THE DIRECT MEASUREMENT OF THE

OXIDATION-REDUCTION POTENTIAL OR ALCOHOLS.

By

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I. INTRODUCTION.

A. PURPOSE OF THIS INVESTIGATION.

For many years Organic Chemistry has been developed entirely apart from Inorganic, with the belief that the two were entirely separate and distinct, but in recent years Organic and Physical chemists have been led to investigate this difference, to determine whether it is really one of kind or only one of degree.

It was with the idea of helping to clear up this situation that Dr. Brewster started an investigation into the nature of some organic oxidation and reduction cells, with the idea that from the data obtained one might build up an electromotive series of the organic groups, methyl, ethyl, propyl, etc. just as has been done with the metals in Inorganic Chemistry.

B. HISTORICAL AND THEORETICAL.

Dr. F. B. Dains, Mr. Markley[1] and Mr. Shields[2], of this University, made a study of the relative reactivity of certain organic esters such as methyl, ethyl, propyl, butyl formates in one series and methyl, ethyl, propyl, and butyl oxalates in another series with organic bases such as aniline. The experimenters found that with each series the percentage yield of formanilide or oxanilide ran in the order of increasing yield as follows: methyl, ethyl, propyl. The maximum yield was with propyl and the yield dropped off with butyl[3].

Other reactions such as the change of propyl alcohol to isopropyl on heating, etc. point to the fact that there might be a difference in energy content of an organic compound depending on the groups associated with it.

Until very recently, but very little work has been done in connection with this subject of the potential of organic oxidation and reduction cells. In 1892, Bancroft[4] made a study of a large number of more or less common oxidizing and reducing agents and these included alkaline solutions of pyrogallol and hydroquinone. In this work, Bancroft measured the potential against other oxidizing and reducing agents but not against a standard electrode. A few years later, Neumann[5] put Bancroft's work upon a better basis by repeating his work and determining the potentials of the solutions against a calomel electrode.

In 1892, Slaboszewicz made some admittedly rough measurements on acetaldehyde and ethyl alcohol in 2M H_2SO_4. Briefly, he measured the potential of the alcohol solution against the aldehyde using a salt bridge of KCl and platinized platinum electrodes. He checked the potentials of aldehyde against alcohol by measuring each against a calomel electrode. He allowed his solutions to stand over relatively long periods of time and at concentrations varying from one per cent. to thirty per cent. alcohol. He found that after the first twenty-four hours there was less change in the potential difference though it was only after

120 hours the change ceased in the centivolt column. He
does not mention any attempt to repeat his results.

In 1921, F. S. Granger and J. M. Nelson[6] made a stu-
dy of the potentials of mixtures of an organic compound and
its oxidation product, namely hydroquinone and quinone.
The solutions were made up of HCl varying from molar to
.01 molar concentration and a saturated solution of hydro-
quinone and quinone. The bridge between the saturated
calomel half cell and the quinone-hydroquinone cell was
a saturated solution of KCl. Possible contact potentials
at the boundaries were not taken into consideration. A
platinum electrode was used in the quinone-hydroquinone
cell and nitrogen was bubbled through at the start to pro-
vide agitation and remove the air. The nitrogen was later
cut off and the cell sealed off when it remained fairly
constant for 180 hours. They found that most of the ir-
regularities disappeared after the first 48 hours. The po-
tential differences which they measured were in good agree-
ment with those calculated from the Van't Hoff equation:

$$\pi_1 - \pi_2 = \frac{RT}{2F}\left[\ln\frac{(Quin)_1}{(Hydroquin)_1} - \ln\frac{(Quin)_2}{(Hydroquin)_2}\right]$$

since the concentration of the Quinone and Hydroquinone in
saturated solutions were known. Granger and Nelson empha-
size the fact that in order for this method to work the
reaction by which the oxidized product is changed to the
reduced product must be a reversible reaction. They men-
tion the fact that since an alcohol and aldehyde mixture

does not give a reversible reaction their method is not applicable to this system.

In 1922, J. B. Conant[7] of Harvard and his students undertook an electrochemical study of systems similar to quinone-hydroquinone in acid solution in order to determine, if possible, the difference between the reversible reaction involved in the change of quinone to hydroquinone and the irreversible reaction involved in the change of alcohol to aldehyde. Conant says that since the reaction in the former case is strictly reversible the oxidation-reduction potential should be easily measured just as that of ferric-ferrous salts and goes on to say that such reactions involve merely the loss or gain of electrons. The application of the principles of electrochemistry is amply justified by the results although many of the more usual cases of reduction of organic substances do not seem to involve electron transfer alone. It is worth while to note at this point that while the oxidation of hydroquinone to quinone is strictly reversible in acid solution, in alkaline solution it is not and no constant E.M.F. values could be obtained with quinone-hydroquinone in alkaline solution. For this reason Conant chose salts of anthraquinone sulfonic acids since the oxidation and reduction of these salts is a reversible reaction in either alkaline or acid solution.

Briefly, Conant's method was as follows:- He introduced 350 c.c. of a buffer solution into a 400 c.c. glass cell and determined the hydrogen ion concentration by means of an electrode of the Hildebrand type. Then, he

introduced 1/1000 of a mole of anthraquinone sulfonic acid in the form of its sodium salt. The cell was swept free from air by means of oxygen-free nitrogen and the stirrer started. The reducing agent, titanous chloride, was added in suitable increments from a burette.

