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# The adaptation of the sodium and potassium electrodes to biological measurements

Emerson W. Bird
*Iowa State College*

# THE ADAPTATION OF THE SODIUM AND POTASSIUM ELECTRODES TO BIOLOGICAL MEASUREMENTS

BY

Emerson W. Bird

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Head of Major Department

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MOLECULAR AND IONIC SPECIES IN A SIMPLE NUTRIENT SOLUTION

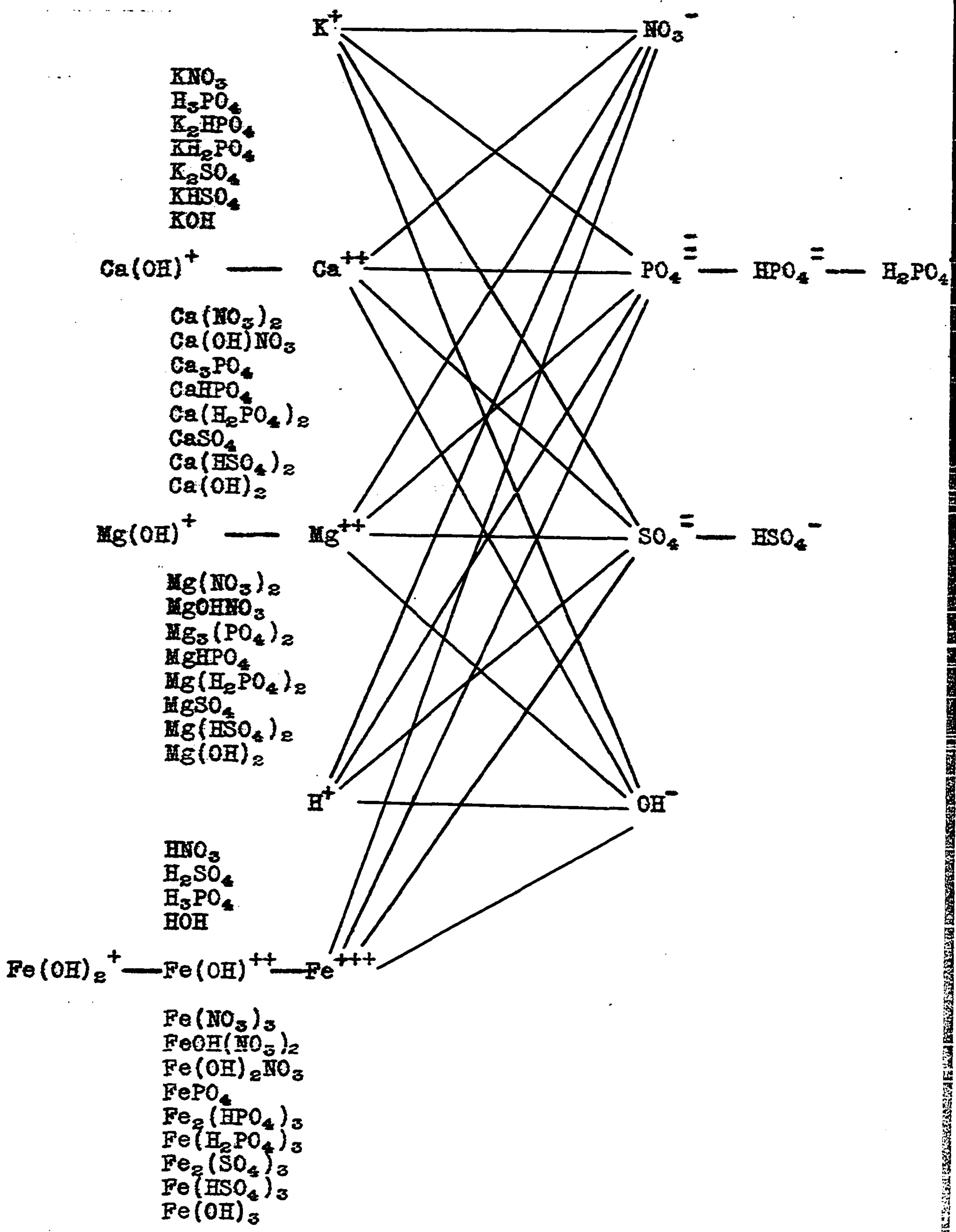


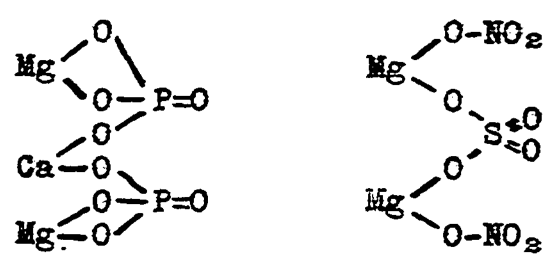

Chart 1.

## INTRODUCTION

A study of the simplest water culture used as a plant nutrient shows a large number of ionic equilibria. An idea of the numbers of ionic and molecular species that might arise in a nutrient solution can be obtained from a consideration of the following ions in solution:

$K^+$, $Ca^{++}$, $Mg^{++}$, $H^+$, $Fe^{+++}$, $NO_3^-$, $PO_4^{\equiv}$, $SO_4^=$, $OH^-$

This is the simplest combination of ions that would support plant growth. The simple ionic and molecular species that would arise is demonstrated in Chart 1. This does not take into account such complexes as illustrated in the following formulae:



in which salts with mixed cations and mixed anions might exist in solution in the molecular state.

A change in the concentration of any one salt in the nutrient solution would cause a change in the concentration of the ions of that salt in the solution. This, in turn, would cause a rearrangement of all the equilibria, and consequently a change in the concentration of each of the molecular and ionic species shown. How great this shift would be is difficult to predict. It would depend on the salt varied, the amount of the variation and the total salt concentration.

Assuming that such equilibrium changes occur, is the change in growth or virility of the plant that results, due primarily to the change in concentration of the ions varied or is it more nearly dependent on the total equilibrium changes? In the light of the recognized "antagonistic" roles, which certain ions seem to play, it would appear probable that the transfer of certain metallic elements - as calcium - from the molecular species to the ionic species, or the reverse, might be responsible for at least a portion of the changes in the growth rate. It seemed highly desirable, therefore, that an attempt be made to study nutrient solutions from the standpoint of tracing the shifts in equilibria in these solutions.

Concentration cell methods seemed the most logical ones to employ in such a study. Much valuable data has been obtained by the use of the hydrogen electrode. Unfortunately, such work as has been done with other electrodes (the sodium, potassium, and calcium) has been primarily for the accumulation of thermodynamic data. Consequently, quantities of solution, rapidity of measurement and simplicity of apparatus, has been sacrificed for the sake of accuracy. Moreover, such measurements as have been made were done either in pure salt solutions or with apparatus not adaptable to biological work.

Before any study could be made the adaptation of the amalgam types of electrodes to biological measurements was necessary. This required a simplification of the design of the electrode, the material reduction of the quantities of solution and of amalgam necessary for making the measurements and the retention of the accuracy of the more cumbersome methods. It was thought that the alkali amalgam electrodes would be as reactive and as difficult to manipulate as any of this type — especially so in acid solutions. For this reason the sodium and potassium electrodes were chosen as the ones for adaptation to the usage desired.

# A SIMPLE FLOWING JUNCTION FOR USE WITH A MODIFIED ALKALI AMALGAM ELECTRODE

## Theoretical Part

In the use of the alkali amalgam electrodes, it has been recognized that the following reactions would tend to affect the measured potential

$$2K\ (\text{amalgam}) + H_2O \longrightarrow 2KOH + H_2$$

$$2K\ (\text{amalgam}) + 1/2\ O_2 + H_2O \longrightarrow 2KOH$$

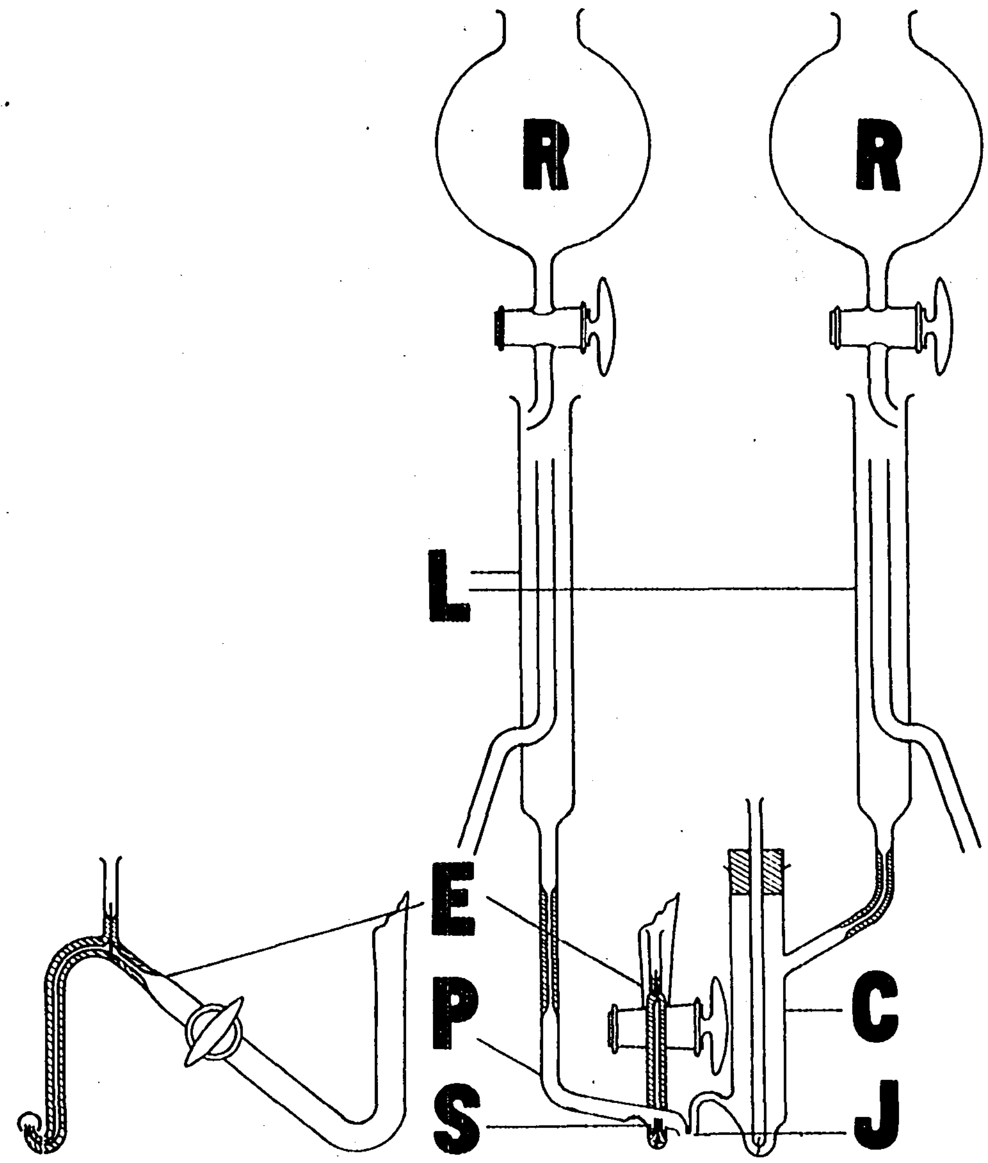
In the literature (MacInnes and Parker, 1915 pg.1452) it has been presumed that the first reaction is eliminated by rapidly flowing both the solution and the amalgam. It would seem that the same technique would eliminate the second reaction (with oxygen) since it would appear that water would react much more easily with the amalgam than molecular oxygen. However, recent workers [MacInnes and Parker (1915, pg.1453), MacInnes and Beattie (1920, pg.1120), Knobel (1923, pg.71), Harned (1925, pg.676)] have consistently excluded oxygen from the solutions. MacInnes and Parker (1915, pg.1452) state that "...when, however, the results of several series...were plotted, irregularities appeared which could only be explained by assuming that the small amounts of dissolved oxygen remaining in the solution reacted instantaneously with the amalgam".

