tammann and Schneider [112] found that Pd formed oxides on heating to 400°C, but that much thicker films were formed by anodic polarisation at 20°C in 1.6 N H_2SO_4. Pennycuick [113] and Kolthoff and Pineda [114] have found that finely divided Pt, e.g. Pt black, forms hexahydroxi platinic acid in aqueous solutions in the presence of oxygen gas. Bowden [115], while engaged in measuring the quantity of current required to change the potential of a Pt electrode from that of hydrogen to that of oxygen or vice versa, found that definite arrests occurred during the process, and these he attributed to the formation or solution

of oxides of Pt on the electrode. From similar evidence, however, Butler and Armstrong[116], Armstrong, Himsworth and Butler[117], and Butler and Drever[118] arrive at the conclusion that these breaks are not due to oxide formation and decomposition, but to the removal and formation of adsorbed layers of oxygen and hydrogen. They agree, however, that in H_2SO_4 Au does form an oxide, but not in NaOH. Shutt and Walton[119], in a paper on the anodic passivation of Au in chloride solutions, decide that the passivity of the metal is due to the presence of high oxides of Au formed on the electrode. In a later paper[120] they found evidence that Au reacts in alkalis forming a film of oxide, which is directly opposed to the views of Butler and his co-workers (loc. cit.). Shutt and Walton also found that, after prolonged exposure to air, the time of passivation for the Au electrode is shortened, and explain this by assuming that an oxide film has already been formed.

More direct evidence has been forthcoming from the work of Müller and Low[121]. They showed, by means of photographs, that a clean, (no oxide), Au plate on exposure to the atmosphere gradually darkens, and this the authors explain as being due to the slow formation of an oxide film. From these photographs it appears that the film takes 60-70 hours before it is complete, i.e. when no more darkening occurs.

Jacobs and Whalley[122], in studying the phase boundary potentials of adsorbed films on metals, found that both Au and Pt, on exposure to air, are immediately covered with a film of chemi-adsorbed oxygen. They affirm that, on heating the Pt in air, the metal acquires a film of oxide, which, however, is unstable and decomposes slowly. Mann[123], using the method of electron diffraction, is doubtful as to whether or no an oxide film is formed on heating a Pt wire in oxygen. Erscher, Leberin and Frumkin[124] state that, on heating Pt in oxygen to 900°C for 10 secs., a monatomic

film of oxygen is formed on the Pt surface, one atom of oxygen combining with one atom of Pt. An electrolytically reduced Pt electrode was oxidised most rapidly in solutions with a pH greater than 7, i.e. in alkalis. Günther-Schulze and Betz[125] showed, by means of electrons set free from a glow discharge, that Pt oxidises superficially in air. This view is not supported by Dobinski[126] or Plessing[127] both of whom used the electron diffraction method for studying the growth of oxide films on Au and Ag. Both authors agree that Au and Ag do not form an oxide film during exposure to the air, or even on polishing the metal in air. Finally Auerbach and Luthardt[128] have recently shown, during measurements of electrical resistance of thin films of metals, that on heating thin films of Pt and Pd in contact with oxygen superficial layers of oxide are formed.

There is, therefore, considerable evidence for the existence of oxide films on the Pt metals after anodic polarisation, or heating in air or oxygen, but not so much evidence that the metals acquire an oxide film merely by exposure to air.

Although the earlier workers all accepted the total oxidic theory, later workers, e.g. Britton[64] and Richards[70], have realised that the potential cannot be totally oxidic since, as was shown in the introduction, the oxygen electrode is reversible to some extent. Richards has shown that the oxygen electrode is immediately sensitive to changes in the oxygen gas concentration - he even showed that the % of oxygen in gaseous mixtures could be determined by means of this electrode- and he points out that, on a totally oxidic theory, this would mean that high oxides of Pt must be reversibly formed at ordinary temperatures, whereas Koehler[54] and Miller and Low[121] have shown that they are only

formed with great difficulty after prolonged exposure to air or oxygen.

In addition to this, Richards quotes the work of Harding and Smith[129] as affording evidence for the oxygen absorbed by Pd being to some extent in the uncombined state. These workers found that, on making Pd cathodic, a sudden decrease in resistance due to occluded hydrogen, was observed. This hydrogen is usually taken as being uncombined. When made the anode, a similar, but smaller decrease of resistance was observed, followed by a permanent increase due to oxide formation. By analogy to the case of hydrogen, it is fairly safe to say that the oxygen is also in the uncombined state.

There is further, more direct evidence, however, that oxygen gas is dissociated by Ag.[130] Johnson and Larose showed that the diffusion of oxygen through Ag obeys a square root law just as the diffusion of hydrogen through Pt or Ni does. This is very strong evidence for the formation of oxygen ions when the gas is dissolved in metallic Ag. In support of their view, the authors quote similar work done by Hartley[131], Steacie and Johnson[132]. Johnson and Larose found no similar evidence to suggest that Pt behaves towards oxygen as Ag does. The work of Haber and his Co-workers[10-12], Baur[13] and Baur and Brunner[14], all of whom found the oxygen electrode thermodynamically reversible above about 400°C, does, however, that at higher temperatures there must be considerable dissociation of oxygen taking place. There is every possibility, then, that at ordinary temperatures there is an oxygen ion potential manifesting itself, to some extent at any rate. The idea that the oxygen potential, as measured, may be due, in part, to an oxygen ion potential is not then altogether fantastic.

There are several fairly obvious deductions which could be made from a theory, which supposes an oxide to be

the only material determining the potential of the electrode. Some of these, however, are irreconcilable with observations made during the present investigation. Au is a metal which, it is most commonly conceded, does form an oxide film. Os is a metal which is known to have the greatest affinity for oxygen of all the Pt metals, and yet Au and Os give totally different types of curve. If an oxide were the only cause of the potential one would expect, at least, that a similar type of curve would be shown by these two metals and probably by others. The curves illustrated, however, show that even in the same electrolyte we get greatly varied types of curve.

Another striking fact is that, although the initial potentials of the electrodes differ widely, they all tend to settle down to approximately the same value eventually. In NaOH especially, it is noticeable how many metals give final values of between .94 and .97 volts for the O_2- H_2 cell. It is highly improbable that all these metals would give stable oxides with the same single potential. Although the Pt metals are very closely allied in many properties, yet among them we have stable oxides where the metals exhibit widely differing valencies; the hydration of the oxides would also differ from metal to metal, and Lorenz and his co-workers[47-51] found the single potential of the oxides of Pt differed considerably, both with the state of oxidation of the metal and with the degree of hydration of the oxide. It seems far more likely that the very similar final potentials are due to some cause outside the differing chemical properties of the individual metals - probably to the influence of an oxygen ion potential analogous to the hydrogen potential, which potential should be the same for any metal capable of dissolving and dissociating the gas.

The very high initial values of Ir and Rh especially, would require oxides with exceedingly high single potentials. Spielmann[9] measured the potential of a Pt plate covered

with various known Pt oxides, in varying degrees of hydration, and found that none gave a sufficiently high potential to account for the potential of the oxygen electrode. He therefore found it necessary to postulate higher oxides than any known to exist in accounting for the potentials then found, and even these were considerably lower than the highest reported in this investigation. Grube[60], however, later claimed to have prepared an oxide, PtO_3, which gave a single potential of 1.5 volts in 2N H_2SO_4 - this high value fell rapidly with the evolution of oxygen as the oxide decomposed.

This very high initial value, falling rapidly with time, is characteristic of the potentials given by Rh and Ir immediately after heating to redness and cooling in air. Thus it seems very likely that the cause of these transient initial values, actually exceeding the theoretical potential of the oxygen electrode in some cases, is the formation of high, unstable, electromotively active oxides of Rh and Ir. In the case of the other metals, including Pt, these higher oxides are evidently very much more difficult to prepare, or are very much less stable than those of Rh and Ir, decomposing completely during the time the electrode is cooling. This, however, is contrary to the experience of Foerster[61], who found the oxides of Ir to be less stable than those of Pt.

If the ordinary potential of the electrode were due primarily to an oxide film, one would expect bright, oxidised and grey electrodes all to give much the same results as, and more reproducible results than the black, since the first three forms are prepared by heating to redness in air, thus having the best opportunity of acquiring an oxide film, whereas the black electrodes have been prepared in the presence of hydrogen (during electrolysis) and consequently might be expected to give erratic results before the oxide coating

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had formed completely. (Müller and Low showed that the oxide film on Au requires 60-70 hours before it is completely formed). This, however, is not the case, as the data show that black electrodes, in general, give the most constant and reproducible results of all the forms of electrode surface.

In some cases the curves of the bright and oxidised forms of metal are almost identical, e.g.Pd, Rh and Ru in H_2SO_4 or Pd in NaOH. Visible oxidation in these cases appears to have very little effect on the potential of the electrode. This would appear to be strong evidence in favour of the theory that the potential of the bright metal is simply due to an oxide film already present. Further investigation, however, showed that the electro-deposited or black form, and the heat treated or grey form also give, in some cases, almost identical curves. This is especially the case for Au and Ag, but Pt in NaOH also gives very similar curves for the black and grey forms of metal. As has been pointed out, it does not seem possible that the electro-deposited form could have an oxide film on the metal surface, whereas the heat treated form is in the most favourable position for acquiring such a film.

The problem is further complicated by the fact that, in the case of some metals where oxidised and bright metal give different potentials, the oxidised metal is at a lower potential than the bright, whereas for other metals the position is reversed. The same applies to the black and grey forms - sometimes the one form gives the higher potential, and sometimes the other form does. It seems that there must be two or more components combining to give the measured potential, and it depends on the properties of the particular metal and on the conditions under which it is used, as to which component will have the greatest effect on the "compromise potential". Thus with one metal under a certain set of conditions one component of the total

potential may predominate producing, say, a low potential for the grey metal compared with the black metal; under different conditions a second component may predominate, producing a high potential for the grey form compared with the black metal.

/ Theory proposed as a Tentative Explanation of Some of the Experimental Results:-

An indication of what the several effects mentioned above are, can be obtained from the results of heating the metals in vacuo, i.e. from the change in the initial potential of the metals after heating in vacuo. The most striking point evident from these results is that the initial potential of the electrode is markedly effected by vacuum treatment, (becomes less noble) if the electrode is used in neutral or acid solution, but that in alkaline solution the effect is negligible in most cases. For the time being the irregularities of Ag and Sb are ignored, but a tentative explanation is offered later. If the drop in initial potential on heating in vacuo is assumed to be due to the decomposition of oxide films on the metal surface, these results may be explained as follows: The big effect on the potential in KCL and H_2SO_4 is due to the fact that the ordinary potentials, given by air treated electrodes in these two electrolytes, are in the main oxidic and consequently, when these oxides disappear, a big effect on the potential of the electrode is to be expected. On the other hand, the effect of heating the electrode in vacuo, in alkaline electrolyte, is almost nil. This can be explained as being due to the ordinary air treated electrode potential consisting, in the main, not of an oxidic, but very probably of an oxygen ion potential, and consequently the effect of decomposing any oxide film is negligible in the same proportion as the oxidic potential is negligible compared with the oxygen ion potential.