After the addition of each increment, the potentials of the solution in the cell was measured. The course of the reduction was followed by plotting the potential against the increments of reducing agent added. By inspection of these curves, it was possible to determine the end point of the titration; this value was taken as 100% reduction. The value of the potential at the mid point, 50% reduction, was then determined by graphical interpolation of the curve. Moreover, the data on the potential so measured and the amount of reducing agent added enabled them to calculate the value of the ratio of

$$\frac{(A)}{(AH_2)}$$

where (A) = concentration of unreduced and (AH_2) = concentration of reduced material. When the reaction was carried out in acid solution, the results so obtained were in accord with the following equation:

$$\pi = \pi_0' + .0295 \log\left(\frac{(A)}{(AH_2)}\right) - .0295 \log K_1 K_2 + .059 \log(H^+)$$

$$K_1 = \frac{(H^+)(AH^-)}{(AH_2)} \qquad K_2 = \frac{(H^+)(A^{--})}{(AH^-)}$$

Conant[8] and his students also devised an indirect me-

thod for the measurement of the potentials of substances
whose oxidized and reduced forms are not in mobile equi-
librium with the oxidizing or reducing agents. In the re-
duction of such compounds as nitro benzene, the reducing
agent is either without effect or causes complete reduc-
tion. It is impossible to find a reducing agent with which
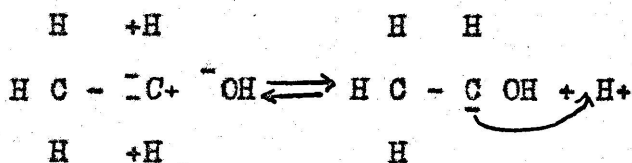the reaction will proceed to a measurable equilibrium.

To quote Mr. Conant, "However, while no real oxida-
tion-reduction potential of such irreversible systems can
be formulated or measured, it is possible to characterize
them with considerable precision by determining the poten-
tial of the weakest reducing agent, (i. e., the reducing
agent of highest oxidation-reduction potential) which will
just cause reduction." If a series of reducing agents of
known potential are available, it is possible to determine
which one will just reduce the compound. For example, if
it is found that a compound, dibenzoylethylene, is not re-
duced by a reagent "A" of potential +.31 but is reduced by
reagent "B" of potential +.24 then some value within this
range +.31 to +.24 can be considered as the potential of
the critical reducing agent; the potential of such a hy-
pothetical reducing agent Conant calls the "Apparent Re-
duction Potential", of the substance in question.

It is apparent that the accuracy of this method is
dependent primarily upon the possibility of obtaining a
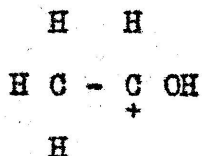series of reducing agents such that the potential of each

member is only slightly lower than that of the preceding member. It is very difficult to get a series of reducing agents closely enough graded to be satisfactory, Conant admits, and in some cases the scheme fails completely.

The cumbersomeness and limited application of the foregoing experimental work together with the following hypotheses of the electronic theory led Dr. Brewster to try to work out a more direct system of potential measurement of simple organic compounds by simply introducing a platinum electrode into a water solution of the compound, using KCl as the electrolyte, and measuring the E.M.F. of the cell against a normal calomel half cell by means of the potentiometer.

The hypotheses of the electronic theory which partially led to this investigation are as follows: In order to explain the reducing action of alcohols, the electronic theory assumes this action to take place.

$$
\begin{array}{ccc}
\text{H} & +\text{H} & & \text{H} & \text{H}\\
\text{H C} - \text{C+}\ \ \text{OH} & \rightleftharpoons & \text{H C} - \text{C OH} +\text{H+}\\
\text{H} & +\text{H} & & \text{H}
\end{array}
$$

Alcohol in this form gives up two electrons and becomes positive.

$$
\begin{array}{cc}
\text{H} & \text{H}\\
\text{H C} - \text{C OH}\\
& + \\
\text{H}
\end{array}
$$

An OH group
adds on

H   H   H

H C - C OH   and water splits   H C - CHO + H₂O
                off giving
H   OH

$$HC-C(OH) \xrightarrow{\text{and water splits off giving}} HC-CHO + H_2O$$
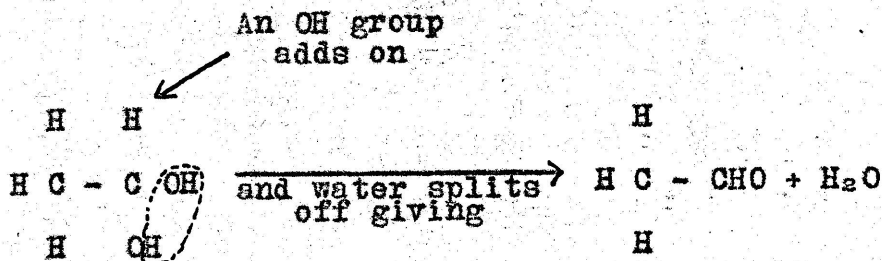
Now, if this theory be true, one should be able to
measure this tendency to give up electrons or reducing
power by means of a platinum electrode in contact with the
solution using a normal calomel electrode as the other
half of the cell.

Likewise, in the case of aldehydes, it is known that
when vinyl bromide is hydrolyzed in place of giving vinyl
alcohol, $HC = C - OH$, as would be expected, it gives
$CH_3 - CHO$ by the following shift of the hydrogen:

$$HC = C - OH \longrightarrow HC - C = O$$
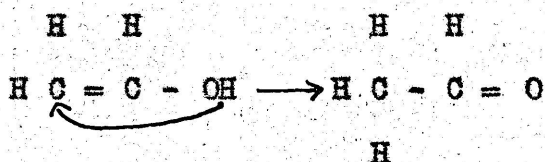
Since one hydrogen can shift, it seems possible that others
might do likewise. The reducing action of aldehydes is ac-
counted for by the electronic theory as follows:

$$HC - C^+ {}^-O \longrightarrow HC = C \, OH$$
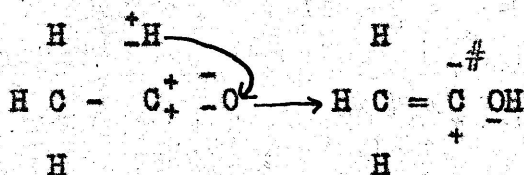
#Electron free to go off. The tendency to
leave as measured by its potential would
be a measure of the strength of its reduc-
ing action.