Allmand and Polack (1919, pg.1023) report similar difficulties in dilute solutions which they eliminated by altering the construction of their cells so as to reduce the high resistance offered by long columns of these dilute solutions. In view of the fact that no precautions toward exclusion of air were taken in this work and yet values of the activity of the sodium ion consistent with other measurements were calculated by Lewis and Randall (1921, pg.1124), it seemed probable that consistent readings could be obtained in solutions exposed to the atmosphere as they must be in biological work.

This conclusion seems justified by the experimental results reported in this paper, since no irregularities at high dilutions were encountered, as reported by MacInnes and Parker (1915, pg.1452). Since the primary object of this investigation is the adaptation of these electrodes to measurements in biological media, no attempt has been made to determine whether these potentials are identical with potentials obtained by exclusion of oxygen.

## Design of Apparatus

The electrode used was similar in design to that of Richards and Conant (1922, pg.604) which in turn was a modification of that of Lewis and Krause (1910). Both types have been used in this laboratory and preference was given to the former since the amalgam kept a mirror-like surface indefinitely under an atmosphere of perfectly dried hydrogen, whereas it seemed impossible to retain a like surface over long periods


R
R
L
E
E
P
S
C
J

of time in an atmosphere of air, dried by passing it over phosphorus pentoxide. The electrode differed in that the amalgam delivery tube E, Fig.1 (front and side view) was bent to the form of a rough S. This change reduced the pressure of the amalgam at the stopcock and permitted better control of the amalgam flow. The contact chamber of the electrode differed radically from those previously reported. The solution made contact with the amalgam in a small tube, P, Fig.1, through which the solution flowed at a fairly high linear velocity. The contact point of the amalgam electrode entered this tube through a small opening, S, in the under side of the chamber. Leakage of the solution at this junction was prevented by paraffining the opening in the tube S and likewise the sides of the amalgam electrode tip. The coating of paraffin seemed to reduce the amount of wetting and likewise the rate of decomposition of the amalgam. The angle at which the electrode chamber, P, was set, discharged the used amalgam through the opening, J, along with the rapidly flowing solution. When not in use, the amalgam electrode tip was well flushed with amalgam and was then coated with paraffin to prevent the action of air and moisture on the amalgam in the capillary. This operation was best performed by immersing the tip in a beaker of molten paraffin, flushing it well with the amalgam and then removing the tip from the paraffin.

The liquid junction is shown at J, Fig.1. The solution from the electrode EP, and likewise, from the calomel half cell

C, make contact at the openings J. The constant flow of the two solutions is obtained partly by means of the constant level devices L, and partly by means of the capillaries sealed at the bottoms of the constant level devices. These capillaries are 1.0 mm in diameter and 12 cm long. Stop cocks or cleaned pieces of rubber tubing with pinch clamps (not shown in the sketch) were sealed on or attached to the devices L at the lower ends of the capillaries, so that the flow of the solutions could be stopped when it was desired. The height of the columns of liquids in L was 30 cm above the junction J. The two openings at J were 2.5 mm in diameter. The adjoining surfaces at J were ground flat to facilitate a smooth and even contact. The best results were obtained when the surfaces of the delivery tubes at J were vertical.

## Preparation of Materials Used

The mercury used throughout this investigation was purified by passing it through a mercurous nitrate — nitric acid column, and then twice distilling under reduced pressure in a current of air. The potassium chloride was Mallinckrodt's C.P. product, twice recrystallized from conductivity water. The sodium chloride was Mallinckrodt's C.P. product, precipitated twice from conductivity water solutions by HCl gas. The sodium chloride was washed free from HCl gas with 98% alcohol after the second precipitation. The HCl gas was generated from concentrated C.P. quality sulfuric and hydrochloric acids. The gas stream was passed through a long tube filled with glass wool to remove entrained sulfuric acid, then through a sulfuric acid bottle to remove water, and finally through two towers filled with glass wool. Calomel was prepared by treating dilute mercurous nitrate solution with a dilute solution of hydrochloric acid. The product so obtained was washed with conductivity water until no precipitate was obtained when the wash water was treated with silver nitrate solution. The potassium and sodium amalgams were prepared by the methods described by MacInnes and Parker (1915, pg.1445).

## Experimental Part

At first a junction of the type devised by Lamb and Larson (1920, pg.229) was employed. However, the column of liquid between the calomel and the amalgam half cells was so long that the internal resistances in this column made the readings meaningless for low concentrations. This fact will be demonstrated later in the paper in connection with Table II. This is in accord with the findings of Allmand and Polack (1919) and of Byers (1908).

To eliminate the internal resistance and at the same time simplify the operation of the electrodes, the design of the apparatus was gradually altered until the set-up described above was obtained. The constancy and reproducibility of the apparatus has been confirmed in three ways:

1. Cells of the type Hg, $Hg_2Cl_2$ KCL(xM)/KCl(1M)$Hg_2Cl_2$,Hg.
2. Cells of the type Hg, $Hg_2Cl_2$ KCl(1M)/KCl(xM), K(amalgam).
3. Cells of the type Hg, $Hg_2Cl_2$, NaCl(xM), Na(amalgam).

1. Cells of the type Hg, $Hg_2Cl_2$ KCl(xM)/KCl(1M) $Hg_2Cl_2$, Hg. This step was taken in order to dispel a doubt which was entertained relative to the constancy and the reproducibility of the calomel half cells when the solutions were flowed through them at a rapid rate. The electrode vessels, of these calomel half cells, were of the type C, Fig.1. The measured values of these cells are recorded in Table I, together with the calculated electromotive forces for the same cell combinations. Concentrations in Table I and likewise in the other tables in this paper are expressed in terms of gram molecular weights of sodium or potassium chloride per 1000 gm. of water (at 25°C) unless otherwise specified. The measurements were made in all cases in an air thermostat at 25° ± 0.05°C.

Table I.

Measurements with Cells of the Type
Hg, $Hg_2Cl_2$ KCl(xM)/KCl(1M) $Hg_2Cl_2$, Hg.

| I<br>Hg,HgCl,KCl(1M)<br>against<br>Hg,HgCl,KCl(xM) | II<br>Values of the combinations calculated from existing data. Expressed in volts. | III<br>Measured values. Two half cells of type C, Fig. I. used. Expressed in volts. | IV<br>Measured values. Half cells used without constant levels. Reservoirs R attached directly to half cells. Expressed in volts. |
|---|---|---|---|
| 0.5 M | 0.01570 | 0.01543 | 0.01620 |
| 0.2 M | 0.03650 | 0.03639 | 0.03825 |
| 0.1 M | 0.05250 | 0.05228 | 0.05270 |
| 0.05 M | 0.06867 | 0.06794 | 0.06886 |
| 0.02 M | 0.09048 | 0.08944 | 0.09100 |
| 0.01 M | 0.10704 | 0.10580 | 0.10498 |
| 0.001 M | 0.16385 | 0.16323 | 0.15360 |

To obtain the calculated values in the second column of Table I, the following equation was used

$$E_{Cell} = E(Hg,HgCl,KCl\ 1M) - E(Hg,HgCl,KCl xM) \pm E_L$$

where $E_L$ is the potential between the solutions KCl 1M and KCl xM. This value $E_L$ was calculated by the modified Nernst equation

$$E_L = (N_c - N_a)\ RT \ln \frac{C_1 a_1}{C_2 a_2}$$

where $N_c$ and $N_a$ are respectively the transference numbers of the cation and anion and $a_1$ and $a_2$ are the activity coefficients of KCl at concentrations $C_1$ and $C_2$. The value of $N_c$ was taken as 0.493 /Noyes and Falk (1911, pg.1455); MacInnes and Smith (1923, pg.2254)/.

According to the theory of transference numbers $N_c$ plus $N_a$ should equal unity. This is substantiated by the work of MacInnes and Brighton (1925, pg.998). The transference number of the chlorine ion should then be 0.507 if that of the potassium ion is 0.493. This value is in agreement with that of Smith and MacInnes (1925, pg.1014) who obtained the value 0.508 ± 0.001. The values $N_c = 0.493$ and $N_a$ 0.507 were used in the calculation of $E_L$ throughout the entire range of concentrations employed.

The values of the half cells were calculated according to the following equation

$$E(Hg, HgCl, KCl xM) = E°(Hg, HgCl, KCl) - \frac{RT}{nF} \ln \frac{1}{Cl^- x a}$$

where E° is the standard electrode potential of mercury-calomel, $Cl^-$ represents the concentration of $Cl^-$ at a concentration of KCl XM and $a$ is the activity coefficient of KCl at that concentration. -0.2700 V was the value for E°. /Lewis and Randall (1923, pg.406)/. The values for $a$ for KCl were likewise obtained from the Lewis and Randall text (1923, pg. 360).

The values in column III were reproducible over a period of several days during which they were measured. The widest deviations measured were $\pm 0.05$ mv. The values in column IV were obtained on another series of half cells without the use of the constant levels L, Fig.1. The reservoirs R, Fig.1, were attached directly to the calomel half cells by short lengths of cleaned rubber tubing, and the flow of the solutions was regulated by screw clamps. Under even these crude conditions the values were constant to $\pm 0.5$ mv. over several days time. In making these measurements a Leeds and Northrup Type K potentiometer was used. The solutions were prepared with conductivity water to insure freedom from all but gaseous impurities. No attempt was made to prevent the absorption of air and other gases by the solutions. Gases must be present in biological media, and it was decided, therefore, to check the junction under conditions approaching as nearly as was possible, those of practical usage.