It still remains to be explained why the initial potential of the vacuum treated electrodes

in KCL and H_2SO_4 is lower and not higher then the corresponding potential of the air treated electrodes, since a purely oxygen/ion potential would be the theoretical one. This may be explained by assuming that the oxygen electrode under some conditions will also show H_2O_2 potential. If the oxygen ion potential is negligible in KCL and H_2SO_4, and the oxidic potential is eliminated by decomposing the oxides, the H_2O_2 potential will become evident. It is well known that H_2O_2 depresses the potential of the oxygen electrode, thus explaining the low initial potentials found after heating the electrodes in vacuo. In NaOH the oxygen ion potential is the predominating factor, is not influenced by heating in vacuo, and consequently remains predominate after heating the vacuo - no fall in initial potential is found in NaOH.

The three main effects combining to give the "compromise potential" of the oxygen electrode appear to be:

(1) The single potential of an oxide film present on the metal surface.

(2) An oxygen ion potential on the lines of the theoretical oxygen electrode.

(3) A H_2O_2 potential produced by the hydration of oxygen ions. The effect of this potential is usually suppressed by the bigger effects due to (1) and (2). The effect predominating in the measured compromise potential of the electrode, will depend on the properties of the metal used, on the previous history of the electrode and on the conditions under which the electrode is used.

In H_2SO_4 the vacuum treatment causes a big initial potential difference between the vacuum and air treated electrodes, and this was explained as due to the air treated electrode potential being in the main due to an oxidic plus H_2O_2 potential. On the decomposition of the oxides, by heating in vacuo, the H_2O_2 potential exerts its depressing effect on the compromise potential. Here again outside

evidence is confirmatory, since H_2O_2 is known to be more stable in H_2SO_4 than in alkalic - H_2SO_4 is a negative catalyst for the decomposition of H_2O_2 - and consequently the H_2O_2 factor is greater in H_2SO_4 than in NaOH. The predominating factors in KCL must also be the oxidic and H_2O_2 effects, since heating in vacuo produces much the same effect as it does in H_2SO_4. In each electrolyte the extent to which one effect suppresses the others will depend on the metal used and the previous history of the electrode.

In the case of KCL and H_2SO_4 the electrode potential rises, sometimes rapidly, sometimes considerably more slowly, as the oxide film reforms and the oxidic potential begins to superimpose itself upon the more feeble H_2O_2 potential. The varying rate, at which the oxide films of the different metals are built up, provides the explanation of the varying rates at which the initial potentials of the vacuum treated metals rise. The ordinary potential of the air treated metal was attained immediately , if the metal was heated in air, cooled and used. This is obviously due to the fact that the heat treatment builds up the oxide film, which is then present when the electrode is immersed in the electrolyte, and therefore exerts its influence on the compromise potential of the electrode immediately.

In explaining the results of heating in vacuo, it was merely assumed that in H_2SO_4 and KCL the potential is mainly oxidic and that in NaOH it is mainly an oxygen ion potential, but there are definite grounds for believing that an oxygen ion potential would be shown to the greatest extent in NaOH and, as has already been pointed out at considerable length, there must be an oxygen ion potential, in part at any rate, in all electrolytes in order to explain the change of E.M.F. with pH etc. (see Introduction , the reversibility of O_2 electrode.)

Of the three electrolytes used, the strongly alkaline solution of NaOH has the greatest concentration of hydroxyl ions - approximately pH 14 - consequently it is to be expected that there will be less hydration of ions in this solution. The hydration of the oxygen ions produces still more hydroxyl ions, and this would be inhibited by the common ion effect. In NaOH, in other words, there is the greatest possibility of finding an appreciable number of unhydrated oxygen ions, and the greatest possibility of an oxygen ion potential becoming predominate in the usual compromise potential of the electrode. The oxidic potential will also be present and, to a lesser extent, that due to Ag_2O. The Ag_2O potential will be a small factor in the compromise potential since, as stated above, there is less hydration of oxygen ions in this electrolyte, and also because alkalis, as well as the Pt metal, are known to be decomposition catalysts for Ag_2O. Thus, on heating in vacuo, there is almost no lowering of the initial potential due to the Ag_2O suppressing the oxygen ion potential. The effect of the Ag_2O potential plus the effect of any undecomposed oxide is still sufficient, however, to prevent the oxygen ion potential reaching the reversible oxygen potential. In the case of black Ag in NaOH, the only heating in vacuo with curve which falls, time is found, i.e. Ag has, in this electrolyte, a greater tendency than the other Pt metals to evince the theoretical oxygen potential, but the oxidic potential rapidly overcomes this tendency.

In NaOH, then, the main factor in the compromise potential is the oxygen ion potential. The important influence of the oxygen ion potential explains the facts brought out in the section "Discussion and Generalisation of experimental results". Time and again it was stated that the best electrolyte to use was NaOH, the reason being, of course, that in this solution we have the nearest approach to the theoretical oxygen electrode.

The fact that the oxygen ion potential even in NaOH, never actually reaches the reversible oxygen potential may be due to removal of electromotively active material from the oxide film surface as proposed by Hoar[71], or simply to the depressing effect of the lower oxidic and H_2O_2 potentials on the oxygen ion potential. On the basis of Hoar's theory the oxygen electrode values will be higher, in NaOH since hydroxyl ions are supposed to be particularly effective in repairing any breaks in the oxide film[133, 134].

The slow potential drift, in either a positive or negative direction, can be explained as due to the slow formation and decomposition respectively of the higher oxides. Since the oxygen electrode potential, in addition to being oxidic, is in part an oxygen ion potential, this will in all probability be going on concurrently with a positive drift due to increasing resistance of the pores in the oxide film to the self-polarising current, as suggested by Hoar.

There still remains to be explained the fact that Ag and Rh, when heated in vacuo, suffer no change of initial potential in any electrolyte. This may be due to the fact that the oxide films on these two metals are not decomposed by the vacuum treatment, and consequently, if the potential is mainly oxidic in all electrolytes, the heating in vacuo produces no lowering of the initial potential. On the other hand, Johnson and Larose[130] showed that Ag has the power of dissociating oxygen to an extent comparable with the dissociation of hydrogen by Ni. * It seems possible, therefore, that in a case of Ag the ordinary air treated electrode potential is, in the main, an oxygen

* In a recent paper Gerassimoff[135] has found that the heat of adsorption of oxygen by Ag is approximately the same as the heat of formation of Ag_2O, and regards this as evidence that the adsorption is really chemical combination.

ion potential, and since, in this case, the increased effect of the oxygen ion potential is due to the metal and not to the electrolyte, it will be evident in all three electrolytes, and heating in vacuo has therefore little effect even in KCl or H_2SO_4. The case of Rh may be similar to that of Ag, and it would be interesting to investigate whether the diffusion of oxygen through Rh obeys a square root law, i.e. whether Rh, as well as Ag, has the power of dissociating O_2. On the other hand Rh_2O_3 is one of the most difficult of the oxides of the Pt metals to decompose by heat under ordinary atmospheric pressure. Carter[136] gives the decomposition temperature as 1150°C. From the very high initial results found for freshly heated Rh electrodes during this investigation, it seems that the high oxides of Rh are particularly active electromotively. It is, therefore, a reasonable possibility that the lower oxide will have the predominating influence on the compromise potential. It seems, then, that, in the case of Rh, the ineffectiveness of the vacuum treatment in producing a low initial potential may be due either to the inability of the treatment to decompose the oxide film, or to the fact that Rh, like Ag, is giving mainly an oxygen ion potential.

In putting forward these suggestions it has been assumed that the vacuum treatment has decomposed the oxide film present on the metal. Richards[70] found that electrodes, which had attained a stable potential, on being made cathode in H_3BO_3, gave a potential considerably higher than before. This he attributed to cathodic reduction of the oxide film, i.e. by reducing the oxides he attained a higher initial potential, due to the now unsuppressed oxygen ion potential, which is just the opposite to what was found on heating in vacuo. Is it possible, then, that heating in vacuo produces a different effect, not the decomposition of the oxide film? The

only other possible effects seem to be the removal of uncombined oxygen from the metal, or else decomposition of the oxides, not to free metal, but to some very low oxide with an extremely low single potential. It does not appear that the first could be the case, since some of the electrodes require a length of time of the order of days before the original air treated potential is reached. The metal would hardly take all that time to take up the oxygen again, but, as mentioned earlier, Müller & Low[121] have shown that some of the metals do require periods of the order of days for the completion of the oxide film, and Foehler[54] showed that the higher oxides of Pt are only formed with difficulty, and after considerable periods of time.

In addition the work of Butler & Armstrong[28] casts doubt on the work of Richards (loc.cit.). Butler & Armstrong found that an electrode anodically polarised set up an oxygen overvoltage, which gradually decayed, finally approaching a 'constant' value after a few hours. By cathodic polarisation they claim to have eliminated the slow decay, and attain the "constant" and lower potential in a few seconds. This cathodic polarisation, carried out in H_2SO_4, gave results more like those here reported from heating in vacuo, and quite different from the high values reported, on cathodic polarisation in H_3BO_3, by Richards.

The suggestion that the decomposition of the original oxide film is not complete but only produces lower oxides with very low single potentials is still a possibility. Even if this were the case, however, the original theory suggested would stand almost unaltered - the postulated H_2O_2 potential, however, would then become less essential to the theory as a whole.

THEORIES PROPOSED TO ACCOUNT FOR MOTOR ELECTROLYTIC POTENTIAL:

Theories of the Oxygen Electrode as Applied to Gas Electrode M.E.P: As was mentioned in the introduction, the phenomenon of M.E.P., as far as the oxygen electrode is concerned, is almost an untouched field. Tarter and Walker[76] applied their adsorption potential theory to the subject of M.E.P. after finding that the H_2O_2 theory was unable to explain the phenomenon[75]. The objections to this adsorption theory, mentioned earlier, still apply when the theory is applied to the problem of M.E.P.

The purely oxidic theory cannot explain M.E.P., nor has an explanation ever been attempted by the advocates of this theory. The only way the bubbling of oxygen could affect a purely oxidic potential would be by the influence of an increased concentration of gas on the stability of the oxide. As Richards[70] has pointed out, these oxides are not reversibly formed at ordinary temperatures. The theory proposed by Kahlenberg and his co-workers[77,78], based on the destruction, by relative motion of the electrode and the electrolyte, of a condensed gas film usually present on the electrode, is quite inadequate to explain the widely differing values for M.E.P. found during this investigation. In the work they did on Pt, Pd and Ag with bubbling of oxygen, they always found a negative M.E.P although for metals other than noble metals a positive M.E.P. was usually observed. The destruction of a film of condensed oxygen on the electrode surface cannot explain why the M.E.P. should sometimes be a positive and sometimes a negative quantity, as was found even among the Pt metals during this investigation. Neither can such a theory explain the maximum and minimum potentials found by French and Kahlenberg during the bubbling of the gas. The authors never attempted to apply their theory to these more complicated cases, since it obviously

cannot supply an adequate explanation.

