VOL. XL. SEPTEMBER, 1918. NO. 9.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, COLUMBIA UNIVERSITY, NO. 314.]

PLANCK'S FORMULA FOR THE POTENTIAL DIFFERENCE BETWEEN SOLUTIONS AND THE VALUES OF CERTAIN IMPORTANT CELLS.

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Received May 17, 1918.

In many instances, in the determination of ionic concentrations by means of electromotive force combinations of the type

$$\underset{(1)}{\mathrm{Hg} - \mathrm{HgCl}}\ 0.1\,M\ \mathrm{KCl} \underset{(2)}{-} 3.5\,M\ \mathrm{KCl} \underset{(3)}{-} 0.1\,M\ \mathrm{HCl} \underset{(4)}{-} \mathrm{H_2Pt},$$

it becomes of primary importance to be able to attach precise values to the various component voltages which go to make up the observed voltage of the combination. Thus considering the combination just given, we have as component voltages: (1) The potential difference existing between the mercury and the mercurous ion, (2) that existing between the 0.1 *M* potassium chloride solution and the 3.5 *M* potassium chloride solution, (3) that existing between the 3.5 *M* potassium chloride solution and the 0.1 *M* hydrochloric acid, (4) that existing between the hydrogen ion of the 0.1 *M* hydrochloric acid and the hydrogen gas.

At this point let us define two terms of which it will be advantageous to make use when referring to potential differences of the kind under consideration; these terms are, electrode potential difference, and contact potential difference. By the first we shall mean the potential difference which exists between a metal (or non-metal) and a solution of its ion, which bathes it. By the second we shall mean the potential difference which exists across the liquid junction when two different solutions, which are electrolytes, are in contact.

Now, in order to assign definite values to the electrode potential differences (1) and (4), we must first know the values of the contact potential differences (2) and (3). Unfortunately, however, contact potential differences cannot be measured separately because they always form an element in a combination. Thus we are forced to reason in a circle, because the values of the electrode potential differences cannot be known until the values of the contact potential differences have been ascertained, and a knowledge of the latter is dependent upon a knowledge of the former.

To get around this difficulty there have been several attempts to deduce more or less general formulas for the calculation of contact potential differences upon theoretical considerations.[1] Of these formulas, the one due to Planck is the one that has been applied most frequently, at least for the case which is most often met, that of two binary salts of the 1 : 1 type with an ion in common, the two solutions being at different or similar concentrations.

Now an extended application of Planck's formula to the contact potential differences of various combinations leads to results for any given pole potential difference which are not consistent.[2] It, therefore, becomes necessary to investigate the validity of this formula more closely.

Such an investigation is the purpose of the present work, and as a case of especial importance the authors have chosen the one which embraces the contact potential differences between solutions of potassium chloride and hydrochloric acid, because this choice enables us to arrive at a closer approximation than has heretofore been obtained of the values of the following important pole potential differences:

(*a*) Hg — HgCl 1.0 *M* KCl; (*b*) Hg — HgCl 0.1 *M* KCl; (*c*) Hg — HgCl 1.0 *M* HCl; (*d*) Hg — HgCl 0.1 *M* HCl; (*e*) PtH_2(1 Atmos.) — 1.0 *M* HCl; (*f*) PtH_2 (1 Atmos.) — 0.1 *M* HCl. These pole potential differences we will respectively designate by the letters *a*, *b*, *c*, *d*, *e* and *f*.

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[1] Nernst, *Z. physik. Chem.*, **2**, 613 (1888) and **4**, 129 (1889); Planck, *Ann. Physik*, **4**, 581 (1890); Löven, *Z. physik. Chem.*, **20**, 593 (1896); Johnson, *Ann. Physik*, **14**, 995 (1904); Henderson, *Z. physik. Chem.*, **59**, 118 (1907) and **63**, 325 (1908); Guyot, *J. chim. phys.*, **6**, 424 (1908); Weinstein, *Thermodynamik*, Bd. III, **1908**; Lewis and Sargent, This Journal, **31**, 363 (1909); Pleijel, *Z. physik. Chem.*, **72**, 1 (1910); Cumming, *Trans. Faraday Soc.*, **8**, 87 (1912); Melander, *Z. physik. Chem.*, **90**, 59 (1915).

[2] This can easily be verified, for instance, by substituting in combinations (1) and (6) below, the values given by Planck's formula and then solving for the pole potential difference (*c*).