The measured values in column III of Table I are in good agreement with the calculated values (column II). The potentials of the cell

$$Hg,\ Hg_2Cl_2\ KCl(0.1M)/KCl(1M)\ Hg_2Cl_2,\ Hg$$

are 0.0523 V and 0.0527 V. These are in accord with the value 0.0529 V as given by Lewis, Brighton and Sebastian (1917, pg. 2255). It is evident, therefore, that the rapid flow of the solution through the half cells does not alter the accuracy, or reproducibility of the calomel cell as a reference electrode.

2. Cells of the type Hg, $Hg_2Cl_2KCl(1M)/KCl(xM)$ K(amalgam). The measurements made with these cells are recorded in Table II. This material is presented to illustrate the magnitude of the deviations caused by the resistance encountered in long columns of dilute solution. That such internal resistance should alter the measured E.M.F. is contrary to the theory of the potentiometric set-up. It has been encountered in concentration cell studies by Allmand and Polack (1919) and by Byers (1908). That such resistances should affect the potentiometric measurement seems apparent if the situation is reduced to an absurdity. If two half cells such as are illustrated in Fig.1 are separated so that a layer of air exists between them, the resistance of that air layer is infinite. Consequently it is impossible to obtain a reading. If the theory were valid the introduction of this infinite resistance between the half cells should not affect the reading and the difficulties attending liquid junctions would be a matter of no further concern.

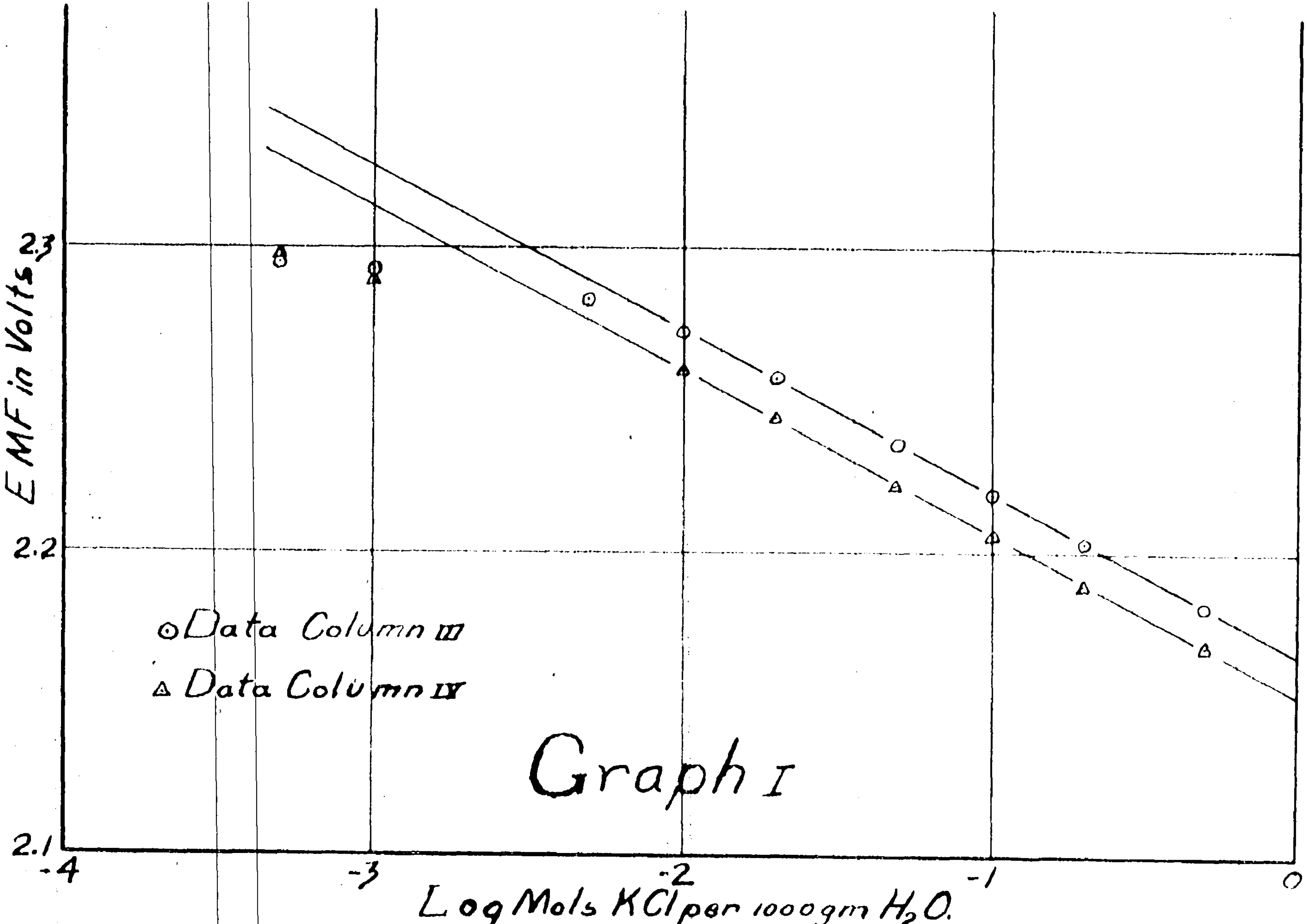

EMF in Volts
2.3
2.2
2.1
-4
-3
-2
-1
0
Log Mols KCl per 1000 gm $H_2O$.
Data Column III
Data Column IV
Graph I

Table II.

Measurements with Cells of the Type
$Hg, Hg_2Cl_2, KCl(1M)/KCl(xM), K(amalgam)$

| I<br>Hg,HgCl,KCl 1M against the K amalgam electrode and KCl solutions of concentration. | II<br>Junction of the Lamb type used. E.M.F. in volts | III<br>Junction of the type shown in Fig.1 used. No constant levels. E.M.F. in volts | IV<br>Junction of the type shown in Fig.1 used. With constant levels. E.M.F. in volts. |
|---|---|---|---|
| 0.5 M | ---- | 2.1820 | 2.16832 |
| 0.2 M | 2.2038 | 2.2036 | 2.18914 |
| 0.1 M | 2.2182 | 2.2196 | 2.20514 |
| 0.05 M | 2.2315 | 2.2362 | 2.22212 |
| 0.02 M | 2.2422 | 2.2574 | 2.24414 |
| 0.01 M | 2.2400 | 2.2720 | 2.26028 |
| 0.001 M | 2.0320 | 2.2934 | 2.28830 |
| 0.0005 M | 1.8420 | 2.2952 | 2.29756 |

The data in columns III and IV are analyzed graphically in Graph I. The electromotive force in a concentration cell of the type under discussion should be a logarithmic function of the concentration of the ion under investigation. Therefore, if the measured E.M.F. is plotted against the logarithm of the corresponding concentrations of KCl a straight line should result. The data in column III (Table II) are so treated. In addition a value for 0.005 MKCl (2.2834V), not recorded in Table II, is included. It is seen that to concentrations as low as 0.01 M KCl the agreement is perfect. At 0.005 M KCl a slight deviation occurs. The points corresponding to 0.001 M KCl and 0.0005 M KCl are not concordant with the theory. The agreement to as low a concentration as 0.005 M KCl is surprisingly good. No measurement at 0.005 M KCl was made in obtaining the value in column IV. However, the results are in agreement to a concentration of 0.01 M KCl. Allmand and Polack (1919) treated the data they obtained in similar fashion. Below 0.02 N NaCl their measured values did not fall on the curve. The value used by them for 0.01 N NaCl was obtained by extrapolating the curve to that concentration.

The data in columns II and III were obtained with a Leeds and Northrup Student potentiometer. For those in column IV, the Type K potentiometer was used. No constant level devices were used in making the measurements given in columns II and III. These readings (II and III) were constant to ±1.0 mv. Further these readings were made, not with the amalgam flowing, but merely with single drop surfaces exposed. To obtain the data in column IV where the more sensitive potentiometer was used, it was necessary to flow the amalgam from the electrode in order to get results more constant than ±0.1 mv. With this method the greatest deviation in the measurements was ±0.05 mv. The amalgam used in the electrode with which the readings in columns II and II were made analyzed 0.186% potassium. That used in the electrode with which the readings in column IV were made analyzed 0.164% potassium.

3. Cells of the type Hg, $Hg_2Cl_2$, NaCl(xM), Na(amalgam). These cells are identical with those used by Allmand and Polack (1919). Sodium chloride solutions were used in the calomel half cells as well as in the amalgam electrode contact chambers. Sodium amalgam was used in place of potassium amalgam. Apparatus of the type described in Fig.1 was used, to determine whether the readings of Allmand and Polack (1919) could be duplicated. The composition of the sodium amalgam employed was different from that of either of the amalgams used by these workers. However, for purposes of comparison the values measured will be subjected to the same treatment as was used by these authors. Table III is a reproduction of some of the data of Allmand and Polack (1919). They were obtained using three concentrations of sodium amalgam. The concentrations used were were respectively

(a) 0.2234% Na (b) 0.1657% Na (c) 0.1389 % Na

Column V (Table III) gives the values of the cells calculated to a concentration of sodium amalgam, 0.1389 % Na, by a method which will be described later.

Table III.

Date of Allmand and Polack (1919)
Cell Type Hg, $Hg_2Cl_2$, NaCl(xM), Na(amalgam)

| I<br>Normality NaCl | II<br>Amalgam (a) E.M.F. in volts. | III<br>Amalgam (b) E.M.F. in volts. | IV<br>Amalgam (c) E.M.F. in volts. | V<br>Calculation to 0.1389% amalgam. E.M.F. in volts. |
|---|---|---|---|---|
| 1.00 | --- | 2.1499 | 2.1430 | 2.1430 |
| 0.50 | --- | 2.1838 | --- | 2.1769 |
| 0.10 | 2.2710 | 2.2596 | --- | 2.2527 |
| 0.02 | 2.3450 | 2.3336 | --- | 2.3267 |
| 0.01 | --- | --- | 2.358 | 2.3585 |

The data presented in Table IV were obtained with the apparatus shown in Fig.1. Sodium chloride solution of the same concentration was used in both half cells. This necessitated a separate calomel half cell for each measurement made. The composition of the amalgam used was 0.194% Na.