EXPERIMENTAL.

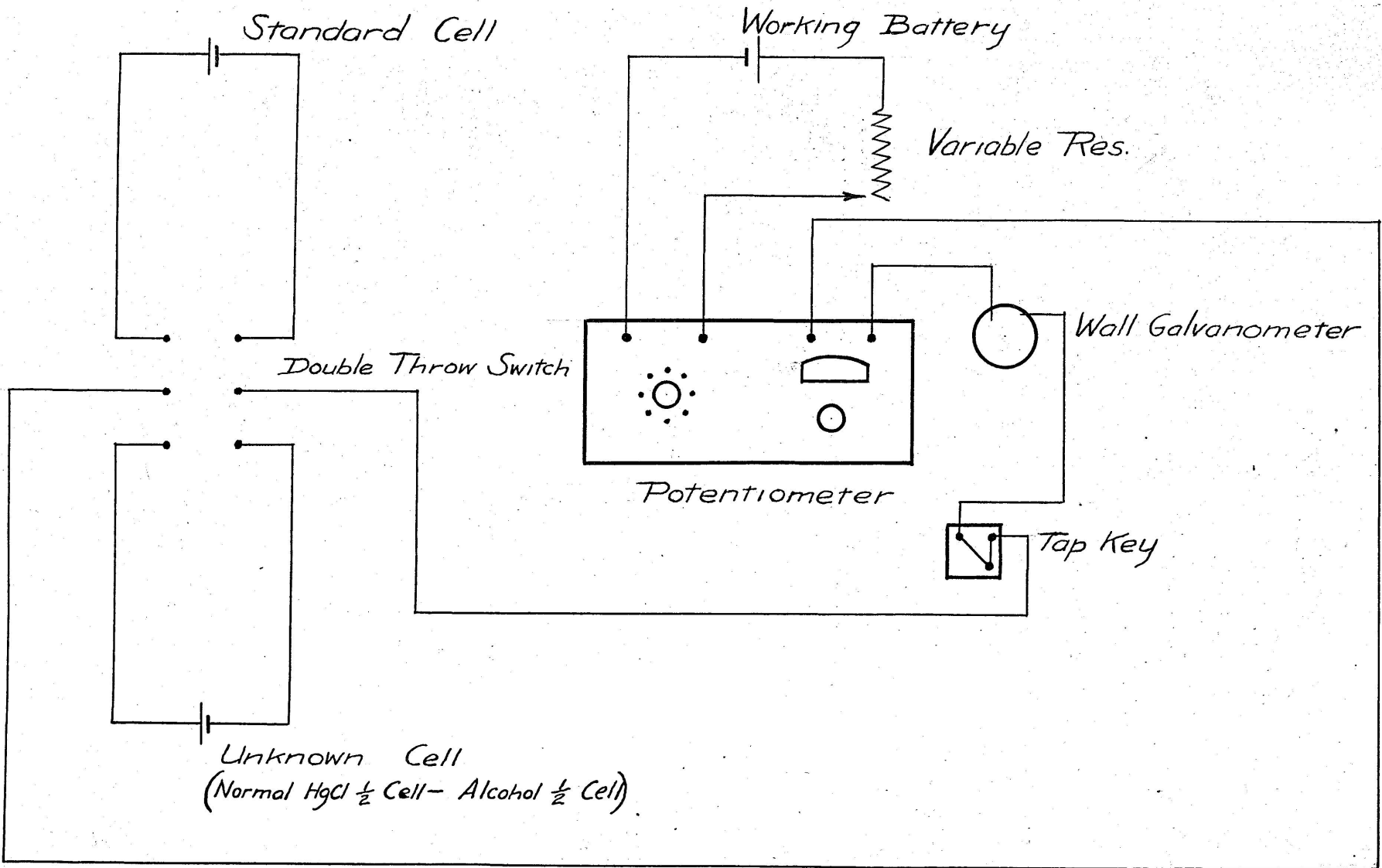In recording the experimental work, since the results were admittedly incomplete and not entirely satisfactory, it was thought best to record the entire history of the investigation for the benefit of those who might wish to carry it further. In outlining the experimental work, it was decided for the sake of clearness to divide it arbitrarily into three stages related to the three major modifications in the type of cell and electrode used. The fundamental idea as alluded to in the introduction was adhered to throughout.

PART I.

The original idea as conceived by Dr. Brewster was to make up solutions of a series of alcohols methyl, ethyl, propyl, etc. of accurately known concentration, 2 molar, and when ready to make a run to mix a portion of the alcohol solution with an equal portion of 2 normal KCl solution making the whole solution normal with respect to both the alcohol and the KCl. This solution was introduced into a glass cell into which a bright platinum electrode has been sealed. This cell was connected to a normal calomel half cell by a salt bridge of normal KCl thus eliminating contact potential. The E.M.F. of this combination was measured by means of the potentiometer scheme illustrated in the wiring diagram, Figure I, Plate I, page 10. A standard Leeds and Northrup Student Potentiometer reading to .0001 volt together with a Leeds Northrup Wall Galvanometer and other standard equipment throughout was employed in making the potential measurements.

Standard Cell

Working Battery

Variable Res.

Double Throw Switch

Wall Galvanometer

Potentiometer

Tap Key

Unknown Cell
(Normal HgCl ½ Cell— Alcohol ½ Cell)

Wiring Diagram

Plate I.

10.

The solutions in this first stage were made up of distilled water boiled down one half to remove dissolved oxygen. One hundred forty-nine and two tenths grams of dry KCl (Baker's or Merck's graded as C. P. by the makers) was weighed out and dissolved in eough of the distilled and reboiled water to make a liter of solution. 32.04, 46.06, and 60.08 grams of methyl ethyl and normal propyl alcohol respectively were weighed out and each dissolved in enough distilled and reboiled water to make 500 c.c. of solution. Alcohols were prepared by using the best grades obtainable and refluxing them over quicklime for four hours. After refluxing, the alcohols were distilled from the quicklime and redistilled using only that fraction whose boiling point varied no more than two degrees from the correct boiling point. Solutions were checked for concentration on the dipping refractometer. The cell used is shown in Figure II, Plate II, page 12, and has been described above.