Planck, as a result of integrating the differential equations with which he expressed his assumptions, finally obtained the expression that

$$E = RT \log \xi \qquad (1)$$

where E is the contact potential difference in volts, $R = 0.000198$, T is the absolute temperature, and ξ is a transcendental function defined by the equation

$$\frac{\xi U_2 - U_1}{V_2 - \xi V_1} = \frac{\log c_2/c_1 - \log \xi}{\log c_2/c_1 + \log \xi} \cdot \frac{\xi c_2 - c_1}{c_2 - \xi c_1}, \qquad (2)$$

in which U_1 is the sum of the products of the mobilities of the positive ions in the dilute solution times their respective concentrations; V_1 is the sum of the products of the mobilities of the negative ions in the dilute solution times their respective concentrations; c_1 is the sum of the concentrations of the positive and negative ions in the dilute solution; and U_2, V_2, and c_2 have a similar significance with regard to the concentrated solution.

In order to find the value of ξ for any given case, we proceed as follows: first we simplify the right hand member of (2) by putting $c_2/c_1 = k$, which gives us,

$$\frac{\xi U_2 - U_1}{V_2 - \xi V_1} = \frac{\log k - \log \xi}{\log k + \log \xi} \cdot \frac{k\xi - 1}{k - \xi}. \qquad (3)$$

Next, we introduce a new variable, η, and construct two auxiliary equations by respectively equating η to the first and second members of (3), thus obtaining,

$$\frac{\xi U_2 - U_1}{V_2 - \xi V_1} = \eta \qquad (4)$$

$$\frac{\log k - \log \xi}{\log k + \log \xi} \cdot \frac{k\xi - 1}{k - \xi} = \eta. \qquad (5)$$

From (5) we construct a table of double entry by assigning arbitrary values to k and ξ, and solving for η. Thus, to take some of the values so found, we have:

Value of k. **Value of ξ.**	1.	2.	4. Value of η.	8.	20.
0.1	1.000	0.784	0.619	0.497	0.384
0.4	1.000	0.902	0.817	0.746	0.672
0.7	1.000	0.960	0.923	0.891	0.856
1.0	1.000	1.000	1.000	1.000	1.000
1.5	1.000	1.047	1.094	1.140	1.194
3.3	1.000	1.143	1.300	1.462	1.673

Finally, we select such a pair of values for ξ and η (the latter to be taken from the appropriate k column) as will satisfy (4). The value of ξ satisfying this requirement is the value to employ in (1).

Using Planck's formula and the values given in the next paragraph for the mobilities and the concentrations of the ions at 25°, we get as the calculated values for the contact potential differences existing at 25° for xM KCl — 1.0 M HCl and for xM KCl — 0.1 M HCl, the values given herewith and represented graphically in Fig. 1.

Value of x	0.05	0.1	0.3	0.5	1.0	2.0	3.3
Volt (1.0 M HCl)	0.0630	0.0532	0.0401	0.0348	0.0280	0.0221	0.0181
Volt (0.1 M HCl)	0.0351	0.0282	0.0184	0.0153	0.0112	0.0080	0.0061

In each case the direction in which the positive current tends to flow across the liquid junction is from the hydrochloric acid to the potassium chloride solution.