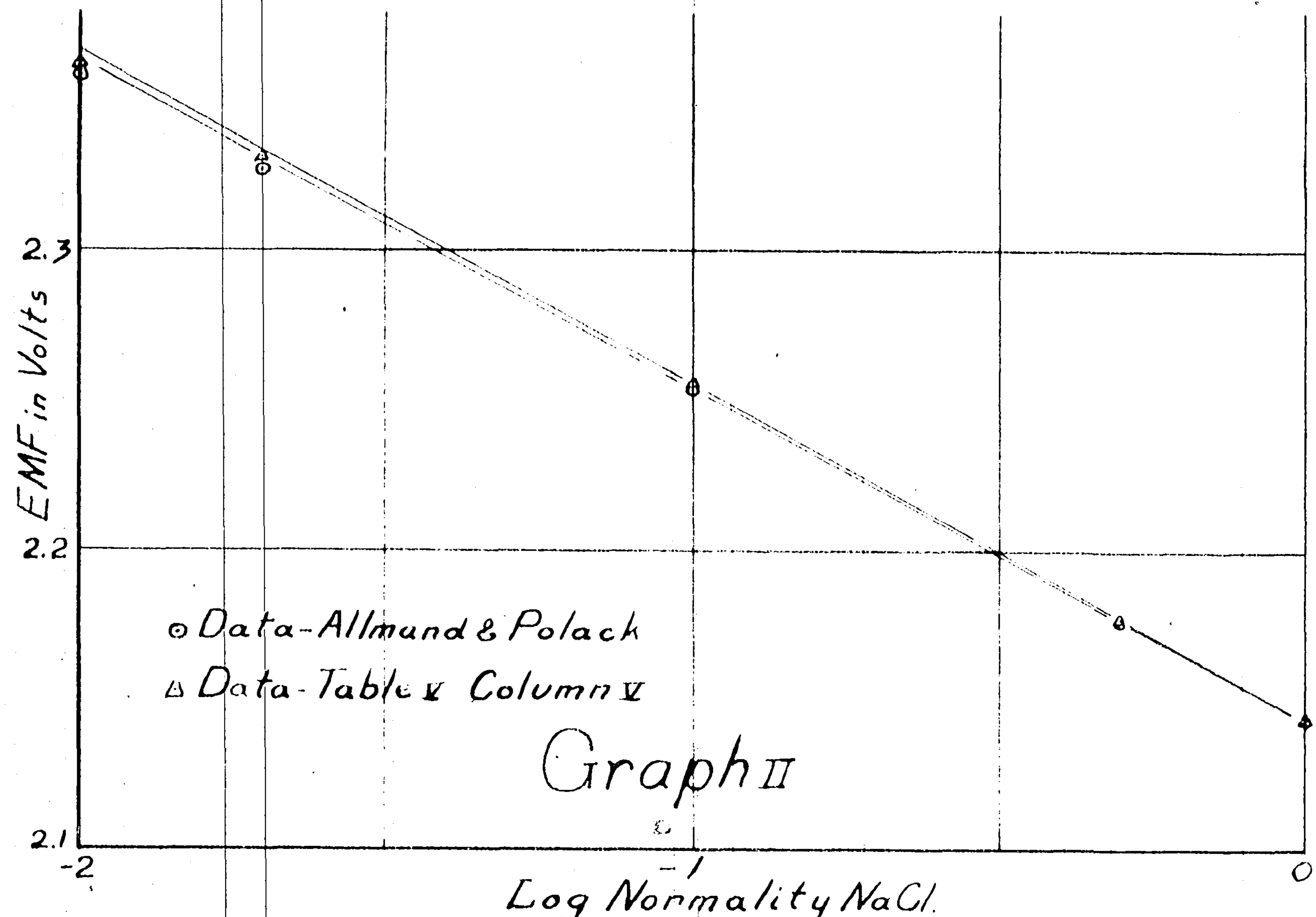
Table IV.

Cells-type, Hg, $Hg_2Cl_2$, NaCl(xM), NaHg(amalgam)
Apparatus Fig.1.

| I<br>Normality NaCl | II<br>Amalgam 0.194%<br>E.M.F. in volts. |
|---|---|
| 1.00 | 2.1549 |
| 0.50 | 2.1893 |
| 0.10 | 2.2672 |
| 0.02 | 2.3426 |
| 0.01 | 2.3740 |

The measurements in Tables III and IV were made at 25°C. Those in Table IV were measured with a Leeds and Northrup Type K potentiometer.

In obtaining the values calculated to 0.1389% Na amalgam, Allmand and Polack (1919) subtracted the reading for the 1.0 N NaCl solution obtained with amalgam (c) from that measured with amalgam (b). They then assumed that the difference was constant throughout the entire range of concentrations of sodium chloride used and applied it to all the values obtained with amalgam (b). That this proceedure is reasonably valid will be pointed out later in connection with the measurements presented in Table VI. The same method of treatment is applied to the data in Table IV in order to compare them with those of Allmand and Polack (1919). The comparison of the two sets of


Graph II
⊙ Data-Allmand & Polack
△ Data-Table V Column V
EMF in Volts
2.3
2.2
2.1
-2
-1
0
Log Normality NaCl.

data is made in Table V.

Table V.

Comparison data Allmand and Polack with data Table IV

| I<br>Normality of NaCl | II<br>Allmand and Polack readings corrected 0.1389% amalgam. E.M.F. in volts | III<br>Data Table IV 0.194% amalgam. E.M.F. in volts. | IV<br>1.0 N value Column III less 1.0 N value Column II. Diff. in volts. | V<br>Data Table IV corrected to 0.1389% alamgam. E.M.F. in volts | VI<br>Values Column V less A. and P. readings 0.1389% amalg. Diff. in volts |
|---|---|---|---|---|---|
| 1.00 | 2.1430 | 2.1549 | 0.0119 | 2.1430 | 0.0000 |
| 0.50 | 2.1769 | 2.1893 | | 2.1774 | 0.0003 |
| 0.10 | 2.2527 | 2.2672 | | 2.2553 | 0.0026 |
| 0.02 | 2.3267 | 2.3426 | | 2.3307 | 0.0040 |
| 0.01 | 2.3587 | 2.3740 | | 2.3621 | 0.0034 |

An analysis (Graph II) of the data is columns II and V shows no greater deviation from the theoretical in the data obtained with the apparatus of Fig.1 than does that of Allmand and Polack (1919). The three high concentrations in each set of measurements are in perfect agreement with the theoretical requirement. The two lowest concentrations in each case fall just below the curve drawn through the first three points. Since the data presented show no wider deviation than do those of Allmand and Polack (1919) it is considered that these measurements complete the proof of the accuracy, constancy and reproducibility of the electrode set-up described. The fact that the readings in Table V column V are consistently higher than those of Allmand and Polack (1919) would seem to indicate that the internal resistance of the solutions was more nearly completely eliminated than was the case in their measurements.

The validity of the method of converting the potentials measured with amalgams of one concentration to a different amalgam concentration is illustrated by Table VI. These measurements were made in KCl solutions with potassium amalgam electrodes at 25° C. The concentrations of the amalgams are given in the table. The variations encountered are in most cases below 0.05 M, and are probably due to experimental error, which is to be expected in extremely dilute solutions.

Table VI.

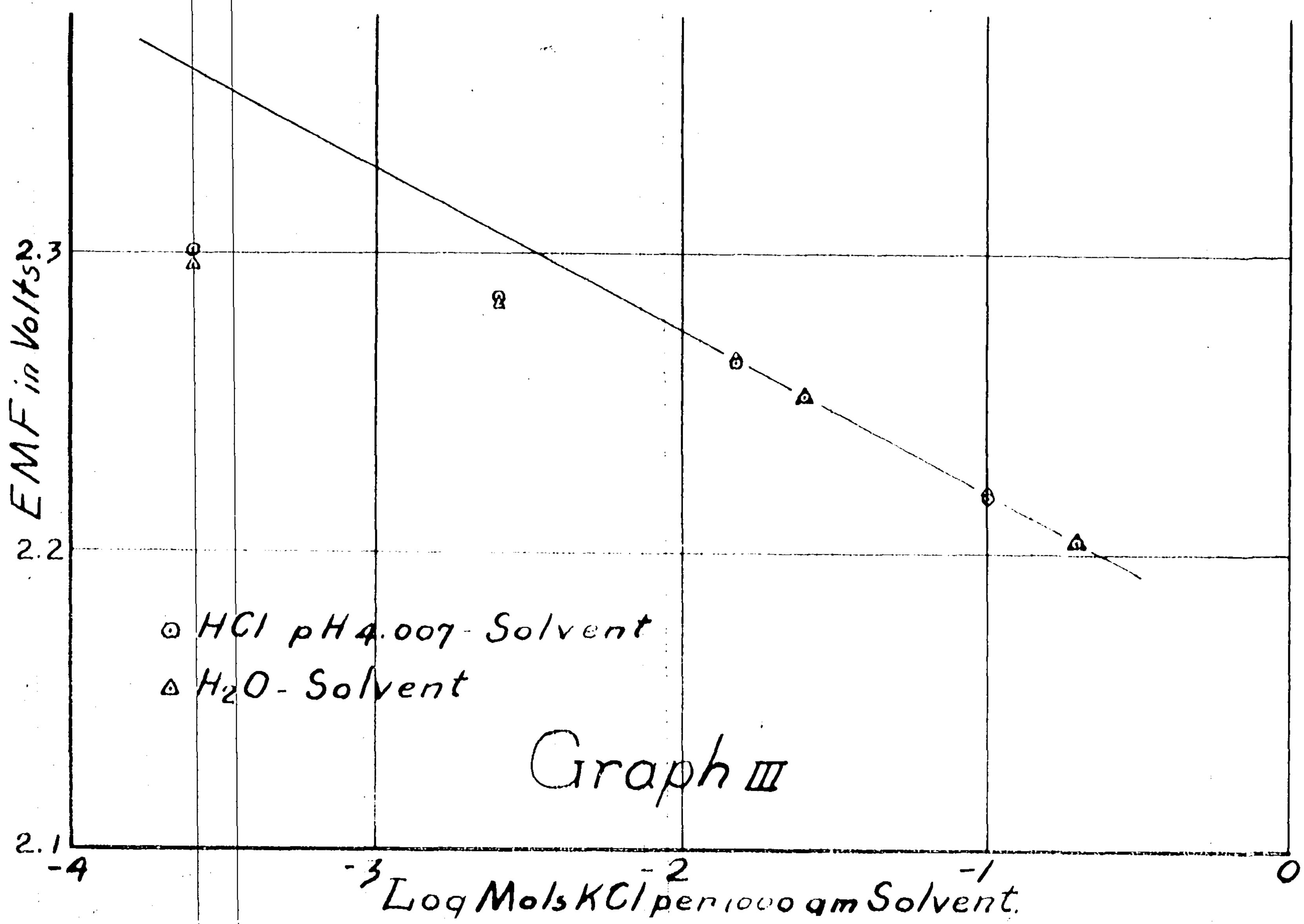
A Comparison of the Potentials Measured with Amalgams of Different Concentrations

| I<br>Mols KCl per 1000 gm $H_2O$. | II<br>K-amalgam A (0.186%)<br>E.M.F. in volts. | III<br>K-amalgam B (0.164%)<br>E.M.F. in volts. | IV<br>K-amalgam C (0.215%)<br>E.M.F. in volts. | V<br>A - B<br>Diff. in volts. | VI<br>C - A<br>Diff. in volts. | VII<br>C - B<br>Diff. in volts. |
|---|---|---|---|---|---|---|
| 0.50 | 2.1820 | 2.1683 | 2.1874 | 0.0137 | 0.0054 | 0.0191 |
| 0.20 | 2.2036 | 2.1891 | 2.2080 | 0.0145 | 0.0044 | 0.0189 |
| 0.10 | 2.2196 | 2.2051 | 2.2245 | 0.0145 | 0.0049 | 0.0194 |
| 0.05 | 2.2362 | 2.2221 | 2.2414 | 0.0141 | 0.0042 | 0.0183 |
| 0.02 | 2.2574 | 2.2441 | 2.2610 | 0.0133 | 0.0036 | 0.0169 |
| 0.01 | 2.2720 | 2.2603 | 2.2784 | 0.0117 | 0.0064 | 0.0181 |

## MEASUREMENTS IN ACID SOLUTIONS

The work of various authors, [Lewis and Krause (1910); Lewis and Keyes (1913, 1912); Chow (1920)] has shown that the alkali amalgam electrodes operate satisfactorily in alkaline as in neutral solutions.