E.M.F. Readings for the System.

2 M. Alcohol + 2 M. KCl	Pt	N/1 KCl	Normal Calomel Half cell

This type of alcohol cell exhibited a decided "drift" in potential, that is, each successive reading was a little greater than the one just preceding. This "drift" slowed down in the course of several hours and in some instances gave nearly constant readings at the end of twenty-four hours. However, if the cell was emptied and a fresh

Cu Wire

Brass

Hg

Glass Bearing

Hg
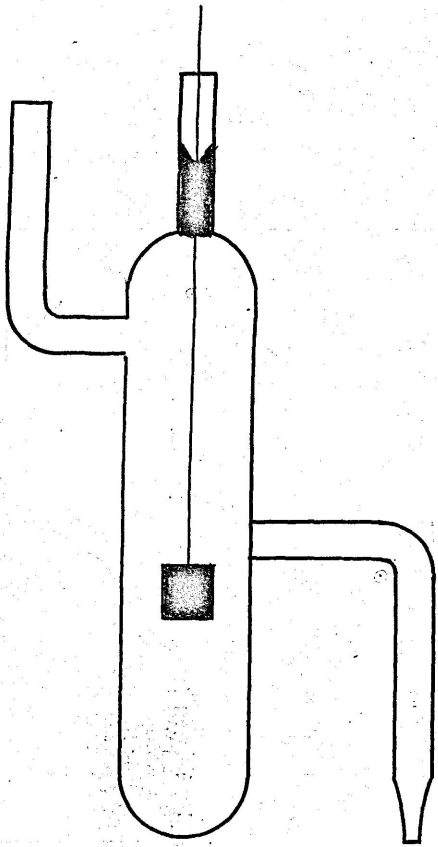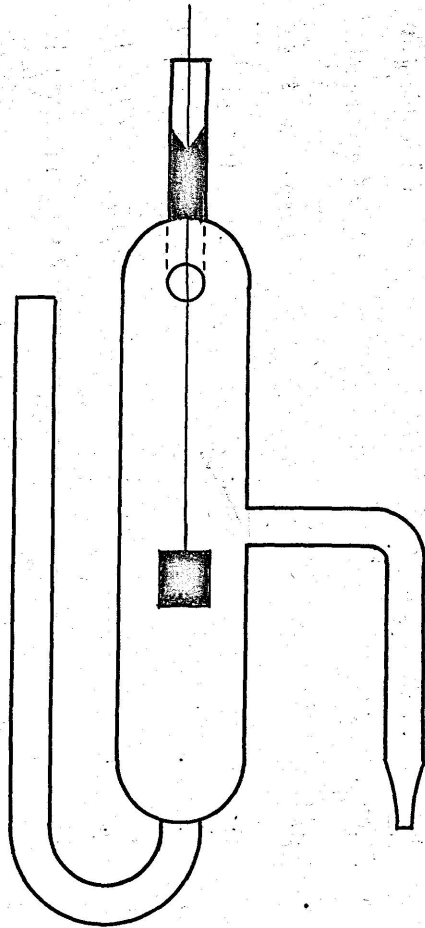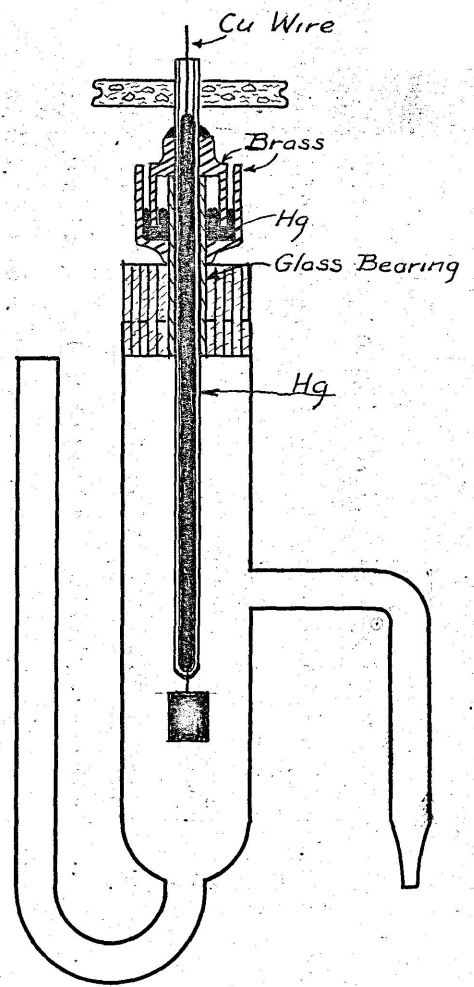
Fig. II.   Fig. III.   Fig. IV.

Cross Section of Three Types of Cells

Plate II.

solution of the alcohol placed in it, it was not possible
to reproduce the former readings, and when fairly con-
stant readings were again reached, they would not be the
same as previous constant readings for the same alcohol.
The accompanying table illustrates a typical set of read-
ings for three alcohols. The first column gives the time,
the second gives the E.M.F. of the combination alcohol
half cell and calomel half cell, the third gives the E.M.F.
of the alcohol half cell assuming the E.M.F. of the calomel
to be .56 volts. (See Page 14.)

The starred value in the Propyl alcohol series in
Table I is where the cell was placed in an ice water bath to
test the effect of temperature change on the cell. The drop,
as will be explained later, was not due to change in tempera-
ture but to shaking and stirring the contents of the cell
during the process of putting it in the ice bath.

TABLE I.