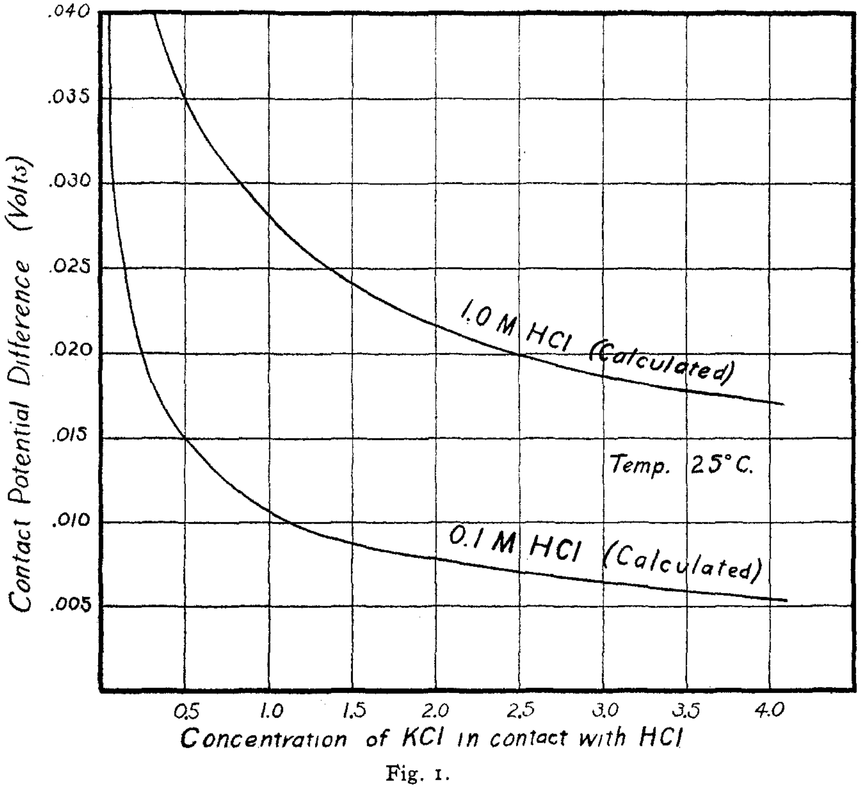

Fig. 1.

The values used in the preceding paragraph are as follows: for the mobilities of the ions at 25°, the values $H^+ = 347.9$, $K^+ = 74.6$, $Cl^- = 75.6$; for the ionic concentrations at 25°, the values obtained by multiplying the molar concentrations by the percentage ionization as derived from conductance ratios without correcting for viscosity,[1] the figures so employed being,[2]

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[1] It is to be noted that for concentrations greater than 0.1 N it is now generally accepted that the values of ionization as given by conductance ratios without correcting

Conc. in moles per liter	0.05	0.1	0.5	1.0	2.0	3.0
% ionization of KCl at 25°	88.72	85.76	77.97	74.54	69.45	65.70
% ionization of HCl at 25°	...	92.04	...	78.94	...	...

Method of Determining Contact Potential Differences.

The method that the authors have devised is essentially a differential method. Consider a system of combinations, which have the same pole potential differences but which differ in their contact potential differences, and let the resultant voltage of each combination be known.

Thus, at 25°, we have the following observed voltages, the component voltages being directed through the solution as indicated:

(1) Hg—HgCl 1.0M KCl—4.1M KCl—1.0M HCl HgCl—Hg; 0.0083 volt

$$\xleftarrow{a}\qquad\qquad\xleftarrow{q_1}\qquad\xleftarrow{r_1}\qquad\qquad\xrightarrow{c}$$

(2) Hg—HgCl 1.0M KCl—3.5M KCl—1.0M HCl HgCl—Hg; 0.0114 volt

$$\xleftarrow{a}\qquad\qquad\xleftarrow{q_2}\qquad\xleftarrow{r_2}\qquad\qquad\xrightarrow{c}$$

(3) Hg—HgCl 1.0M KCl—2.5M KCl—1.0M HCl HgCl—Hg; 0.0172 volt

$$\xleftarrow{a}\qquad\qquad\xleftarrow{q_3}\qquad\xleftarrow{r_3}\qquad\qquad\xrightarrow{c}$$

The other combinations of the system we will specify by saying that (4) q_4r_4 shall correspond to a 1.75 M KCl salt bridge; (5) q_5r_5 to 1.0 M KCl; (6) q_6r_6 to 0.1 M KCl, the observed voltages being, respectively, 0.0227, 0.0319 and 0.0669 volt; see Expts. 1 to 6.

By subtracting (1) from (2) we get that $q_2 + r_2 - q_1 - r_1 = 0.0114 - 0.0083 = 0.0031$ volt, or $r_2 = 0.0031 + r_1 - (q_2 - q_1)$. In a similar manner $r_3 = 0.0089 + r_1 - (q_3 - q_1)$; and so on for r_4, r_5 and r_6.

It now remains to determine the value of r_1 and the values of the differences $(q_2 - q_1)$, $(q_3 - q_1)$, etc. In regard to the latter we may assume that there is no contact potential difference between potassium chloride solutions of different concentrations because of the fact that the mobility of the potassium ion is so very nearly equal to that of the chloride ion, in which case the values assigned to q_1, q_2, ... q_6 would be each equal to zero. Or we may assume that there is a contact potential difference and that it is correctly expressed by Nernst's formula,[3]

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for viscosity are to be considered only as approximations, and that values much nearer the truth are given by conductance ratios corrected for viscosity; see Noyes and Falk, THIS JOURNAL, **34**, 454 (1912).