If the electrodes were useful in biological work it would be necessary that they function equally well in acid solutions, with pH values ranging from 7.0 to 4.0. The ease of reactivity of the alkali metals and their amalgams is well known. The fact that in static solutions the reactions of the amalgams with water is a factor which must be overcome has been mentioned. Therefore, doubt was entertained regarding the utility of the electrodes in acid solution. In order to determine the effect of the highest concentration of acids likely to be encountered in plant nutrients, the following experiment was devised. Solutions of KCl ranging in concentration from 0.2 M to 0.0005 M were prepared using HCl solution as the solvent. An aqueous solution was prepared which should have had a pH of 4.00; potentiometric measurement gave the value pH 4.007. Weighed quantities of purified and dried potassium chloride were added to weighed amounts of the HCl solution in such manner that the concentrations expressed for solutions in Table VII are in terms of gram molecular weights of KCl per 1000 gm. of the HCl solution (pH 4.007). The KCl solution measurements, used as comparative data, were made in aqueous


EMF in Volts
2.3
2.2
2.1
-4
-3
-2
-1
0
Log Mols KCl per 1000 gm Solvent.
⊙ HCl pH 4.007 - Solvent
△ H2O - Solvent

Graph III

KCl solutions prepared from purified and dried KCl and conductivity water. The two groups of measurements are recorded in Table VII.

Table VII.

Comparison of Potentials in Neutral and Acid (pH 4.007) Solutions

| I<br>Mols KCl per 1000 gm. solvent. | II<br>Solvent water. E.M.F. in volts | III<br>Solvent HCl Soln. pH(4.007): E.M.F. in volts | IV<br>Difference II - III Expressed in volts |
|---|---|---|---|
| 0.2000 | 2.2036 | 2.2036 | 0.0000 |
| 0.1000 | 2.2196 | 2.2192 | +0.0004 |
| 0.0250 | 2.2516 | 2.2516 | 0.0000 |
| 0.0150 | 2.2644 | 2.2636 | +0.0008 |
| 0.0050 | 2.2834 | 2.2848 | -0.0014 |
| 0.0005 | 2.2952 | 2.3007 | -0.0055 |

Table VII and Graph III show good correlation between the two sets of measurements. It seems, therefore, that the alkali amalgam electrodes will not be affected by such concentrations of hydrogen ion as would be encountered in plant nutrients. This raises the question of the importance of the reaction of the amalgam electrodes with water. If measurements of the type shown in column III, above, can be made in solutions of pH 4.0 with salt concentrations as low as 0.0005 M, it is doubtful that reaction between the amalgam and water would affect the potential in neutral solutions.

The measurements are well in accord with the theory on the linear curve (Graph III) to concentrations of about 0.01 M. No constant level devices were used in making these measurements; a fact which may explain the deviations at 0.005 M. A 0.186% K amalgam was used in obtaining all the potentials in Table VII.

The extremely low concentrations of KCl were purposely used in the above comparison, since it was thought that deviations between the two sets of readings would be most pronounced at the lowest concentrations.

## MEASUREMENTS IN SALT SOLUTIONS WITH MIXED CATIONS

At the time of the initiation of this study practically no work had been attempted using amalgam electrodes in solutions containing mixed cations. Byers (1908) found difficulty in using the calcium and sodium electrodes in dilute solutions of single electrolytes due to the low current transfer in these solutions. To overcome this he added "indifferent" salts to the solutions he was studying to increase the current flow. In all cases where salts were added, abnormal readings were obtained. Neuhausen (1922), preparatory to a determination of sodium ion concentrations in blood serums with the sodium amalgam electrode, checked this electrode in pure and mixed salt solutions. He recognized abnormalities in the readings in solutions of mixed cations. However, in a later paper Neuhausen and Marshall (1922, pg.366) state that "both when sodium salts are present alone and when admixed with salts of other cations, it was shown by Neuhausen (1922) that in the range of concentration present in the blood the sodium amalgam electrode is reliable and that furthermore potassium and calcium ions in concentrations, such as are present in the blood, do not interfere".

During the time that this work was in progress Ringer (1923) published data indicating that the potential measured in solutions of sodium salts (with the sodium electrode) is strongly influenced by the presence of potassium salts. Likewise, the potential of the potassium electrode in solutions of potassium salts was affected by the addition of sodium salts. Additional measurements indicate that calcium and magnesium salts have little if any effect on the sodium or potassium electrodes. Michaelis and Kawai (1925) published data confirming Ringer's results regarding the negligible effect of the calcium salts. However, they were unable to obtain any difference in the potential measured in 0.2 N NaCl (with the sodium electrode) on the addition of potassium chloride in concentrations from 0.2 N to 0.002 N.

It was proposed at the beginning of this study to investigate the behavior of the sodium and the potassium electrodes in various solutions of mixed cations. However, the nature of the preliminary results obtained with the potassium electrode in mixtures of NaCl and KCl led to a prolonged study of the sodium and potassium electrodes in solutions containing only sodium and potassium chlorides and further work was abandoned.

Table VIII gives a summary of the preliminary measurements made with the potassium electrode in solutions containing both sodium and potassium chlorides. These measurements are compared in two ways in Table VIII with potentials measured in pure potassium chloride solution.

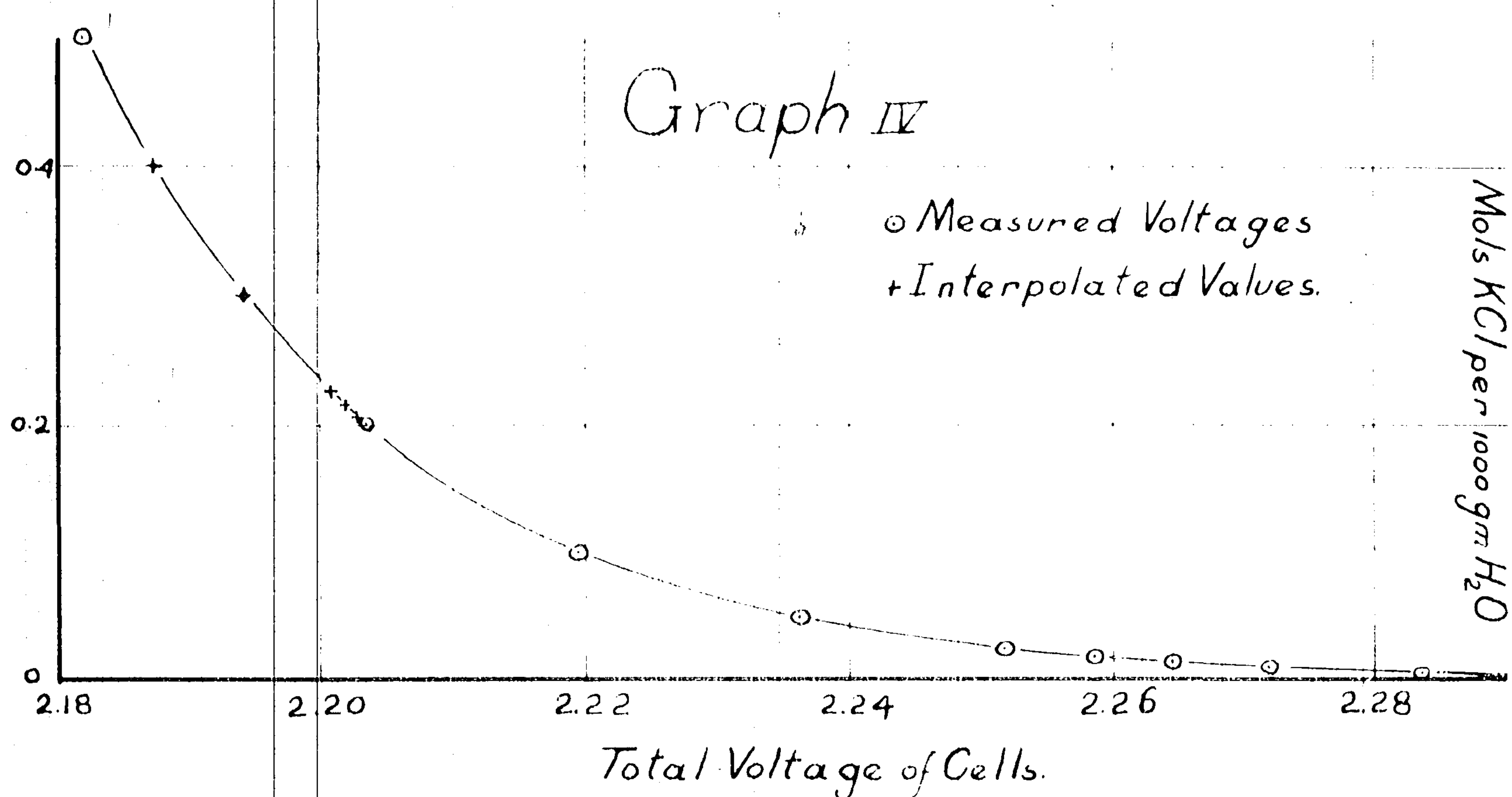

Graph IV
⊙ Measured Voltages
+ Interpolated Values.
Mols KCl per 1000 gm $H_2O$
0.4
0.2
0
2.18
2.20
2.22
2.24
2.26
2.28
Total Voltage of Cells.