Time in Minutes	METHYL ALCOHOL		ETHYL ALCOHOL		N. PROPYL ALCOHOL	
	E.M.F. HgCl 1/2 cell +	E.M.F. Alcohol 1/2 cell	E.M.F. HgCl 1/2 cell +	E.M.F. Alcohol 1/2 cell	E.M.F. HgCl 1/2 cell +	E.M.F. Alcohol 1/2 cell
0	.3845	+.1755	.3275	+.2325	.1665	+.3935
3	.3790	.1810	.3400	.2200	.1755	.3845
6	.3784	.1816	.3450	.2150	.1805	.3795
9	.3770	.1830	.3650	.1950	.1840	.3760
12	.3100	.2500	.3670	.1930	.1870	.3730
15	.3280	.2320	.3710	.1890	.1900#	.3700
18	.3405	.2195	.3750	.1850	.1655#	.3945
21	.3430	.2165	.3800	.1800	.1640	.3960
24	.3440	.2155	.3840	.1760	.1675	.3925
27	.3455	.2145	.3880	.1720	.1655	.3945
30	.3465	.2135	.3895	.1705	.1640	.3960
33	.3480	.2120	.3900	.1700	.1639	.3961
36	.3495	.2105	.3950	.1650	.1641	.3959
39	.3495	.2105	.3965	.1635	.1650	.3950
42	.3496	.2104	.3972	.1628	.1650	.3950
45	.3495	.2104	.4000	.1600	.1655	.3945
48	.3497	.2103	.4000	.1600	.1660	.3940
51			.4020	.1580	.1690	.3910
54			.4021	.1579	.1701	.3899
57			.4026	.1574	.1715	.3885
60			.4030	.1570	.1720	.3880
63			.4042	.1558	.1740	.3860
66			.4000+		.1740	.3860
69					.1744	.3856
72					.1784	.3816
75			+Constant 48 hours		.1805	.3795
78			later.		.1810	.3790
81					.1845	.3755
84					.1850	.3750
87					.1850	.3750

The data in Table I shows that there is a tendency for the "drift" to slow down the end of about forty-five minutes and to become fairly constant at the end of forty-eight hours. However, the results do not appear to be reproducible as the following Table II shows: The results given in this table were obtained with new solution of two molar propyl alcohol freshly made up and two molar KCl. The E.M.F. readings are in volts and the results were all positive.

TABLE II.

Time in Minutes	E.M.F. Calomel Half Cell+	E.M.F. of Alcohol Half Cell
0	.1385	.4215
3	.1390	.4210
6	.1398	.4208
9	.1402	.4198
12	.1450	.4150
15	.1449	.4151
18	.1446	.4154
21	.1445	.4155
24	.1475	.4125
27	.1490	.4110
30	.1515	.4085
33	.1550	.4050
36	.1595	.4005
39	.1595	.4005
42	.1595	.4005
45	.1595	.4005
48	.1595	.4005

PART II.

In the experimental work of Part I, an attempt was made to investigate the effect of temperature changes on the E.M.F. of the alcohol cells. A cell, formerly at room temperature,

was placed in an ice water bath and a very decided rise in the E.M.F. of the cell was observed[#]. As this was in the direction opposite to that which was expected, the phenomenon was further investigated and it was found that shaking the cell and contents incident to putting the cell in the ice bath caused the rise in E.M.F.[9], and that if the shaking was done before cooling the cell and continued while the cell was in the bath there was no sudden change, the E.M.F. beginning to "drift" down again as before but more slowly so long as the shaking was continued.

Tests on the distilled and reboiled water which had been used for making up alcohol and KCl solutions showed that not all of the dissolved oxygen had been removed by boiling the distilled water down to one-half its original volume. The test was carried out by the Winkler method for dissolved oxygen outlined in Standard Methods of Water Analysis.

The Winkler test is as follows: Fill a 300 c.c. bottle fitted with a ground glass stopper with the water in which the dissolved oxygen is to be determined completely full and put in the stopper being careful that no air bubbles are trapped in the bottle. Remove the stopper and add successively one c.c. of $MnSO_4$ (425.5 grams per liter) and 3 c.c. of alkaline KI (700 grams NaOH and 150 grams KI per liter). Replace stopper, shake contents of bottle and allow to set-

[#]See starred value in propyl alcohol column in Table I, page 14.

tle. Add 1 c.c. of concentrated H_2SO_4 and when the precipitate is dissolved measure out 250 c.c. of the contents of the bottle into a volumetric flask and titrate to faint yellow with $Na_2S_2O_3$ solution containing .025 grams of $Na_2S_2O_3$ per liter, add starch solution and complete titration. The number of c.c. of $Na_2S_2O_3$ solution is the number of parts per million of dissolved O_2.

The failure to remove all of the dissolved oxygen and the desire to try agitating the solution in the cell led to the design of the second type of the cell illustrated in Figure III, Plate II, page 12. In this cell gas was bubbled up through the solution in the cell by means of the side tube "A" and the hole in the bottom of the cell. The gas was to serve the double purpose of providing agitation and removing the remaining oxygen. The gas chosen for this purpose was nitrogen. As no tank nitrogen was available, it was generated from NH_4Cl and $NaNO_2$ by heating a solution of NH_4Cl to boiling and adding a solution of $NaNO_2$ slowly drop by drop. A steady and fairly uniform stream of nitrogen was thus generated and stored in a large gas holder over water. This nitrogen gas was analyzed[#] for oxygen and found to contain from .09 to .11% O_2. Before bubbling it through the cell it was passed through a wash tower of alkaline pyrogallol and another of sulfuric acid, the pyro to remove as much oxygen as possible and the acid to remove any NH_3 which

[#]This gas analysis through courtesy of I. L. Malm.

might have come over from hydrolysis of NH_4Cl.

The alcohol solutions in the runs with this type of cell were made up from alcohol prepared as in Part I and in exactly the same concentration, etc. The electrodes in this type of cell were platinized platinum in place of the bright platinum used in the previous cell.