As a matter of fact, the usual theories proposed to account for the irreversibility and other anomalies of the oxygen electrode will, in all probability, be insufficient to explain the phenomenon of M.E.P., as the following points make clear.

(1) Very often the potential of an electrode is, at first, moved in the less noble direction by bubbling, but towards the end of the five minute period of bubbling the potential begins to rise again.

(2) Continued bubbling for the full thirty minutes gave, when tried in some cases, the same final values, within the limits of reproducibility of the experiment, as an electrode which had been used in undisturbed electrolyte.

(3) A bright Pt electrode showed a rise of potential at the beginning of the five minute period, while oxygen gas was being bubbled at a slow rate, but on increasing the rate of bubbling, the potential became less noble again, i.e. if the bubbling is not sufficiently vigorous the usual slow positive drift given in undisturbed electrolyte, can still make itself evident.

These three observations suggest that the final equilibrium potential of the electrode is the same, whether the electrolyte has been disturbed or not, i.e. the potential of the oxygen electrode during bubbling is still, in the main, controlled by the same factors as when the electrolyte is undisturbed. However, small, superficial changes in the potential of the order of 10-20 mv. (i.e. M.E.P.) still do occur due to some new, and very much less important factors, which in the undisturbed electrolyte do not affect the potential to any appreciable extent. These new factors, brought into play by the bubbling of the oxygen gas, are not important from the point of view of the irreversibility of the oxygen electrode, but are exceedingly important from the point of view of the

constancy or reproducibility, since the reproducibility of 10-20 mv. is not good enough for direct pH determination with the electrodes.

The only other authors to tackle directly the subject of oxygen electrode M.E.P. were Newbery and Smith[79]. They put forward an oxidation - reduction theory for metal electrode M.E.P., and the M.E.P. of hydrogen electrodes, but stated that it was inadequate to explain oxygen electrode M.E.P.

Theories of Metal Electrode M.E.P. and their Relationship to Gas Electrode M.E.P. In turning to theories of metal electrode M.E.P. in an endeavour to find one which might be applied to the case of M.E.P. of the oxygen electrode, it appears that there is a considerable need for standardisation of the procedure used in obtaining M.E.P's. French and Kahlenberg[77] obtained an M.E.P. by stirring the electrolyte, thereby moving it relative to the electrode, and propose that the difference in potential observed is due to the destruction of the gas film on the metal. They add that the slightest jar given the electrode or even a patch of dirt on the surface is sufficient partially to destroy this film, and so to change the electrode potential.

On the other hand, Fink and Linford[94] obtained their relative motion between electrode and electrolyte by rotating their electrodes at peripheral speeds of up to 10,000 f.p.m., and stated that these speeds were essential to break down the unstirrable liquid layer against the electrode. These authors affirm that bubbling gas or stirring the electrolyte produces a change of potential quite distinct from that brought about by rotating the electrode.

In between these two extremes we have Newbery and Smith[79], who rotated their electrodes at speeds of 900r.p.m.

and find that bubbling gas round the electrode has exactly the same effect. Chittum and Hunt[100] used speeds of 1,700 r.p.m., and also stated that bubbling gas produces an "electrokinetic" potential, the term which they apply, without much justification, to M.E.P. Müller and Konopicky[96] rapidly rotated one of a pair of electrodes and found a M.E.P., if the electrode was not "perfect" or unattackable. Koenig[97] used an electromagnetic vibrator of unknown frequency and also a stirrer working in the electrolyte at 2,000 r.p.m. Bonnewitz and Schulz[89] and Bonnewitz and Bigalke[90], using two Ag electrode, scraped the surface of the one Ag electrode with a movable diamond point and found a M.E.P. even in $AgNO_3$, whereas most workers[79,97,98,100] have stated that Ag in $AgNO_3$ gives zero or very low M.E.P. values. Bonnewitz and Schulz mentioned, however, that, in order to get an M.E.P., the electrode must be scraped. Mere rotation of the electrode is not sufficient to break down the unstirrable liquid layer on the electrode, without which no M.E.P. is obtained for Ag in $AgNO_3$.

There appear to be two distinct phenomena comprising metal electrode M.E.P. apparently being regarded as identical. The one effect can be caused merely by a slight jar given the electrode, by a patch dirt on the electrode, or by moderates of stirring or rotating the electrode. The other requires electrode speeds of 10,000 r.p.m. to break down the unstirrable liquid layer on the electrode, as stated by Fink and Linford, or requires the electrode to be scraped as Bonnewitz and his co-workers found.

It hardly seems possible, then, that an explanation of one of these could be applied to the other with any degree of success, even though Fink and Linford's change of potential would of necessity include any change brought about simply by a slight jar or moderate rates of rotation of the electrode. Some standardisation of procedure

is therefore essential, in order to separate and identify these two effects, and afford a means of comparing the work of different investigators.

Gas electrode M.E.P. is brought into play merely by gentle bubbling of the gas round the electrode, and therefore must be governed by factors quite distinct from those governing metal electrode M.E.P., which are measured by methods similar to that of Fink and Linford or Bennewitz and his co-workers.

The theory of metal electrode M.E.P., which has probably received the largest amount of support in the literature,[89,90,92-94], is the electrokinetic theory of Procopiu[87]. This theory demands the sweeping away of the diffuse portion of the Helmholtz double layer by the relative motion of electrode and electrolyte. Koenig[97] points out that electrokinetic phenomena depend only on the slip or displacement of the diffuse part of the double layer relative to the immobile part, whereas the electrokinetic theory of M.E.P. demands a complete removal of the diffuse component. Chittum and Hunt[100] have also attacked the validity of Procopiu's use of the electrokinetic theory to explain metal electrode M.E.P. from a similar theoretical point of view. Newbery and Smith[79] have pointed out that the generation of appreciable electric currents by M.E.P. definitely places this phenomenon in quite a distinct category from electrokinetic potentials.

Procopiu's attempted correlation of M.E.P. values with Burton's[88] electrokinetic measurements is not at all conclusive, and it was unfortunate that Chittum and Hunt should apply the term "electrokinetic potential" to M.E.P. phenomena with such little experimental proof of the identity of the two quantities.

Both Chittum and Hunt's M.E.P. theory of the distur-

bance by motion of a modified double layer, the solution side consisting of charged colloidal metal particles, and Procopiu's theory of the disturbance of the outer component of the Helmholtz double layer, are inapplicable to oxygen electrode E.M.F. for the same reason.

The unstirrable liquid layer on the electrode [137-140] is generally conceded to have a depth considerably in excess of the depth of adsorbed layers. According to Davis and Crandall [140] water stirred at 1,000 r.p.m. leaves an unstirred film approximately 4×10^{-2} mm. thick. On the other hand the Helmholtz double layer, according to White, Monaghan and Urban [141], has a depth of approximately 3×10^{-4} cm., and other estimates [142] are even less, i.e. the unstirrable layer is at least one hundredtimes deeper than the electrical double layer.

Consequently in the case of either Procopiu's or Chittum and Hunt's theory, the E.M.F. can only be brought into play by breaking down the unstirrable layer on the electrode, and mere bubbling of oxygen gas, which is sufficient to produce oxygen electrode E.M.F., would certainly fail to do this. Further, either of these two theories is applicable to metal electrode E.M.F., only when the values are obtained by a method such as Finn and Linford's or that of Bennewitz and his co-workers. Even in these cases, however, a large part of the potential thus measured must be due to some factor, which does not involve the breaking down of the unstirrable liquid layer, since moderate rates of stirring also produce a very definite metal electrode E.M.F.

The only theory of metal electrode E.M.F. which remains is that supported by Miller and Konopicky [96], Koenig [97], Evans [95] and Kasper [98]. This theory, when applied to the ordinary metals, has become known as the "differential aeration" theory. As originally proposed [72], the stirring of the electrolyte is supposed to affect the electrode

potential merely by increasing the concentration of oxygen at the one electrode - the stirring, as such, having no effect on the potential. This view has been modified in certain cases of metal electrode M.E.P. by Müller and Konopicky[96]. They found three effects caused by relative motion of electrode and electrolyte.

(a) A small negative effect due to the sweeping away of metallic ions from the electrode. Found with Cu and Pb, and independent of pH.

(b) A second, bigger positive effect, superimposed on (a), due to the removal of the products of the reaction between the electrode and the electrolyte - these products having a higher pH than the remaining solution. Found with Zn, which reacted with the electrolyte.

(c) A third and biggest effect, positive in acid and negative in alkali, due to the increased concentration of an oxidising agent at the electrode.

Thus the effects (a) and (b) have been added to the original idea of Evans that the increased concentration of oxygen at the electrode is the only factor in M.E.P. Kaspar's work[98] was intended to show that, if a system is in true electrochemical equilibrium, then no M.E.P. is evident. He took Ag in $AgNO_3$, in the absence of any gases like oxygen, as being in true electrochemical equilibrium. The system should then show none of the three above effects, although an electrokinetic effect should still be apparent, if present. Kaspar found that there was zero M.E.P., and therefore concluded that the electrokinetic theory of M.E.P. is inapplicable, and that Müller and Konopicky have the correct explanation. This conclusion is probably correct for his experimental results, since, although Kaspar does not mention the speed at which he rotated his electrodes, it is probable that he used moderate speeds, which would be too low to break down the unstirrable film on the electrode, and he would then, of course, find no electrokinetic effect.

On the other hand, had he used methods, such as those used by Fink and Linford or Müller and Konopicky, for measuring his M.E.F., it is probable that, even for Ag in $AgNO_3$, he would have found an appreciable M.E.F., i.e. an electrokinetic effect might then be evident.

Evans[95] in attempting to explain the M.E.F. of Pt, which is usually negative, makes the assumption that noble metals, on agitation in an electrolyte respond preferentially to the decrease in metal ion concentration, i.e. to effect (a), and not to the increase of oxygen concentration, i.e. effect (c). This assumption, then, removes the explanation of the M.E.F. of the Pt metals from the realm of the original "differential aeration" theory. The effect (b) would, of course, be very small or zero for the Pt metals, since they are very nearly "perfect" or unattackable electrodes in most electrolytes.