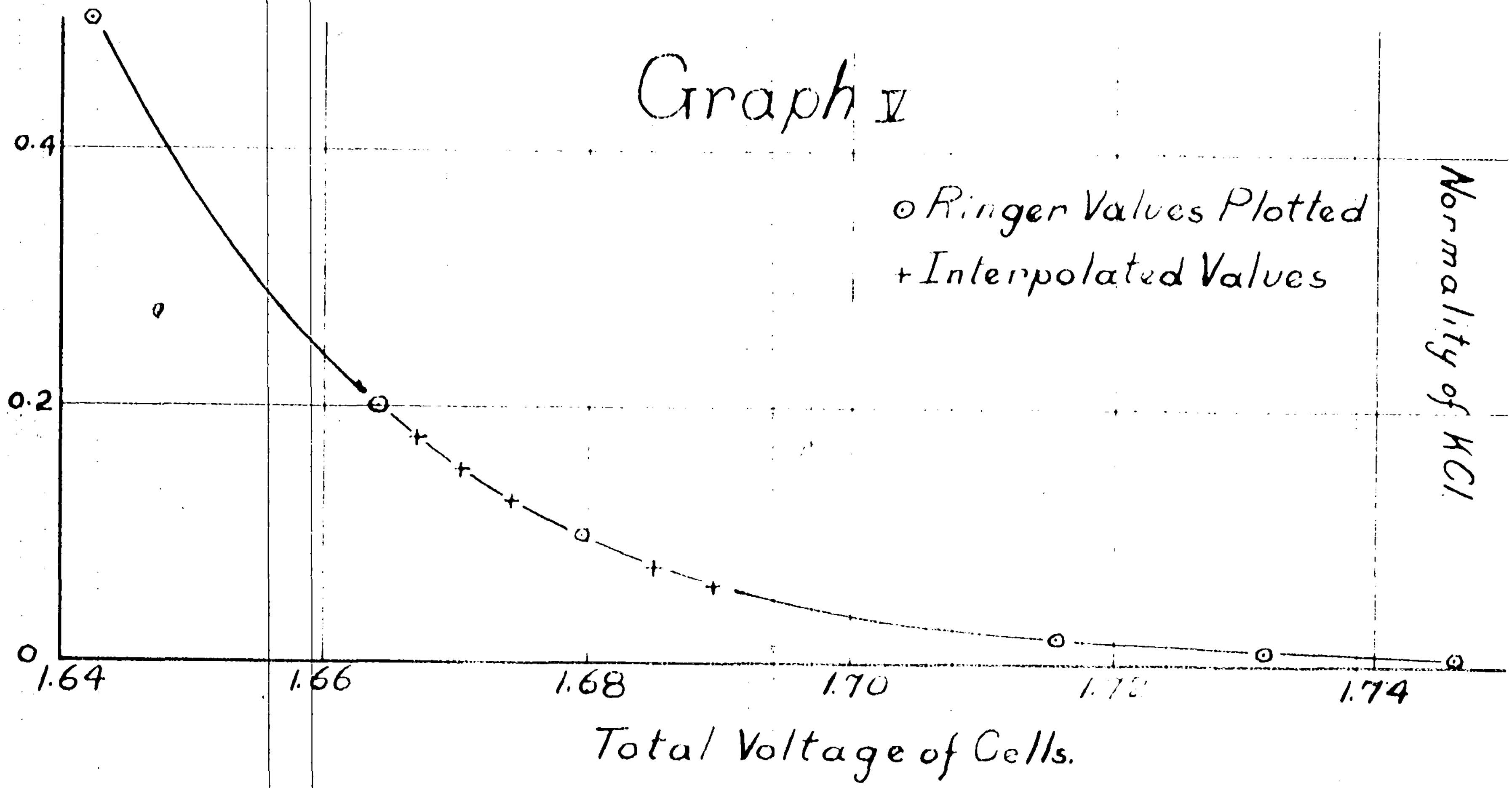
Table VIII.

Measurements with K-electrode (0.186% K-amalgam) in Mixed Salt Solutions Compared with those in Pure KCl Solutions. Potentials measured 25°C.

| I<br>Concentration of salts in Mols per 1000 gm. $H_2O$<br>a<br>KCl | <br><br><br>b<br>NaCl | II<br>Mixed salt solutions (1M)KCl; $Hg_2Cl_2$ Hg reference E.M.F. in volts. | III<br>Pure KCl of conc. col. I-a; (1M)KCl, $Hg_2Cl_2$; Hg reference E.M.F. in volts (From Table II: column III). | IV<br>Total salt concentration. Col. I-a + Col. I-b in Mols per 1000 gm. $H_2O$. | V<br>E.M.F. in pure KCl solution of conc. col. IV. Values read from Graph IV in volts. |
|---|---|---|---|---|---|
| 0.200 | 0.200 | 2.1846 | 2.2036 | 0.400 | 2.1874 |
| 0.100 | 0.200 | 2.1928 | 2.2196 | 0.300 | 2.1943 |
| 0.025 | 0.200 | 2.1992 | 2.2516 | 0.225 | 2.2008 |
| 0.015 | 0.200 | 2.2012 | 2.2644 | 0.215 | 2.2019 |
| 0.005 | 0.200 | 2.2028 | 2.2834 | 0.205 | 2.2029 |
| 0.200 | 0.100 | 2.1888 | 2.2036 | 0.300 | 2.1943 |
| 0.200 | 0.015 | 2.1956 | 2.2036 | 0.215 | 2.2019 |
| 0.200 | 0.005 | 2.1976 | 2.2036 | 0.205 | 2.2034 |

The readings in Table VIII appeared to be in the correct order of magnitude. A comparison of the readings in which the sodium chloride concentration was constant, with those in which the potassium chloride concentration was kept constant showed singular agreement for those values at which the total salt concentrations were the same. Therefore, a comparison with the values in column III, Table II was made. In all cases the measurements in the mixed salt solutions indicated a greater potassium ion concentration than should have been present. This lead to a comparison of the measurements in the mixed chloride solutions with the values in pure potassium chloride solutions at concentrations equivalent to the total salt concentration. In order that this could be done the voltages in column III, Table II were plotted (Graph IV) against the concentration of potassium chloride of the various solutions measured. Potentials for the total salt concentrations in column IV, Table VIII were read from the plot and were recorded in colum V, Table VIII. A close agreement was found to exist between the values measured in the mixed salt solutions (column II) and those interpolated from Graph IV (column V) at concentrations of pure KCl equal to the total salt concentration of the mixed solutions. This was especially true in those cases in which the sodium chloride concentration was a constant. The comparison would seem to indicate that the effect of the sodium chloride was additive and that the potassium electrode was not specific for the potassium ion but reversible to both the sodium and the potassium ions.

A similar treatment of that portion of the data of Ringer (1923) measured with the potassium electrode in potassium chloride - sodium chloride mixtures is given in Table IX. No similar comparison is made of his data with the sodium electrode in sodium chloride - potassium chloride mixtures since but one value is given. The interpolated voltages were read



Graph V
o Ringer Values Plotted
+ Interpolated Values
Normality of KCl
0.4
0.2
0
1.64
1.66
1.68
1.70
1.74
Total Voltage of Cells.

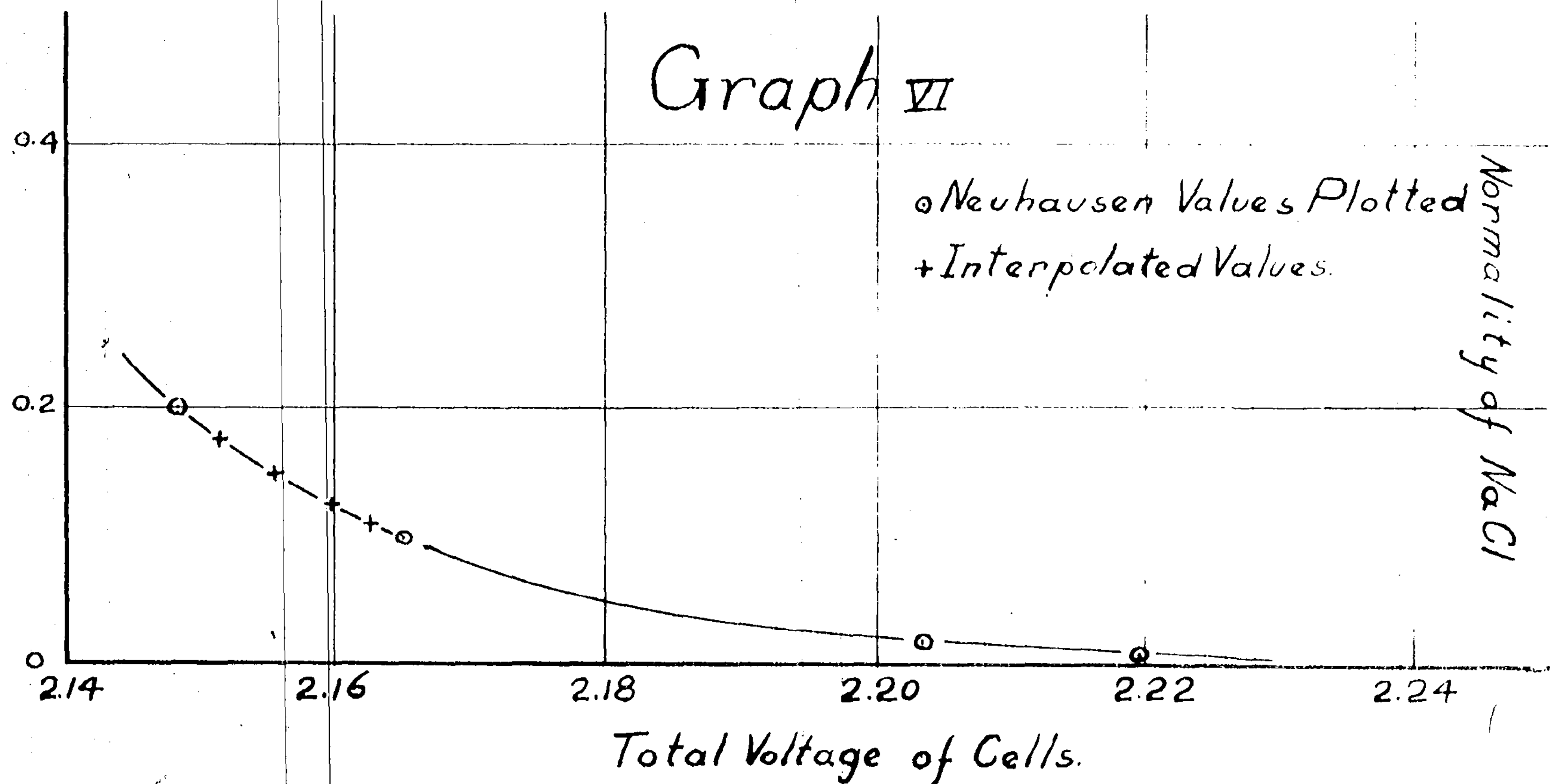
from Graph V which is a plot of Ringer's (1923) data in pure potassium chloride solution, measured with the potassium electrode. In all the data cited he used a potassium amalgam 0.361% K. The measurements were made at 18°C. Table IX shows that his data is in exact accordance with that presented above.

Table IX.