The proceądure in these runs differed a little from that in former runs in that a certain volume of 2 molar KCl solution was placed in the cell first, nitrogen gas bubbled through it continuously and the reading with the KCl solution alone was taken. When the KCl solution and nitrogen system became constant, an equal volume of the 2 molar alcohol solution was added to the KCl and gas bubbling continued. Readings were taken at regular intervals until the cell became fairly constant. It may be well to note at this point that butyl alcohol was not used in these runs since it is not sufficiently soluble in water to make a 2 molar solution.

Column one in Table III, page 19, represents time in minutes; column two the reading of the KCl alone and the calomel half cell; column three represents reading after adding the alcohol; and column four the actual E.M.F. of the alcohol and the reading taken before adding the alcohol.

TABLE III.

Time in Minutes	METHYL ALCOHOL			ETHYL ALCOHOL			PROPYL ALCOHOL.		
	E.M.F. of KCl Cal +	E.M.F. after Adding Alcohol Cal +	Difference E.M.F. of Alcohol	E.M.F. of KCl Cal +	E.M.F. after Adding Alcohol Cal +	Difference E.M.F. of Alcohol	E.M.F. of KCl Cal +	E.M.F. After Adding Alcohol Cal +	Difference E.M.F. of Alcohol
0	.5550	.7710		.5280	.8085		.4900	.7790	
3	.5570	.7825		.5295	.8200		.4920	.7850	
6	.5570	.7860		.5300	.8210		.4925	.7900	
9	.5570	.7861		.5310	.8215		.4930	.7920	
12		.7860		.5310	.8215		.4930	.7930	
15		.7860			.8215		.4930	.7930	
18		.7860						.7930	
			.2270			.2905			.3000

Attempts to reproduce the foregoing values in Table III by making up new solutions and repeating the readings were no more successful than in the former cases as illustrated in Part I.

PART III.

Since agitation appeared to shorten the time required for the E.M.F. to become fairly constant, it was decided to try a rotating electrode in place of bubbling gas as this would obviate the necessity of generating nitrogen and we had no direct proof at this time that the dissolved oxygen remaining in the water had any effect on the potential of the solution.

The design of the new and final type of cell is illustrated in Figure IV, Plate II, page 12. The side arm "A" for bubbling gas up through the solution in case it was desired was retained. The cell was closed at the top with a tight fitting one-hole rubber stopper. A short piece of glass tubing was fitted into this hole to act as a bearing for the rotating electrode. Another piece of glass tubing of such a size as to pass smoothly through the bearing and rotate in it without undue friction was chosen and a platinized platinum electrode sealed on one end. A cork pulley with a small copper burr on the under side to the place at which the pulley came in contact with the glass bearing completed the electrode as first designed. Later it was modified to the form shown in Figure IV, Plate II by substitut-

ing a mercury seal for the former simple type of bearing.

In experimenting with this new type of cell during preliminary runs, it was observed that when the platinized platinum electrode was removed from the solution and exposed to the air for even a brief period of time and then reinserted in the same solution there was a very decided change in the E.M.F. of the cell. The most plausible explanation was that the electrode had adsorbed oxygen during the exposure and on reinserting the electrode in the solution this oxygen caused a change in the E.M.F. reading. The cell after a few minutes run came back to about the same E.M.F. as it had before exposure of the electrode, but was never quite the same. It was decided that if oxygen adsorbed on the surface of the electrode had such an effect then dissolved oxygen in the solution must be a considerable source of error.

With this fact in mind, the solutions used in the new design of cell were made up in a different manner from the previous solutions and the procedure in making the run was slightly different.

The solutions were prepared from absolute alcohols prepared as in Part I, but they were made up one-half molar instead of two molar so as to include normal butyl alcohol. The water was boiled down to one-half of its former volume as before and placed in a one liter volumetric flask tightly corked with a ground glass stopper and allowed to cool. Up-

on cooling to 20° C, enough dry KCl was weighed out to make
a normal solution and placed in the distilled reboiled wa-
ter and the whole made up to the mark with water which had
been similarly treated. This normal solution of KCl was
then placed in a liter distilling flask and nitrogen gas
bubbled through it at a fairly rapid rate for about eight
hours. At the end of this time, 4.00 grams of methyl alco-
hol, 5.75 grams of ethyl alcohol, 7.51 grams of normal pro-
pyl alcohol and 9.26 grams of normal butyl alcohol were
weighed out; each was placed in a 250 c.c. volumetric flask
and made up to the mark with the KCl solution just prepared.
This procedure obviated the necessity of mixing KCl and
alcohol solutions just before the run ʌ eliminated a possible
source of error.

When ready to make the run, the cell was filled about
two-thirds full of solution; nitrogen gas was bubbled through
the solution for a short time to get rid of the air above the
solution and the motor started. The following readings re-
present results before a mercury seal was designed to prevent
air getting back into the cell. The E.M.F. readings were in
volts. Table IV, page 23 contains the data for the first run
and Table V, page 24, the data for the second run using dif-
ferent portions of the same solutions.

TABLE IV.

Time in Minutes	METHYL ALCOHOL		ETHYL ALCOHOL		N PROPYL ALCOHOL		N BUTYL ALCOHOL	
	E.M.F. Cal. -	E.M.F. Alcohol half Cell	E.M.F. Cal. -	E.M.F. Alcohol half Cell	E.M.F. Cal. -	E.M.F. Alcohol half Cell	E.M.F. Cal. -	E.M.F. Alcohol half Cell
0	.0450	.6050	.0620	.6220	.1030	.6630	.0920	.6520
10	.0450	.6050	.0630	.6230	.1055	.6655	.0910	.6510
20	.0455	.6055	.0635	.6235	.1070	.6670	.0930	.6530
30	.0470	.6070	.0635	.6235	.1070	.6670	.0935	.6535
40	.0470	.6070	.0635	.6235	.1070	.6670	.0935	.6535
50	.0470	.6070	.0635	.6235	.1070	.6670	.0935	.6535

TABLE V.