An Attempted Explanation of the M.E.F. of the Oxygen Electrode: Any theory of oxygen electrode M.E.F., to be satisfactory, must be capable of explaining, particularly, why the observed M.E.F. is sometimes positive and sometimes negative even with the same metal, and also the irregular variations of M.E.F. with the nature of electrode surface etc. The only theory, which appears to have any chance of fulfilling these conditions at present, is that of Müller and Konopicky, since it provides for both a positive and a negative effect on relative motion between the electrode and the electrolyte. It seems, from the irregularities of the M.E.F., that the observed values must be a compromise between at least two effects which probably work in opposite directions, i.e. tend to move the potential in opposite directions. The effect, that predominates under any set of conditions, will depend on these conditions. Thus under one set of conditions a positive M.E.F. may result, the negative effect or effects being suppressed, and under another set of conditions the position may be reversed,

the negative effects becoming predominate. The value of the positive M.E.F. will depend on the extent to which the negative effects are suppressed by the particular conditions under which the electrode is being used, and vice versa.

With regard to the M.E.F. of the Pt metals used as oxygen electrodes, it appears that there are only two main effects, and these work in opposite directions; the one effect producing a fall in potential with bubbling (negative M.E.F.) and the other a rise of potential with bubbling (positive M.E.F.). It still remains to decide to what these two effects are due, and the reasons for the suppression of the one effect in certain cases and the other in other cases, thus producing positive and negative M.E.F.'s under different conditions.

From Table 5, where the effect of a collodion coating on the M.E.F. of Pt, Au and Os is tabulated, it appears that the principle effect of this coating is to change the M.E.F. from negative to positive. In the case of Au, which gave a positive M.E.F., in H_2SO_4, the value, but not the sign, is changed, although the two values, + 23 mv. and + 15 mv. respectively, lie within the limits of reproducibility of the experiment. (One uncoated Au electrode in H_2SO_4 gave an M.E.F. as low as + 8 mv.) The collodion coating, of course, prevents any mechanical disturbance of the "diffusion layer" round the electrode, leaving the electrode in much the same condition as it is in undisturbed electrolyte but the excess concentration of oxygen gas produced by bubbling can still diffuse through onto the electrode and effect the potential. It appears, then, that the small positive M.E.F.'s, given by the metals coated with collodion, are due, in the main, to the increased concentration of oxygen gas produced by bubbling. This agrees well with theories of Evans[95], Müller and Konopicky[96] and Hoar[71], all of whom

predict an increase in electrode potential with an increased concentration of oxygen at the electrode.

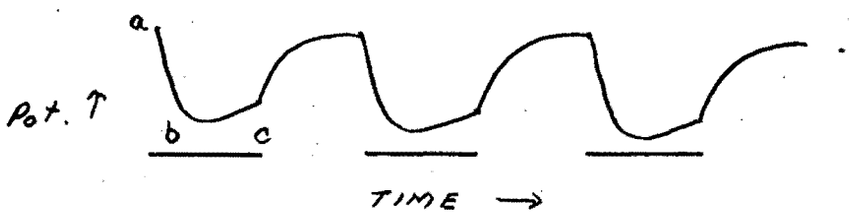
The small positive effect, in other cases, is probably the original positive potential drift, given in undisturbed electrolyte, re-asserting itself when the superficial negative effect on the potential, due to bubbling, ceases. This positive potential drift can be explained, as mentioned before, either on the basis of Hoar's theory or is due to the slow formation of higher oxides or, as is probable in most cases, due to a combination of the two, since Hoar's theory alone cannot explain a negative potential drift. A small positive potential drift would be increased in the positive direction, on the basis of Hoar's theory, by increasing the concentration of oxygen round the electrode. Thus a potential drift which might be slightly in a negative direction in undisturbed electrolyte could become positive in disturbed electrolyte, due to increased concentration of oxygen. Thus even an electrode giving a negative potential drift in undisturbed electrolyte could still show a small positive drift when colloidionised.

This positive effect is, however, usually small and the larger negative effect, which a collodion coat suppresses, has still to be accounted for. Since the pt metals do not react appreciably with the solutions used, the relatively large negative effect, following Müller and Konopicky's theory, must be due to the removal of metal ions by the sweeping away of the "diffusion layer" around the electrode by bubbling. This seems a very probable explanation. The prevalence of the negative drift's among the pt metals has been explained by Evans[95] who states that the noble metals are more sensitive to changes in metal ion concentration than to changes in oxygen concentration.

Some Experimental Facts explained on the Basis of this Theory:

It will be seen that most of these experimental facts, which

are here explained on the basis of the foregoing theory, were actually the clues which led to the theory. When examining the M.E.P. graphs, it was found that every metal had a number of graphs like the following:



M.E.P. Curve, Type 3. (See P. 61)

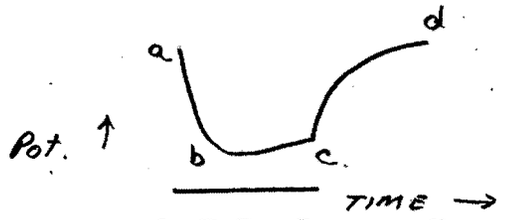
The potential falls rapidly, on bubbling, from a to b, but eventually the fall stops and a slow rise begins, which is usually of the order of a few millivolts or less (b to c).

These are apparently cases, where the electrode has at first responded to the sudden decrease in concentration of the metal ions caused by bubbling, (a to b), then, as the constant potential is reached, (b), the smaller rise in potential due increased concentration of oxygen gas becomes evident (b to c). This latter rise in potential was suppressed at first by the much bigger potential drop due to the decreased metal ion concentration round the electrode. The actual shape of these sections of the curve varies from metal to metal and from solution to solution, depending on the previous history of the electrode. The case of one bright Pt electrode in H_2SO_4, which showed a positive M.E.P. when the rate of bubbling was very slow, and a negative M.E.P. when it was speeded up to three bubbles per second, is an obvious case of how the one effect can be suppressed by varying the conditions under which the electrode is used.

Sometimes the b to c portion, due to increased concentration of oxygen, is almost non-existent, being very small for the conditions involved. In a few cases, e.g. black Pd in KCl, the a to b effect has been small compared with the b to c effect and so, under these conditions, small positive values for the M.E.P. are recorded.

In the case of Au in H_2SO_4 there is a large positive

M.E.P., the value of which is very little dependent on whether the electrode has a collodion coating or not, i.e. not being influenced by mechanical disturbance to any extent. In H_2SO_4 Au apparently behaves more like a base metal than a noble metal, on the basis of Evans' theory, and produces a rise in potential with the increased concentration of oxygen, which is big enough to suppress completely the fall in potential due to the decreased concentration of metal ions. In this case the original potential drift of Au in $HgSO_4$ is not big enough to explain the large positive M.E.P. of the collodionised Au electrode. In addition the potential drift is occasionally in a negative direction, consequently the effect of the increased concentration of oxygen must be exceptionally large for Au, i.e. Au is behaving more like a base metal.



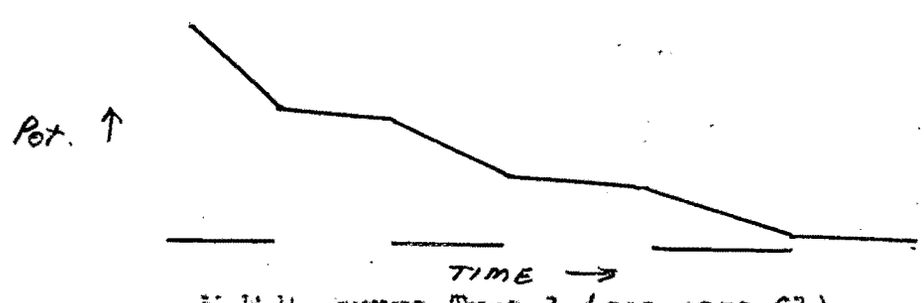
M.E.P. Curve, Type 3.

It will be observed that, in all the curves of type 3, the drop in potential from a to b is very much more rapid than either the rise from b to c or the additional rise in potential which takes place from c to d, on stopping the bubbling of gas. One would expect the fall from a to be to be rapid, since it is caused simply by the sudden sweeping away of metal ions from round the electrode and the potential of the electrode changes with the same speed as the mechanical disturbance sweeps away the metal ions. The slow potential increase from b to c, due to the increased concentration of oxygen which accompanies the mechanical disturbance, has been fully explained by Hoar[71] as due to the slow increase of resistance of the pores in the oxide film preventing the electromotively active material from being too rapidly removed from the film surface. In some cases, where the potential is mainly oxidic, the slow b to c rise may be due in the main to the

slow formation of oxides with higher single potentials. The more rapid increase of potential from c to d, attendant on the stoppage of the mechanical disturbance, can also be explained. The c to d portion must be due to the replacement of whatever was swept away by bubbling (a to b portion), since colloidionising not only cuts out the first rapid fall, but also the rise, c to d, occuring on cessation of bubbling, i.e. the rise from c to d is due to the replacement of the metal ions swept away by the mechanical disturbance. This will be at a ratereletively slow to that at which the concentration would be reduced by the sudden mechanical disturbance. Koenig[97] and Chittum and Hunt[100] have pointed out that the electrokinetic theory would not predict a time interval of the order of minutes for the re-building of the double layer.

This type 3 M.E.F. curve seems to be the most stable form since, as was pointed out before (page 61), the other types of curve all tend to approach to type 3 form of curve with time. The stable, type 3, form of curve is most often found in alkaline solution, whereas the less stable types 1 and 4, are found by far the most in neutral solution.

It is more difficult to explain the other, less stable, types of M.E.F. curve. In the cases where the metal gives very high initial potentials after heating, the first part of the M.E.F. curve invariably consists of the type 1 curve.



M.E.F. curve Type 1 (see page 61).

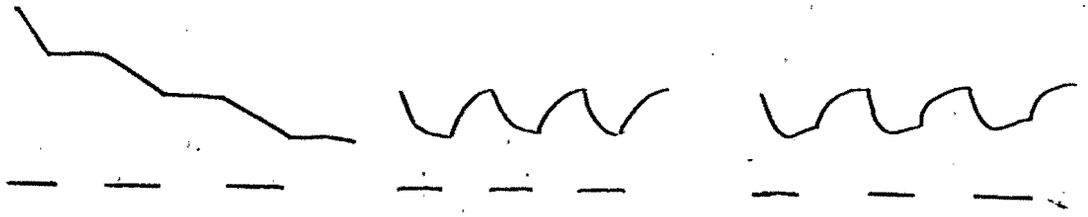
This can be explained by assuming that in the case of M.E.F., as for undisturbed electrolyte, the initial

potential is overwhelmingly that of high electromotively active oxides, which are rapidly decomposing, thus producing the rapid fall of potential. Bubbling has, thong very little effect on the potential at first but as these high oxides decompose the lower, more stable and less electromotively active, oxides appear; the electrode then becomes sensitive to mechanical disturbance , and the type 1 curve develepes into type 2, and finally type 3, with time.