A Comparison of the Data of Ringer (1923) in Mixed KCl - NaCl Solution with Values for Pure KCl at the Total Salt Concentration.

| I Concentration of salt expressed in normality a KCl | I b NaCl | II E.M.F. in volts in mixed solns. : Hg, $Hg_2Cl_2$, KCl (sat.) reference. | III E.M.F. in volts in pure KCl solns. of conc. Col. I-a Sat'd. Calomel reference. | IV Total salt concentration - Col. I-a + Col. I-b in normality. | V E.M.F. in volts in pure KCl solns. of concentration in Col. IV from Graph V. |
|---|---|---|---|---|---|
| 0.10 | 0.025 | 1.6730 | 1.6773 | 0.125 | 1.6740 |
| 0.10 | 0.050 | 1.6692 | 1.6773 | 0.150 | 1.6702 |
| 0.10 | 0.075 | 1.6659 | 1.6773 | 0.175 | 1.6670 |
| 0.05 | 0.010 | 1.6909 | 1.6938 | 0.060 | 1.6895 |
| 0.05 | 0.025 | 1.6865 | 1.6938 | 0.075 | 1.6850 |
| 0.05 | 0.100 | 1.6700 | 1.6938 | 0.150 | 1.6702 |

The values obtained by Neuhausen (1922) with the sodium electrode in pure salt solutions are plotted on Graph VI. His data measured with the sodium electrode in mixed solutions of sodium and potassium chlorides are treated in Table X. by the method employed in Tables VIII and IX. The interpolated values


Graph VI
0.4
0.2
0
⊙ Neuhausen Values Plotted
+ Interpolated Values.
Normality of NaCl
2.14
2.16
2.18
2.20
2.22
2.24
Total Voltage of Cells.

were read from Graph VI. These measurements were made at 25°C. with a sodium electrode (amalgam 0.1659% Na).

Table X.

The Data of Neuhausen (1922) in Mixed
KCl - NaCl Solutions Compared with Values
in Pure NaCl at the Total Salt Concentration.

| I Concentration salts expressed in normality a: NaCl | b: KCl | II E.M.F. in volts of mixed solutions against Hg, $Hg_2Cl_2$, KCl (sat.) | III E.M.F. in volts of pure NaCl soln. conc. col. I-a against Hg, $Hg_2Cl_2$, KCl (sat.) | IV Total salt concentration col. I-a + col. I-b in normality. | V E.M.F. in volts of pure NaCl of total salt concn.-voltages from Graph VI. |
|---|---|---|---|---|---|
| 0.10 | 0.100 | 2.1577 | 2.1650 | 0.200 | 2.1482 |
| 0.10 | 0.075 | 2.1589 | 2.1650 | 0.175 | 2.1515 |
| 0.10 | 0.050 | 2.1595 | 2.1650 | 0.150 | 2.1555 |
| 0.10 | 0.025 | 2.1613 | 2.1650 | 0.125 | 2.1596 |
| 0.10 | 0.010 | 2.1638 | 2.1650 | 0.110 | 2.1626 |

A fair agreement with the data of Tables VIII and IX is shown. It will be noted that when sodium chloride is added to the potassium chloride solutions, the E.M.F. measured with the potassium electrode is lower than that measured in a pure potassium chloride solution, the concentration of which is the same as that of the total mixed salts. When potassium chloride is added to sodium chloride solutions, the E.M.F. measured with the sodium electrode is higher than that measured in a pure sodium chloride solution of the same concentration as that of the total mixed salts. This is in agreement with the data presented in Tables XI and XII. This would indicate that the addition of sodium chloride to potassium chloride causes a greater apparent degree of dissociation of the latter than is caused in sodium chloride solution by the addition of potassium chloride to it. This cannot be explained on the basis of activities since they are practically the same to concentrations as high as 0.2 N.

It was thought quite probable that, if the addition of sodium ion had so great an effect on the potential of the potassium electrode, and the addition of potassium ion so affected the potential of the sodium electrode, that it should be possible to obtain a constant, definite, reproducible potential with the sodium electrode in solutions containing potassium but no sodium ions, and with the potassium electrode in solutions containing sodium but not potassium ions. To this end the following series of solutions were prepared: 1. pure sodium chloride ranging in concentration from 1.0 M to 0.001 M; 2. pure potassium chloride with the same concentrations as in (1); 3. solutions equi-molar with respect to sodium and potassium chlorides, the total salt concentrations of which were identical with those of the pure sodium chloride and potassium chloride solutions at each concentration interval used in the pure salt solutions. These were prepared in sufficiently large volumes that all the measurements recorded in Tables XI and XII could be made on the same group of solutions. All three solutions at each of the concentrations prepared were measured at 25°C in an air thermostat, first against a potassium electrode (amalgam concentration 0.215% K) and then against a sodium electrode (amalgam concentration 0.206% Na). The measurements were made with the apparatus described in this paper. The voltages were read with a Leeds and Northrup Type K potentiometer. A certified Weston standard cell was used as a calibration reference. The 1M KCl - calomel half cell was used as a reference electrode throughout. The cells used may be formulated as follows:

$$Hg,\ Hg_2Cl_2\ KCl(1M)/MeCl(xM)\ MeHg\ (amalgam)$$

and

$$Hg,\ Hg_2Cl_2\ KCl(1M)/KCl(\tfrac{xM}{2}) + NaCl(\tfrac{xM}{2}),\ MeHg\ (amalgam)$$

where Me represents either sodium or potassium,   represents the concentration of the pure sodium or potassium chloride solution at any concentration interval.

The potentials measured are recorded in Tables XI and XII. These data seem to indicate that the alkali amalgam electrodes are not specific for any single alkali ion species when other ions are present. Within narrow limits the same E.M.F. is obtained with the potassium electrode in pure potassium chloride solutions, equi-molal mixtures of potassium and sodium chlorides and in pure sodium chloride solution, when the total salt concentrations are the same in these several solutions.

Table XI.

Measurements with K-electrode in KCl, NaCl, and Mixed KCl-NaCl Solutions

| I<br>Concentration of pure salt. | II<br>Concentration of mixed salt solutions.<br>KCl | <br><br>NaCl | III<br>Pure KCl Measured E.M.F. in volts. | IV<br>KCl-NaCl mixture. Measured E.M.F. in volts | V<br>Pure NaCl Measured E.M.F. in volts. |
|---|---|---|---|---|---|
| 1.0M | .5M | .5M | 2.1818 | 2.1603 | 2.1532 |
| 0.5M | .25M | .25M | 2.1875 | 2.1875 | 2.1782 |
| 0.2M | .10M | .10M | 2.2080 | 2.2073 | 2.2055 |
| 0.1M | .05M | .05M | 2.2246 | 2.2245 | 2.2244 |
| 0.05M | .025M | .025M | 2.2414 | 2.2413 | 2.2427 |
| 0.02M | .010M | .010M | 2.2610 | 2.2609 | 2.2626 |
| 0.01M | .005M | .005M | 2.2784 | 2.2789 | 2.2803 |
| 0.001M | .0005M | .0005M | 2.3121 | 2.3125 | 2.3146 |

Table XII.

Measurements with Na-electrode in NaCl, KCl and Mixed NaCl-KCl Solutions

| I Concentration of pure salt. | II Concentration of mixed salt solutions. | | III Pure KCl Measured E.M.F. in volts. | IV KCl-NaCl mixture. Measured E.M.F. in volts | V Pure NaCl Measured E.M.F. in volts. |
|---|---|---|---|---|---|
| | KCl | NaCl | | | |
| 1.0M | .5M | .5M | 2.1785 | 2.1673 | 2.1531 |
| 0.5M | .25M | .25M | 2.1910 | 2.1806 | 2.1750 |
| 0.2M | .10M | .10M | 2.2049 | 2.1999 | 2.1956 |
| 0.1M | .05M | .05M | 2.2159 | 2.2149 | 2.2147 |
| 0.05M | .025M | .025M | 2.2299 | 2.2293 | 2.2296 |
| 0.02M | .01M | .01M | 2.2490 | 2.2492 | 2.2556 |
| 0.01M | .005M | .005M | 2.2618 | 2.2641 | 2.2665 |
| 0.001M | .0005M | .0005M | 2.2920 | 2.2989 | 2.2967 |

## DISCUSSION OF RESULTS

The potentials measured with the potassium electrode in pure KCl solutions (Table II) show that internal resistances were encountered in extremely dilute solutions. These resistances were of sufficient magnitude to materially affect the measured values of cells of the type

$$Hg,\ Hg_2Cl_2\ KCl(1M)/KCl(xM),\ K(amalgam)$$

They present sufficient justification for the simplification of the apparatus used in such measurements. That such resistances were encountered is in accord with the findings of Allmand and Polack (1919) who simplified the design of the apparatus they used in order to overcome it. Byers (1908) likewise recognized that internal resistances affected his measured potentials. In order to attempt to eliminate this low electrical transfer in his cells, he added "indifferent electrolytes" to the solutions he used.

Measured values of 0.0523V and 0.0527V were obtained for the cell

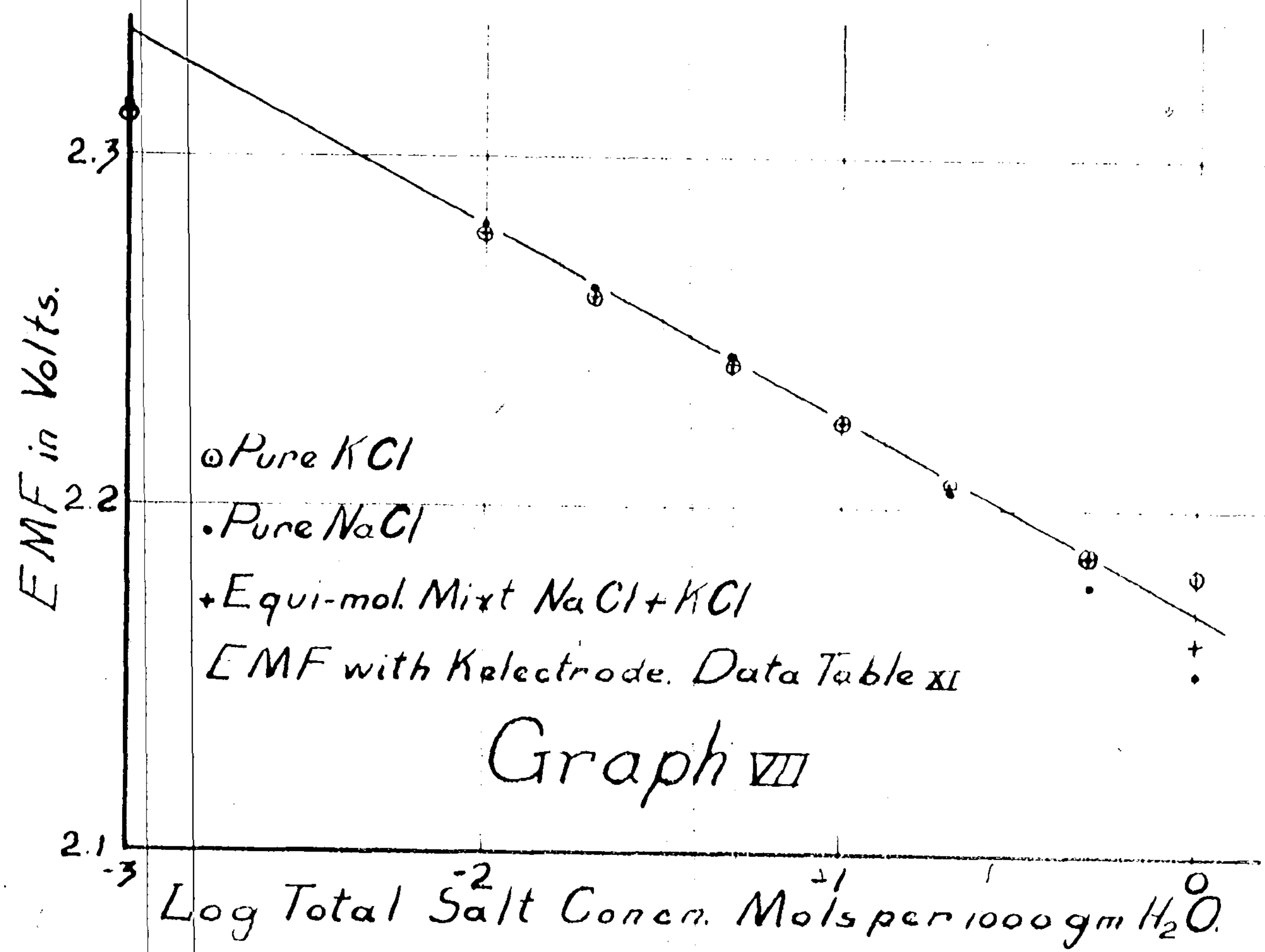
$$Hg,\ Hg_2Cl_2\ KCl(0.1M)/KCl(1M)\ Hg_2Cl_2,\ Hg$$