Time in Minutes	METHYL ALCOHOL		ETHYL ALCOHOL		N PROPYL ALCOHOL		N BUTYL ALCOHOL	
	E.M.F. Cal. -	E.M.F. Alcohol half Cell	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell	E.M.F. Cal. -	E.M.F. Alcohol half Cell
0	.0450	.6050	.0710	.6310	.1050	.6650	.0870	.6470
10	.0450	.6050	.0630	.6230	.1055	.6655	.0890	.6490
20	.0455	.6055	.0630	.6230	.1055	.6655	.0900	.6500
30	.0470	.6070	.0630	.6230	.1070	.6670	.0910	.6510
40	.0470	.6070	.0630	.6230	.1070	.6670	.1920	.6520
50	.0470	.6070	.0630	.6230	.1070	.6670	.1920	.6520

When a run was made on a second portion of the same al-
cohol solution, it was necessary, in order to obtain the con-
sistent results shown in the tables on pages 23 and 24, to
keep the electrode protected from the air by removing it in
a small cup fitted with a long glass rod for a handle. The
cup, of course, was dipped into the cell and the electrode
placed in it. The electrode and cup were then removed and
the alcohol in the cup protected the electrode from the air
until it could be replaced in the cell in a fresh solution
of the same alcohol. In changing from alcohol to alcohol,
of course, the electrode had to be exposed to the air in
rinsing off and drying but before it was placed in the cell
for the run, the most reproducible and consistent results
were obtained when the electrode was allowed to stand in the
solution of the alcohol to be run for five minutes before
placing it in the cell. This was, of course, using the
platinized platinum electrode.

In order to eliminate the above mentioned difficulties,
it was decided to use a gold plated platinum electrode[10].

As a final attempt to get reproducable and consistent
results, two sets of solutions were made up as follows:
two separate lots of water were boiled down the same amount
as checked by weighing on rough balances and allowed to
cool in closely stoppered volumetric flasks. Enough dry
KCl was weighed out and placed in each of the two flasks to
make a normal solution and the solutions made up to the

mark with a few c.c. of distilled, reboiled water. The KCl
solutions were then placed in two separate liter distilling
flasks and methane bubbled through them for about six hours
at a fairly rapid rate. Methane was used here instead of
nitrogen because the limited time prevented the generation
of so much nitrogen. At the end of the six hours, a portion
of the KCl solution was tested for dissolved oxygen and
found to contain less than one part per million. The origi-
nal distilled water contained from seven to six parts per
million before treatment.

4.00, 5.76, 7.51 and 9.26 grams respectively of methyl,
ethyl, propyl, and butyl alcohols were weighed and one put
in each of four 250 c.c. flasks. The alcohols were then di-
luted to the mark with one of the KCl solutions prepared.
A second series of alcohol solutions was similarly prepared
from the other KCl solutions.

A gold plated electrode was used on these runs and so
far as could be observed, the effect of exposure to the air
was so slight as to be negligible. This made manipulation
much easier. The run was conducted just as in Part II and
the results are shown in the tables on page 27 and 28.

The pH was taken on these two sets of solutions and it
was found to be the same. The method used in running the
pH was the colorimetric method outlined in Standard Methods
of Water Analysis for 1923 and although it is not extremely
accurate, comparative values should be close enough and any

TABLE VI.

Time in Minutes	METHYL ALCOHOL		ETHYL ALCOHOL		N PROPYL ALCOHOL		N BUTYL ALCOHOL	
	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell.
0	.1830	.7430	.1730	.7330	.1570	.7170	.1560	.7160
10	.1940	.7540	.1735	.7555	.1455	.7055	.1740	.7340
20	.1915	.7515	.1735	.7335	.1460	.7060	.1740	.7340
30	.1900	.7500	.1735	.7335	.1460	.7060	.1690	.7290
40	.1870	.7470	.1735	.7335	.1460	.7060	.1735	.7335
50	.1870	.7470	.1735	.7335	.1460	.7060	.1735	.7335
60	.1840	.7440	.1735	.7335	.1460	.7060	.1735	.7335
70	.1840	.7440	.				.1750[#]	.7350[#]
80	.1840	.7440						

[#]12 hours later.

TABLE VII.

Time in Minutes	METHYL ALCOHOL		ETHYL ALCOHOL		N PROPYL ALCOHOL		N BUTYL ALCOHOL	
	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell.	E.M.F. Cal. -	E.M.F. Alcohol half Cell.
0	.1750	.7350	.1825	.7425	.1660	.7260	.1600	.7200
10	.1750	.7350	.1785	.7385	.1560	.7160	.1620	.7220
20	.1755	.7355	.1600	.7200	.1580	.7180	.1625	.7225
30	.1755	.7355	.1650	.7250	.1580	.7180	.1625	.7225
40	.1755	.7355	.1630	.7230	.1580	.7180	.1625	.7225
50	.1755	.7355	.1630	.7230	.1580	.7180	.1625	.7225
60	.1755	.7355	.1630	.7230	.1580	.7180	.1625	.7225

differences in the E.M.F. recorded in these two tables for
any one alcohol could scarcely be attributed to that cause.
The dissolved oxygen content, however, might have been a
factor in causing the differences shown since the solutions
take up oxygen fairly rapidly and there was, of necessity,
some time intervening between the time the solutions were
made up and the time when the last sample was run. A way
of getting around this difficulty, which was not tried out
thoroughly on account of the shortage of time, was to make
up each alcohol solution from the oxygen free KCl solution
just as needed and using it immediately in the cell with
the mercury seal so that after the air above the solution
had been swept out by bubbling nitrogen through the cell
and solution the mercury seal could be filled with mercury
and the danger of reabsorbing oxygen done away with. An-
other idea which might be of value, should further work
along this lime be attempted, is to use a buffer solution
with the alcohol to control the pH more carefully so that
errors from this source could be eliminated.