On the other hand, the type 1 M.E.F. curve sometimes occurs throughout the full thirty minutes - this usually appears in KCL and seldom, if ever, in NaOH. Applying Hoar's theory, this may have some connection with the fact that the chloride ion is particularly effective in the breaking down of the oxide film, whereas the hydroxyl ion tends to repair the film[133,134]. In KCL the oxide film would then become more porous, thus allowing the self-polarisation to go on at a more rapid rate and the potential would fall. This effect would be enhanced by bubbling, since the disturbance would continually provide fresh chloride ions to stimulate the breakdown. On ceasing the bubbling the potential rises again as the oxygen then gets a chance to repair the film without the interference of the continual re-inforcements of chloride ions provided by bubbling. This steady breakdown and repair would produce a steady fall and rise in potential as in type 1 M.E.F. curves. In NaOH the hydroxyl ion keeps the film in permanent repair and so the other factors - decrease in metal ion concentration etc. - affect the potential. These latter statements regarding the mechanism of the type 1 M.E.F. curves are, of course, conjecture - there is no direct experimental evidence that such is the case.

Sometimes the types 1 and 3 of M.E.F. curves are superimposed, and the curve of type 2 appears. Sometimes type 3 is modified to a still larger extent by type 1 and so we get curves giving any variation from type 1

with straight line sections, through type 2 with a definite curve in the sections, to type 3.



Type 1. Type 2. Type 3.

M.E.F. curves.

CONCLUSION:

The mechanism of the oxygen electrode in undisturbed electrolyte outlined in this work, was suggested, in the first place, by the results obtained on heating the electrodes in a vacuum. The mechanism for the phenomenon of M.E.F. was suggested by the results obtained for the M.E.F. of metals coated with collodion. In view of the extremely irregular results found with the other oxygen electrode properties of the Pt metals, it would seem, that, in order to make any definite statements about the general effect of heating in vacuo or collodionising, all the previous work would have to be repeated using electrodes heated in vacuo, and again, for the case of M.E.F., with electrodes covered with a collodion coating. Such extensive repetition has, up to the present, not been possible. Consequently, in the paper sent to the Electrochemical Society for publication in its transactions, these rather speculative attempts at suggesting a mechanism for the observed phenomena were not included. It was considered, on the other hand, that such an attempt should find a place in the present thesis.

Further lines of research, along which future investigations might profitably proceed, would include the follwoing:

(1) To investigate whether the diffusion of oxygen

through Ih obeys the square root law, as the diffusion of oxygen through Ag does, on the line of the work of Johnson and Larose[130].

(2) The further investigation of the behaviour of the Pt metals as oxygen electrodes after heat treatment in vacuo, or after any treatment designed to eliminate any possible oxide film on the metal surface.

(3) The further investigation of the phenomenon of H.E.F., using collodionised electrodes, or any device which would suppress a portion of the complex H.E.F., and thus allow the individual effects to be studied alone.

(4) A general attempt to control or eliminate some of the various component effects making up the "compromise potential" of the oxygen electrode, in order to study the individual effects in greater detail with the remaining effects either controlled or eliminated.

(5) An oscillograph study of the very rapid initial changes of potential taking place, to decide exactly what happens when the electrode is first placed in the electrolyte. Up to the present research workers have concentrated on observing the electrode for long periods, sometimes amounting to days on end. Goard and Rideal[65], however, found that electrodes pre-treated in $KMnO_4$ gave a maximum potential, in selected electrolytes, within the first few seconds, which maximum was reproducible within a few millivolts. The potential then shows the usual non-reproducible drift. The authors suggest that the same maximum may occur with ordinary electrodes, but takes place too rapidly to be observed with ordinary methods. In addition to this it would be extremely interesting to follow the behaviour of an electrode heated in vacuo, immediately after immersion in the electrolyte, when the possibility of the presence of an oxide film is very remote.

It is quite certain that no single theory, proposed

up to the present, can explain fully the anomalies of the oxygen electrode as revealed in this investigation. The theory here proposed to explain the widely different results, is therefore, in the main, the combination of earlier theories, with certain additions and modifications.

The previous history of the electrodes and the exact condition of the metallic surface is not amenable to accurate measurement, nor have the conditions under which the electrodes have been used, been sufficiently rigorously controlled during this work. Consequently it has not been possible to establish in any detail the conditions under which one effect or another will predominate, although the general conditions governing the different factors influencing E.M.F. and the equilibrium potential of the oxygen electrode have been suggested.

Bibliography.

1. Nernst & von Hartenberg. Z. phys. Chem. 56,534 (1906)
2. Lewis & Randall. J.A.C.S. 36, 1965 (1914).
3. Löwenstein. Z phys. Chem. 54,715 (1905).
4. Langmuir. J.A.C.S. 28, 1357 (1906),
5. Lewis. J.A.C.S. 28, 158 (1906).
6. Brofisted. Z. phys. Chem. 65, 84, 744 (1909).
7. Taylor & Hulett. J. phys. Chem. 17, 565 (1913).
8. Britton. J.C.S. 127, 2960 (1925).
9. Spielmann. Trans. Far. Soc. 5, 88 (1909).
10. Haber & Fleischmann. Z.anorg. Chem. 51,245, (1906).
11. Haber & Foster. Z. anorg. Chem. 51,289 (1906).
12. Haber. Z anorg. Chem. 51, 356, (1906).
13. Baur. Helv. Chim. Acta. 4, 325 (1921).
14. Baur & Brunner. Z.Elektrochem. 41, 794 (1935).
15. Furman. J.A.C.S. 44, 2685 (1922).
16. Furman. Trans. Electrochem. Soc. 43, 79 (1923).
17. Arthur & Keeler. Power. 55, 768 (1922).
18. Tilley & Halsten. Trans. Electrochem. Soc. 44, 31(1923)
19. van der Meulen & Wilcoxon. J.I. & E. Chem. 15, 62 (1923).
20. Britton. J.C.S. 125, 1578 (1924).
21. Britton. J.C.S. 127, 1911, 2148, 2963 (1925).
22. Britton. J.C.S. 130, 147 (1927).
23. Montillon & Cassel. Trans. Electrochem. Soc. 45, 259 (1924).
24. Brewer & Montillon. Trans. Electrochem. Soc. 55, 357 (1929).
25. Popoff & McHenry. J. Amer. Pharm. Assoc. 14,473(1925)
26. Popoff & McHenry. J.I. & E. Chem. 20, 534 (1928)
27. Elder. Trans. Electrochem. , Soc. 57, 383 (1930).

28. Butler & Armstrong. Trans. Far. Soc. 29, 862 (1933).

29. Willard & Fenwick. J.A.C.S. 44, 2504 (1922).

30. Baylis. J.I. & L. Chem. 15, 852 (1923).

31. Parker. J. I. & L. Chem. 17, 737 (1925).

32. Cluss & Kahlenberg. Trans. Electrochem. Soc. 54,369 (1928).

33. Kahlenberg & Krueger. Trans. Electrochem. Soc. 56, 201 (1929).

34. Holt & Kahlenberg. Trans. Electrochem. Soc. 57, 361 (1930).

35. Britton & Dodd. J.C.S. 829, (1931).

36. Wolf. J. für. prakt. Chem. 147/8, 134 (1936/7).

37. Glaser. Z. Elektrochem. 4, 355 (1898).

38. Wilsmore. Z.phys.Chem. 35, 291 (1900).

39. Bose. Z. phys. Chem. 34, 726 (1900.)

40. Bose. Z. phys. Chem. 38, 1 (1901).

41. Bose. Z Elektrochem. 7, 817 (1901).

42. Brislee. Trans. Far. Soc. 1, 65 (1905).

43. Bornemann. Z. anorg. Chem. 34, 1 (1903).

44. Haber. Z. Elektrochem. 7. 441 (1901).

45. Lewis. J.A.C.S. 28, 161 (1906).

46. Bancroft & Murphy. J. Phys. Chem. 39, 382 (1935).

47. Lorenz & Hauser. Z. anorg. Chem. 51, 61 (1906).

48. ~~Lorenz & Haber. Z. anorg. Chem. 53.~~

49. Lorenz. Z.Elektrochem. 14, 781 (1908)
15, 661 (1909).

50. Lorenz & Lauber. Z.Elektrochem. 15, 157, 206 (1908/9).

51. Lorenz & Spielmann. Z.Elektrochem.15, 293,349 (1909/9).

52. Lond, Ramsay & Shields. Proc. Roy. Soc. 58,242 (1895)
62, 50 (1897).

53. Lond, Ramsay & Shields. Z. phys. Chem. 25, 657 (1898)

54. Koehler. Ber. 36, 3475 (1903).

55. Luther & Brislee. Z. phys. Chem. 45, 216 (1903).

56. Seale. Z. phys. Chem. 14, 577 (1894).

57. Crotogino. Z anorg. Chem. 24, 225 (1900).

58. Csepinski. Z anorg. Chem. 30, 1 (1902).

59. Westhaver. Z. phys. Chem. 51, 65 (1905).

60. Grube. Z. Elektrochem. 16, 621 (1910).

61. Foerster. Z phys. Chem. 69, 236 (1909).

62. Schoch. J. Phys. Chem. 14, 665 (1910).

63. Grube & Lulk. Z Elektrochem. 24, 237 (1918).

64. Britton. "Hyrdogen Ions" p.69 (1932).

65. Goard & Rideal. Trans. Far. Soc. 19, 742 (1924).

66. Tammann & Runge. Z. anorg. Chem. 156, 85 (1926).

67. von Kiray Szabo. Z. Elektrochem. 33, 15 (1927).

68. Knobel. J.A.C.S. 45, 1723 (1923).

69. Schmidt. Helv. Chim. Acta. 7, 370 (1924).

70. Richards. J. Phys. Chem. 32, 990 (1928).

71. Hoar. Proc. Roy. Soc. A 142, 628 (1933).

72. Evans. J. Inst. Metals. 30, 239 (1923).

73. Evans. J. I. & S. Chem. 17, 363 (1925).

74. Bannister & Evans. J.C.S. part I, 1361 (1930).

75. Tartar & Wellman. J. Phys. Chem. 32, 1171 (1928).

76. Tartar & Walker. J.A.C.S. 52, 2256 (1930).

77. French & Kahlenberg. Trans. Electrochem. Soc. 54, 163('28)

78. Krueger & Kahlenberg. Trans. Electrochem. Soc. 58, 107 (1930).

79. Newbery & Smith. Trans. Electrochem. Soc. 63, 116(1938).

80. Billitzer. Z. phys. Chem. 48, 513, 542, (1904).

81. Pionchon. Compt. Rend. 153, 47 (1911).

82. Pionchon. Compt. Rend. 154, 865 (1912).

83. Newbery. J.C.S. 111, 482 (1917).

84. Procopiu. J. chim. Phys. 19, 121 (1921).

85. Procapiu. Ann. Sci. Univ. Jassy. 7, 224.

86. Procopiu. Chem. Zentr. 2, 669 (1912).

87. Procopiu. Z. phys. Chem. A 154, 322 (1931).

88. Burton. Phil. Mag. 11, 425,
12, 472, (1906).
17, 583, (1909).

89.