which are in excellent agreement with the potential (0.0529V) for this cell measured by Lewis, Brighton and Sebastian (1917, pg. 2255). This measurement, together with the close correlation between the measured and calculated values of Table I, is sufficient proof that the constancy, accuracy and reproducibility of the calomel half cell is not altered by flowing solution through it at a fairly rapid rate. The Ml KCl calomel may therefore be used as a reference electrode in an apparatus of the type described in Fig.1.

The agreement between the measured values of Allmand and Polack (1919) and those obtained with the apparatus described establish the validity of measurements obtained with a liquid junction of the type developed.

The further agreement between the potentials measured in neutral potassium chloride solutions and those prepared using hydrochloric acid solution (pH 4.007) as a solvent completed the proof that insofar as design of apparatus was concerned the amalgam electrodes had been successfully adapted to measurements in biological solutions. Measurements could be made on as little as 25 cc. of solution. Furthermore, as many as twelve distinct measurements have been made with 3.0 cc. of amalgam.

Wide deviations were encountered when the sodium and the potassium electrodes were used in solutions containing both sodium and potassium ions. That this was not the fault of the apparatus used was clear since when the preliminary data in mixed salt solutions (Table VIII), those of Ringer (1923)(Table IX), and those of Neuhausen (1922) were treated in the same manner, deviations of like type were encountered in all of them. Michaelis and Kawai (1925) do not agree that the sodium


EMF in Volts.
2.3
2.2
2.1
-3
-2
-1
0
Log Total Salt Concn. Mols per 1000 gm $H_2O$.
⊙ Pure KCl
• Pure NaCl
+ Equi-mol. Mixt NaCl + KCl
EMF with K electrode. Data Table XI

Graph VII

electrode is affected by potassium chloride. This seems peculiar since the apparatus used by them was in effect quite similar in design to that of these other workers.

Subsequent measurements with the sodium and the potassium electrodes in pure potassium chloride, pure sodium chloride and in equi-molal mixtures of sodium and potassium chlorides confirm the results of Neuhausen (1922), of Ringer (1923), and of Byers (1908) but refute those of Michaelis and Kawai (1925). Not only were definite and reproducible potentials measured in mixed salt solutions but like measurements were obtained with the sodium electrode in pure potassium chloride solutions and with the potassium electrode in pure sodium chloride solutions.

These measurements are presented in Tables XI and XII. They are plotted for easy comparison in Graphs VII and VIII. It can be seen that regardless of the electrode used the same form of curve is obtained in sodium chloride solutions; the same is true with regard to potassium chloride. In practically every instance the potentials in the mixed salt solutions (if the same electrode is used) lie between those of the potassium chloride solutions and the sodium chloride solutions. They approximate more nearly the potassium chloride measurements than the sodium chloride ones.

It would appear that either the amalgam electrodes are not specific for a single ion or that the electrode potential and not the activity of the ion measured is a function of the total salt concentration.

The probability that the deviation which existed might be caused by the surging of some calomel into the amalgam electrode reaction chamber, causing the amalgam electrode to act as a calomel half cell was rejected for two reasons — first, that such potentials should have been in the order of magnitude of those in Table I, second, since no constant or reproducible potential could be obtained when pure mercury was used in the amalgam electrode vessel in place of the amalgam.

Byers (1908) attributed the deviations to the replacement of some of the metal in the amalgam by the metal corresponding to the cation in the added salt. This should cause the electrode to be reversible to both ions (the metal in the prepared amalgam and the metal corresponding to the cation of the added salt).

Neuhausen (1922) states that "In the case of 0.1 N sodium chloride solution mixed with other salts three considerations must be kept in mind. The common ion effect ($Cl^-$) will tend to decrease the $Na^+$ concentration; on the other hand the presence of the second salt may activate the sodium ions which would be equivalent to increasing the $Na^+$ concentration....... These two results may balance......The third and most important effect is the replacement of some of the sodium in the amalgam by the cation, the electrode having a lower potential against the solution. The amount of replacement will depend principally on the chemical properties of the cation and its concentration as well as on the character of the amalgam formed by the replacing ion".

From the measurements of Table VI, and the compilation of data by Michalek and Phipps (1928) it is seen that the lower the concentration of the alkali metal in the amalgam the lower the measured E.M.F. of a cell — all other things constant. This would be in accord with Neuhausen's (1922) statement that replacement of some of the sodium in the amalgam results in the electrode having a lower potential against the solution. However, MacInnes and Parker (1915, pg.1453) conclude from the following measured potentials

| | | | |
|---|---|---|---|
| Concn. amalgam | 3.02% app. | 0.002% app. | 0.0002% app. |
| E.M.F. in volts | 0.10603±0.00001 | 0.10600±0.00005 | 0.1060±0.0005 |

in cells of the type

$$Ag/AgCl_{(s)}-KCl_{c_1}/KHg_x-KHg_x/KCl_{c_2}\ AgCl_{(s)}/Ag$$

that the E.M.F. measured was independent of the amalgam concentration. These amalgams were extremely dilute so there is the probability that there is a minimum amalgam concentration below which no change in E.M.F. occurs with a change in the amalgam concentration. If this is true, and these potentials with dilute amalgams indicate that it is, the explanation of the abnormal behavior of the alkali amalgam electrodes in the presence of foreign alkali cations is quite easily and logically explained by the assumption that replacement does occur in the amalgams even in those cases in which both the solution and the amalgam are flowing. A concentration of the replacing alkali metal sufficient to give a constant potential with the added ion is built up and the amalgam electrode becomes reversible for both ions. It will be noted that the lowest concentration of amalgam cited from MacInnes and Parker (1915) is but 0.0002% which lends weight to the above assumption. It is further borne out by a comparison of a portion of the measurements from Tables XI and XII which have been regrouped in Table XIII.

Table XIII.

| I Concentration salt in gm. mol. wt. per 1000 gm. $H_2O$. | II Pure NaCl Na-electrode Measured E.M.F. in volts. | III Pure NaCl K-electrode Measured E.M.F. in volts. | IV Pure KCl Na-electrode Measured E.M.F. in volts. | V Pure KCl K-electrode Measured E.M.F. in volts. |
|---|---|---|---|---|
| 1.000 | 2.1531 | 2.1532 | 2.1785 | 2.1818 |
| 0.500 | 2.1750 | 2.1782 | 2.1910 | 2.1875 |
| 0.200 | 2.1956 | 2.2055 | 2.2049 | 2.2080 |
| 0.100 | 2.2147 | 2.2244 | 2.2159 | 2.2246 |
| 0.050 | 2.2296 | 2.2427 | 2.2299 | 2.2414 |
| 0.020 | 2.2556 | 2.2626 | 2.2490 | 2.2610 |
| 0.010 | 2.2665 | 2.2803 | 2.2618 | 2.2784 |
| 0.001 | 2.2967 | 2.3146 | 2.2920 | 2.3121 |

In fact the agreement, between the two sets of measurements in pure NaCl, and likewise between the two sets in pure KCl, is much closer than would be expected.

## SUMMARY AND CONCLUSIONS

1. A new type of flowing junction has been developed for use with the alkali amalgam electrodes. The calomel half cell of any desired concentration could be used as a reference electrode in the apparatus described. The half cell $Hg/Hg_2Cl_2$, KCl(1M) was used as a reference in all the measurements made except those recorded in Table IV.

2. This type of junction was shown to operate accurately when single salt solutions (either in neutral or in acid solution) were employed.

3. Studies were made with the sodium amalgam and the potassium amalgam electrodes in solutions of (a) pure KCl, (b) pure NaCl, and (c) equi-molecular mixtures of NaCl and KCl at total salt concentrations equal to the pure salt concentrations in series (a) and (b).

4. It was found that the potassium electrode gave definite and reproducible measurements in all three series of solutions. Moreover, the potentials measured were in the same order of magnitude for any one total salt concentration. Results of the same type were obtained with the sodium electrode in the three series of solutions.

5. A comparison of the data presented with that of Neuhausen (1922) and likewise with that of Ringer (1923) was made. All three groups of data show that the sodium ion affects the potassium electrode and that the potassium ion affects the s odium electrode. The effect is such in all cases as to make

the electrode potential appear to be a function of the total salt concentration.

6. The explanation advanced by Byers (1908) and by Neuhausen (1922) that the effect was due to replacement of sodium in the amalgam by some potassium; on the reverse, is confirmed by the data presented. It is further pointed out that in view of the measured potentials of MacInnes and Parker (1915) only very small amounts of the alkali metals are necessary in the amalgams in order to make them electrodes reversible to the particular ionic species they represent. With this in view it seems probable that electrodes reversible to more than one ionic species might exist. This seems to be confirmed by the data in Tables XI, XII, and XIII.

7. The measurements presented would indicate that the alkali amalgam electrodes in their present forms would be of little or no value for plant nutrient work insofar as the study of ionic equilibria (as are described in the introduction to this paper) are concerned. This does not obviate the possibility of following plant growth with these electrodes. In this case, however, the growth would have to be correlated with the measured potentials and not with the concentrations of ions calculated from these potentials.

ACKNOWLEDGMENT

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