SUMMARY AND CONCLUSION.

1. Former methods for the measurement of the potential
   of organic oxidation-reduction cell were reviewed.
   Need for more direct and simpler method was pointed
   out.

2. Three different methods were attempted for the direct
   measurement of the oxidation-reduction potential of

alcohols.

   a. Stationary electrode, bright platinum and plati-
     nized platinum.

   b. Stationary electrode with bubbling gas for agi-
     tation.

   c. Rotating electrode with bubbling gas electrodes
     either platinized platinum or gold plated plati-
     num.

3. Results so far as work goes not consistent or repro-
ducible.

4. Potentials showed a decided tendency to "drift" with
stationary electrodes but finally came to fairly con-
stant readings after about forty-eight hours. Poten-
tials with bubbling gas type of cell still showed
"drift" but came to equilibrium sooner. Rotating
electrode and gas decreased the period of "drift"
to only a few minutes.

5. With one exception, the results even in this crude
state show a gradually increasing E.M.F. to propyl
alcohol and then a drop back with butyl which is to
be expected from the previous work of Mr. Markley
and Mr. Shields on the hydrolysis of esters.

6. Dissolved oxygen was shown to have an effect on the
potential of the alcohol cell and it is an estab-
lished fact that the alkalinity or acidity has a de-
cided effect on the E.M.F. of such cells.

While the results are not satisfactory, the fact remains that there exists a difference in electrode potential in different alcohol solutions and the method will not be proven a failure until it can be demonstrated that all of the alcohol solutions give the same electrode potential.

Further work is needed in the development of proper apparatus and procedure to obtain consistent results.

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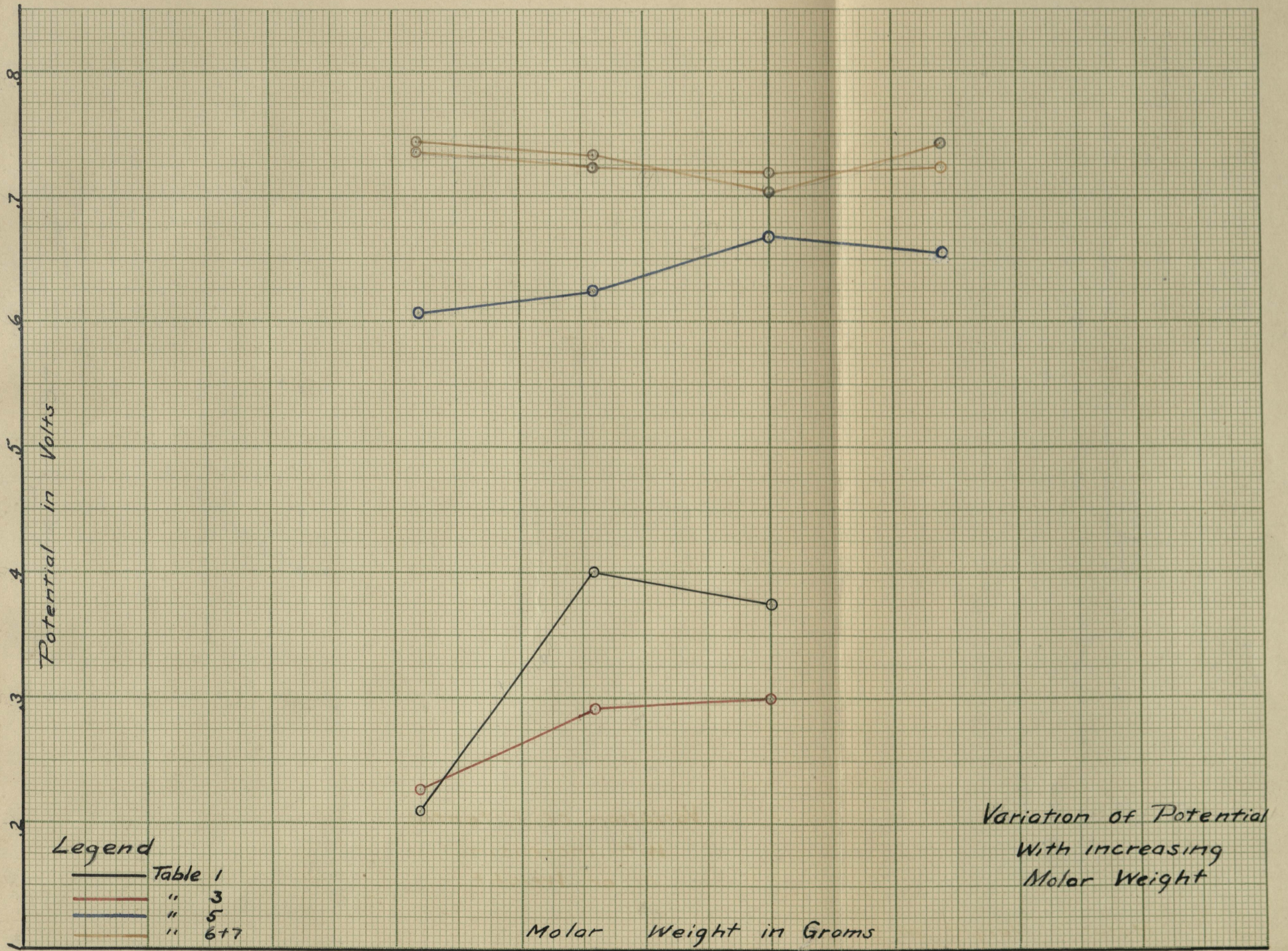
Variation of Potential
With increasing
Molar Weight

Potential in Volts

Molar Weight in Grams

Legend

Table 1	
" 3	
" 5	
" 6+7	

Typical Potential Variation With time
With the three types of Cells.

Type I
Stationary—No Gas

Type II
Gas Agitation

Type III
Rotating Electrode

Potential in Volts

Time in Minutes