89. Bennewitz & Schulz. Z. phys. Chem. 124, 115 (1926).

90. Bennewitz & Bigalke. Z. phys. Chem. A 154, 113 (1931).

91. Charnanderjan & Terwuschin. Z. Elektrochem. 36, 248 (1930).

92. Charnandarjan & Terwuschin. Phys. Z. Sowjetunion. 4, 334 (1933).

93. Gheorghiu. Ann. Sci. Univ. Jassy. 16, 335 (1933).

94. Finn & Linford. Trans. Electrochem. Soc. 72, 461 (1937).

95. Evans. Trans. Electrochem. Soc. 71, 217 (1937).

96. Müller & Konopicky. Monatsh. 53/4, 707 (1929).

97. Koenig. J. Phys. Chem. 39, 455 (1935).

98. Kaspar. Helv. Chim. Acta. 21, 733 (1938).

99. Chittum & Hunt. J. Phys. Chem. 40, 1083 (1936).

100. Chittum & Hunt. Trans. Electrochem. Soc. 71, 207 (1937).

101. Newbery. Trans. Electrochem. Soc., 64, 99 (1933).

102. Cottrell. Z. phys. Chem. 42, 395 (1903).

103. Weischede. "Elektrolytische Bestimmung & Trennung der Platinmetalle Pt. Ir & Os" Darmstadt (1927).

104. Lunenot & Schmid. Z. anorg. Chem. 216, 104 (1933).

105. Godward & Wardlaw. J.C.S. 1422, (1938).

106. Lakio. Trans. Electrochem. Soc. 53, 261 (1928).

107. Donnan & Allmand. J.C.S. 99, 851 (1911).

108. Newman. "Electrolytic Conduction" p.200 (1930).

109. Sederholm & Benedicks. Trans. Electrochem. Soc. 56, 169 (1929).

110. Tartar & McClain. J.A.C.S. 53, 3201 (1931).

111. Tartar & Co.-Workers. J.A.C.S. 59, 1400 (1937).

112. Tammann & Schneider. Z. anorg. Chem. 171, 367 (1928).

113. Pennycuick. J.C.S. 2600 (1927), 551 (1928), 2108 (1928).

114. Kolthoff & Kameda. J.A.C.S. 51, 2888 (1929).

115. Bowden. Proc. Roy. Soc. A 125, 446 (1929).

116. Butler & Armstrong. Proc. Roy. Soc. A 137, 604 (1932).

117. Armstrong, Himsworth & Butler. Proc. Roy. Soc. A 143, 89 (1934).

118. Butler & Drever. Trans. Far. Soc. 32, 427 (1936).

119. Shutt & Walton. Trans. Far. Soc. 28, 741 (1932).

120. Shutt & Walton. Trans. Far. Soc. 29, 1210 (1933).

121. Müller & Low. Trans. Far. Soc. 31, 1291 (1935).

122. Jacobs & Whalley. Proc. Roy. Soc. A 140, 409 (1933).

123. Penn. Proc. Roy. Soc. A 146, 776 (1934)
161, 236 (1937).

124. Ershler, Deborin & Frumkin. Bull. Acad. Sci. U.R.S.S. Ser. Chim. 1065 (1937).

125. Günther-Schulze & Betz. Z. Elektrochem. 44, 253 (1938).

126. Lessing. Phil. Mag. 20, 465 (1937).

127. Wissling. Phys. Zeitschrift p. 618 (1938).

128. Auerbach & Ruthardt Z. Elektrochem. 44, 579 (1938).

129. Harding & Smith. J.A.C.S. 40, 1568 (1918).

130. Johnson & Larose. J.A.C.S. 49, 312 (1927).

131. Hartley. Proc. Roy. Soc. A 90, 61 (1914).

132. Steele & Johnson. Proc. Roy. Soc. A 112, 542 (1926).

133. Evans. J.C.S. p. 1020 (1927)
92 (1929).

134. Britton & Evans. J.C.S. 1773 (1930).

135. Gerassimoff. Z. für. Elektrochem. 44, 709 (1938).

136. Carter. Trans. Electrochem. Soc. 43, 399 (1923).

137. Noyes & Whitney. Z. phys. Chem. 23, 689 (1897).

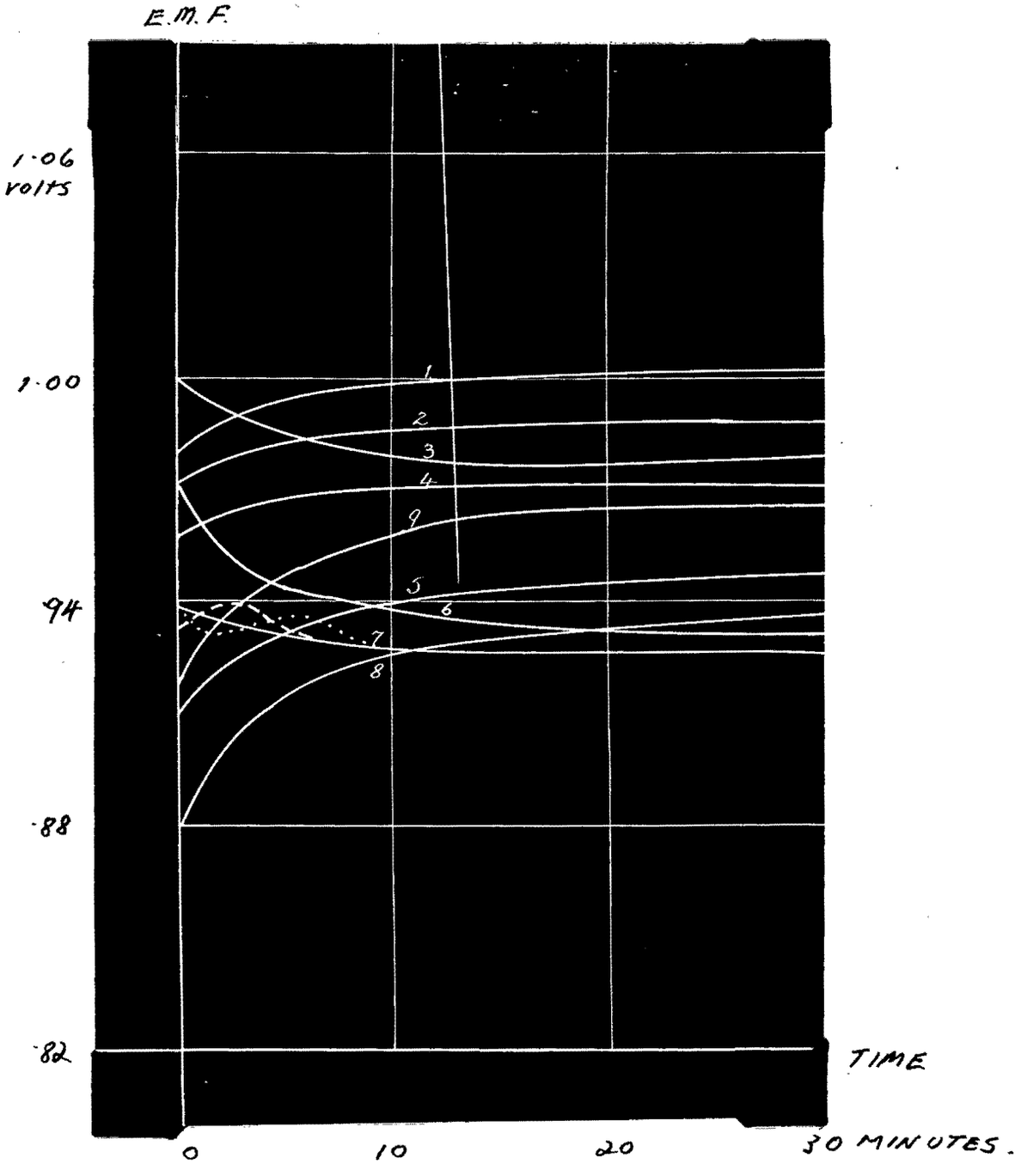
138. Brunner. Z. phys. Chem. 47, 56 (1904).

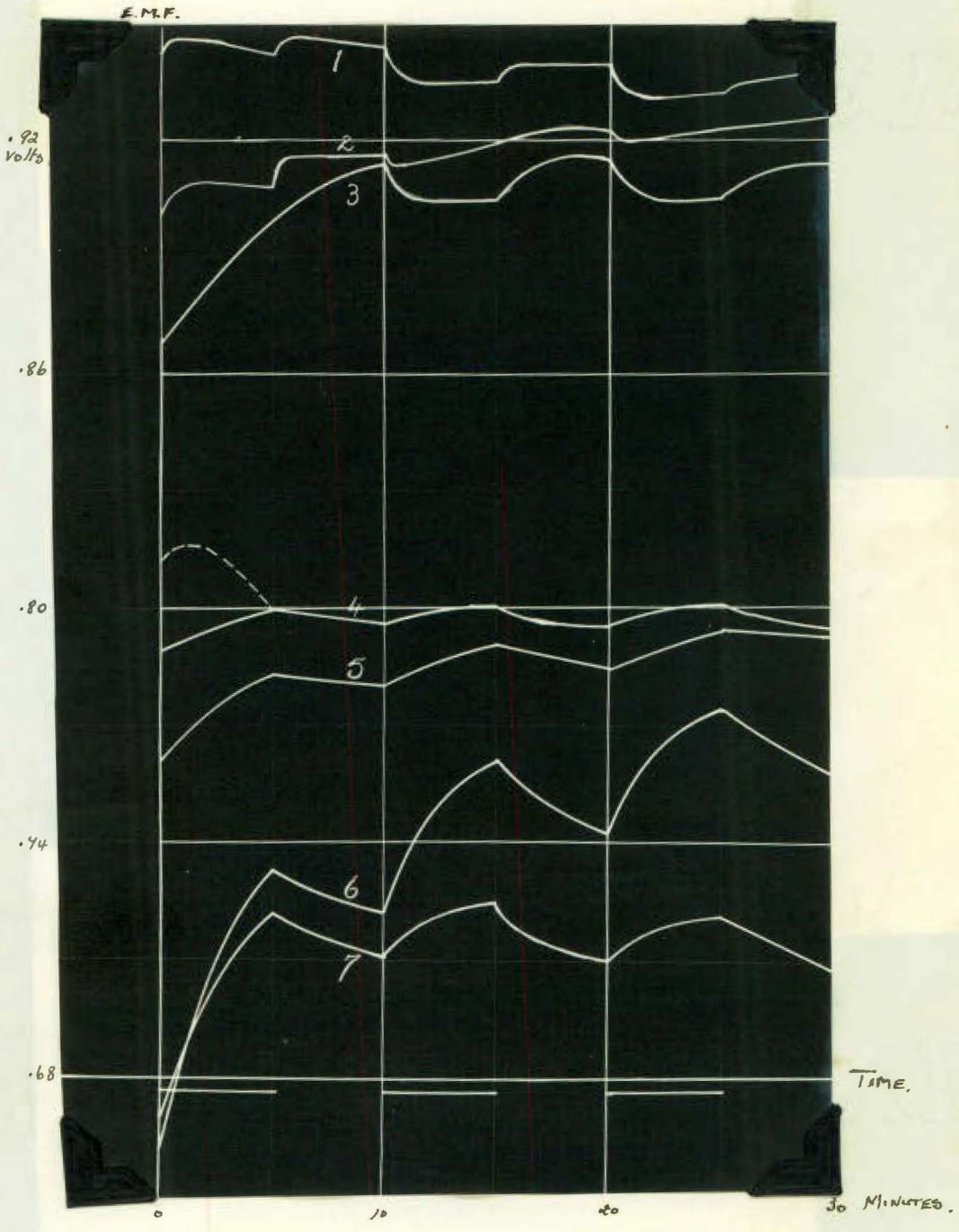
139. Nernst. Z. phys. Chem. 47, 52 (1904).

140. Lewis & Crandall. J.A.C.S. 52, 3757, 3769 (1930).

141. White, Monaghan & Urban. J. Phys. Chem. 39, 619 (1935).

142. Lippmann. Compt. Rend. 95, 686 (1882).

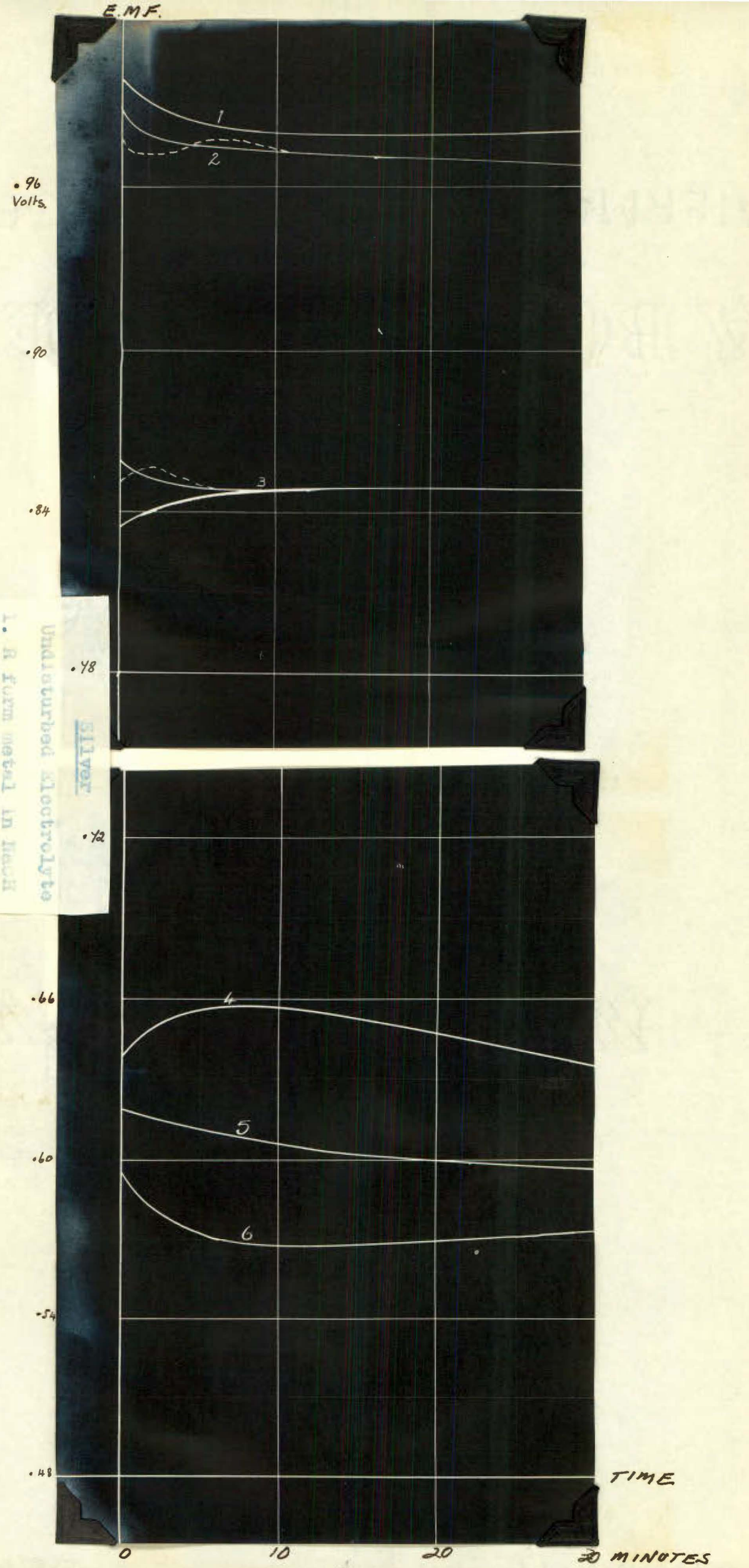

E.M.F.
1·06
VOLTS
1·00
·94
·88
·82
1
2
3
4
9
5
6
7
8
TIME
0
10
20
30 MINUTES.

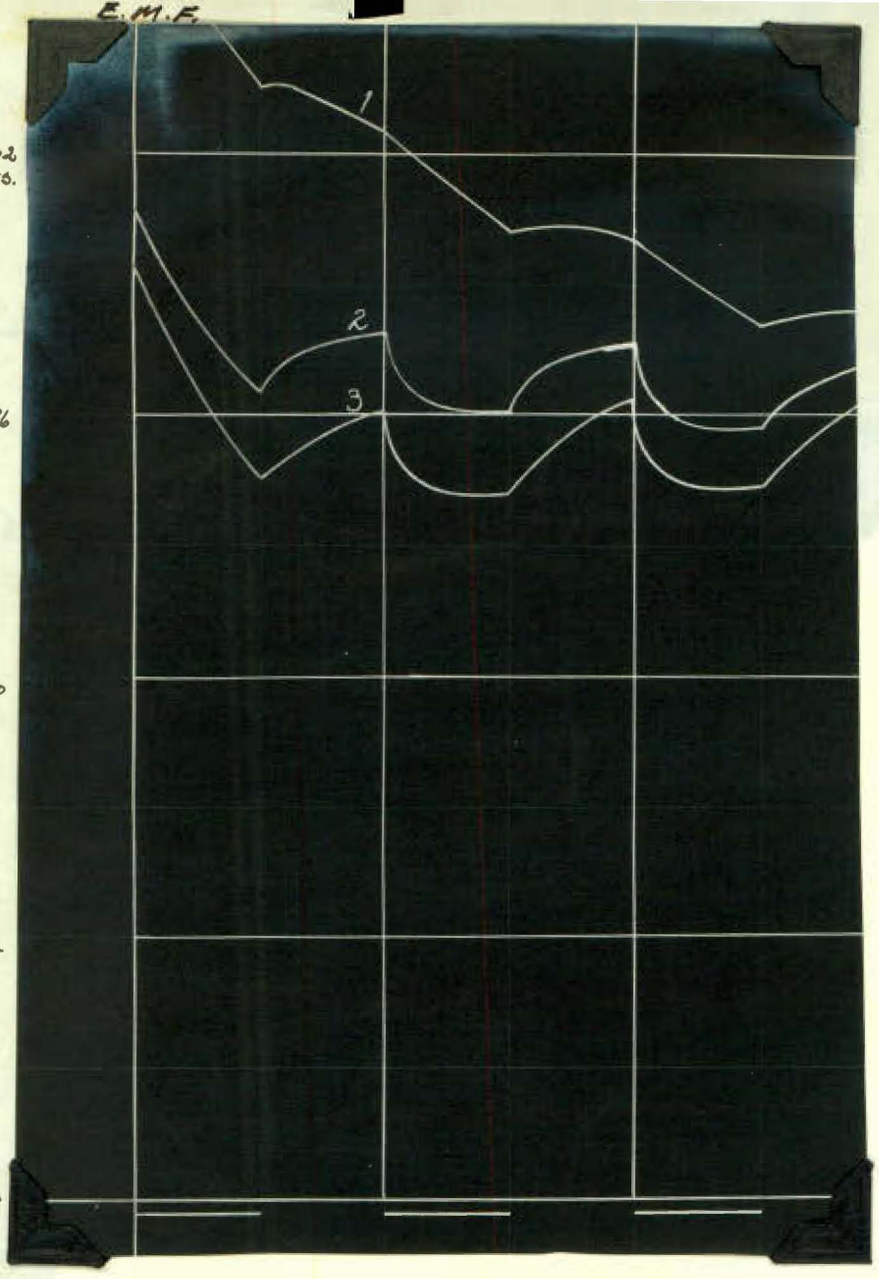


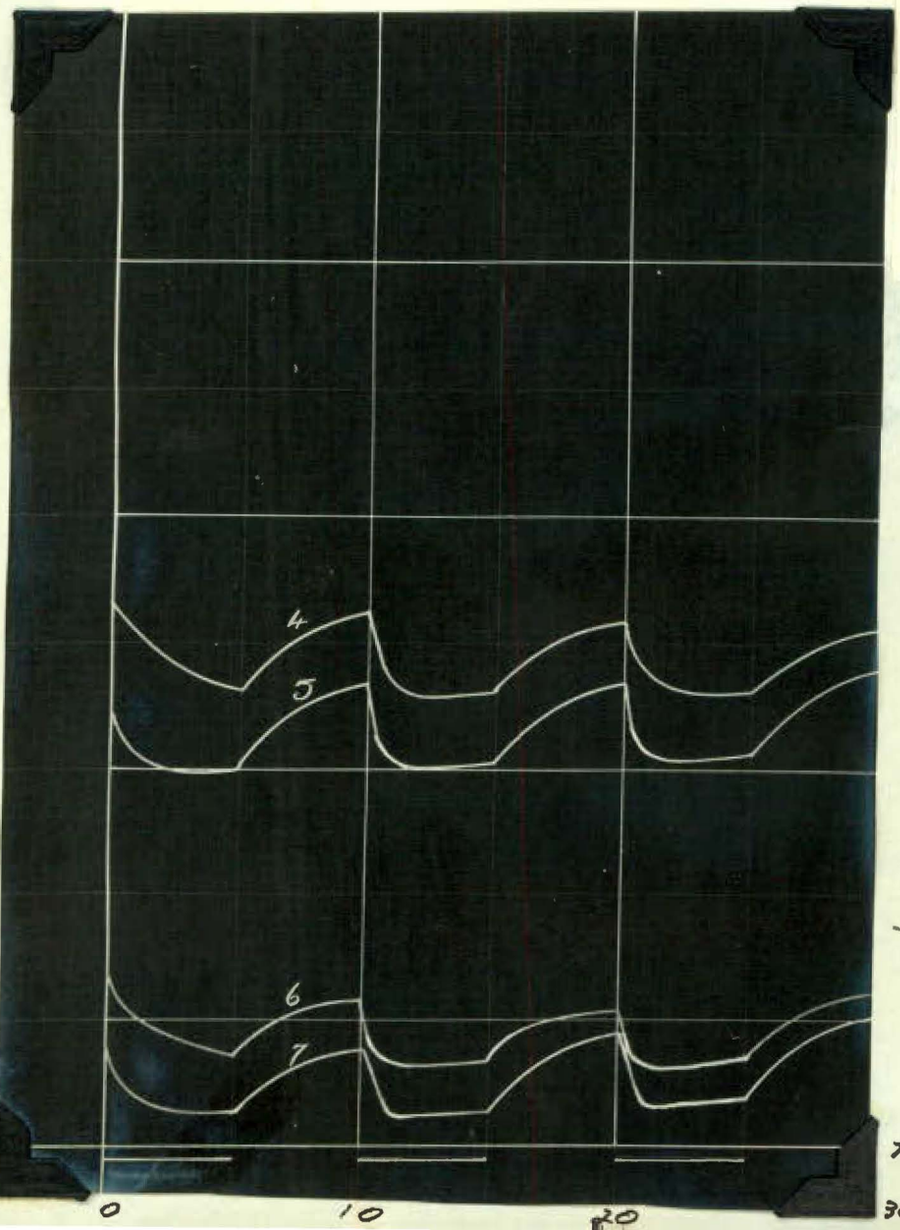
Gold

Disturbed Electrolyte

1. Bright metal in NaOH
2. R form " NaOH
3. Bright " NaOH
4. Bright " KCl
5. R form " KCl
6. Bright " H_2SO_4
7. R form " H_2SO_4


E.M.F.
.96 Volts.
.90
.84
.78
.72
.66
.60
.54
.48
1
2
3
4
5
6
TIME
0
10
20
30 MINUTES
Undisturbed Electrolyte
Silver
1. R form metal in Mech
2. Bright " " Mech
3. R form " " H2SO4
4. R form " " KCl
5. Bright " " KCl
6. R form " " KCl

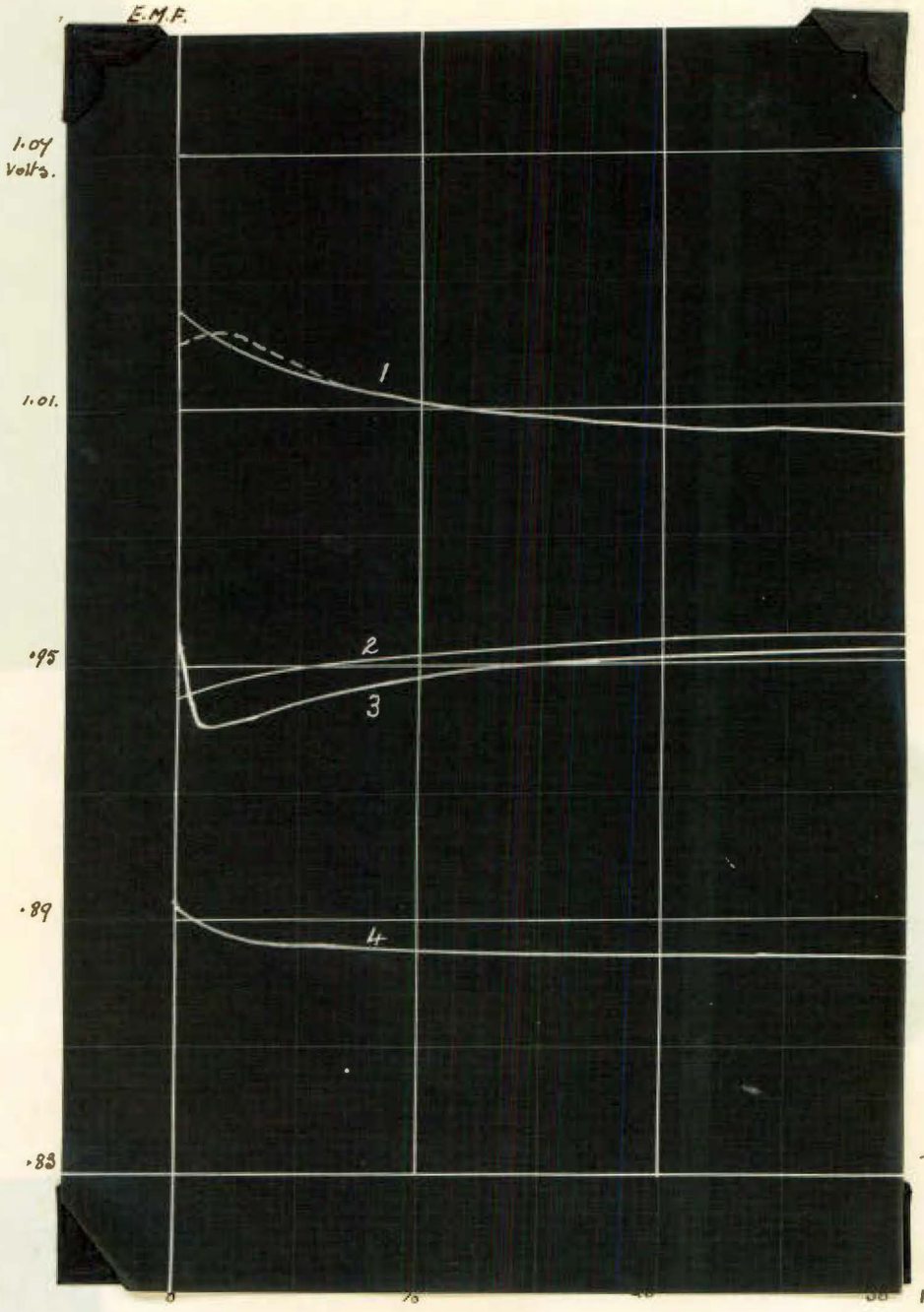




Silver

Disturbed Electrolyte

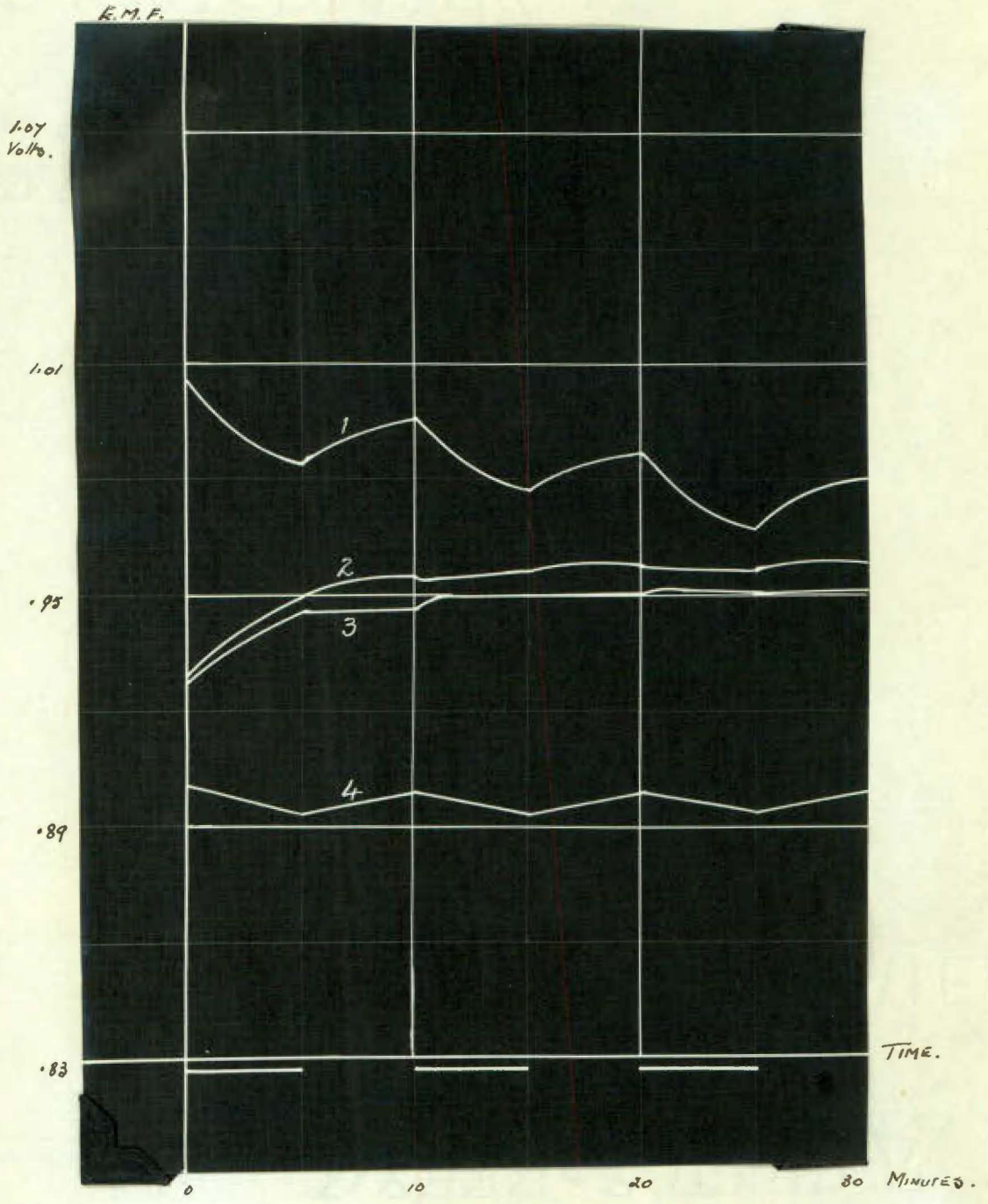
1. Bright metal in NaOH
2. Bright " NaOH
3. H form " NaOH
4. K form " KCl
5. Bright " KCl
6. H form " H_2SO_4
7. Bright " H_2SO_4



Osmium

Undisturbed Electrolyte

1. Black metal in KCl
2. Black " NaOH
3. Black " NaOH
   (on Ag base)
4. Black " H_2SO_4



Osmium

Disturbed Electrolyte

1. Black metal in KOl
2. Black metal " NaOH
3. Black " NaOH
4. Black " H_2SO_4