The reason in this article for taking the values given by conductance ratios without correcting for viscosity is because such values are based upon the assumption that the mobilities of the ions are independent of the concentration, and Planck's formula is predicated upon premises which contain this same assumption; see Planck, *Loc. cit.*, p. 571.

[2] Partly from the data of Kohlrausch; partly from the data of Goodwin and Haskell; as given in Landolt and Börnstein, *Physik.-Chem. Tabellen*, 4th ed., pp. 1104 and 1108.

[3] *Z. physik. Chem.*, 4, 129 (1888). Here u represents the mobility of the positive ion, v that of the negative ion, c_1 the ionic concentration of the dilute solution, c_2 that of the concentrated solution.

$$E = RT\frac{u - v}{u + v}\log\frac{c_2}{c_1};$$

then the assigned values would be $q_1 = 0.00022$; $q_2 = 0.00019$; $q_3 = 0.00014$; $q_4 = 0.00009$; $q_5 =$ zero; $q_6 = 0.00037$ volt at 25°. This second assumption seems to merit the more credence from theoretical considerations and is the one that we will adopt; that we are justified in doing this we will prove later.

It is, of course, possible, though not likely, that the real values of q_1, q_2, . . . q_6 are in excess of the values that we have assigned. Even granting this, it is to be noticed that whatever differences exist between the real and the assigned values of q_1, q_2, . . . q_6, the errors that are introduced into the values of r_2, r_3 . . . r_6 are reduced by virtue of our employing the differences $(q_2 - q_1)$, $(q_3 - q_1)$, etc.

Using the foregoing values we get:

$$\begin{aligned}
r_2 &= 0.0031 + r_1 - (-0.00003) = 0.0031 + r_1\\
r_3 &= 0.0089 + r_1 - (-0.00008) = 0.0090 + r_1\\
r_4 &= 0.0144 + r_1 - (-0.00013) = 0.0145 + r_1\\
r_5 &= 0.0236 + r_1 - (-0.00022) = 0.0238 + r_1\\
r_6 &= 0.0586 + r_1 - (-0.00059) = 0.0592 + r_1
\end{aligned}$$

To determine the value of r_1 let us next consider combinations of the type Hg — HgCl xM HCl — xM HCl — H_2 (1 Atmos.) Pt. In the first place there is no contact potential difference because the concentration of the hydrochloric acid is the same on both sides of the surface of contact of the two solutions. Secondly, as we vary x, the pole potential difference at each pole changes by the same amount, but in an opposite direction.[1]

Now for $x = 1.0$ and $x = 0.1$, respectively, we have the following observed voltages at 25°:

(7) $\text{Hg}\underset{\xleftarrow{c}}{-}\text{HgCl}\ 1.0\,M\ \text{HCl}\underset{\text{none}}{-}1.0\,M\ \text{HCl}\underset{\xrightarrow{e}}{-}H_2$ (1 Atmos.) Pt; 0.2790 volt,

the value from Ellis' work being 0.2788;[2] from the authors' work 0.2791 (Expt. No. 7); average 0.2790.

(8) $\text{Hg}\underset{\xleftarrow{d}}{-}\text{HgCl}\ 0.1\,M\ \text{HCl}\underset{\text{none}}{-}0.1\,M\ \text{HCl}\underset{\xrightarrow{f}}{-}H_2$ (1 Atmos.) Pt; 0.3989 volt,

Ellis having obtained 0.3988;[3] Harned,[4] 0.3991; Loomis and Meacham,[5]

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[1] This assumes that the repression of ionization of mercurous chloride in the presence of hydrochloric acid for the range of concentrations and for the temperature of 25° follows the Law of Mass Action; the validity of this assumption we shall justify later.

[2] THIS JOURNAL, **38**, 752 (1916). This investigator obtained 0.2780 for the combination Hg—HgCl 1.016 M HCl—1.016 M HCl—H_2 (1 Atmos.) Pt, which corrected to exact molarity gives 0.2788.

[3] *Loc. cit.*

[4] THIS JOURNAL, **37**, 2475 (1915).

[5] *Ibid.*, **38**, 2315 (1916).

0.3988; average, 0.3989. Loomis and Acree[1] obtained 0.4001, and Myers and Acree,[2] 0.3998; but these results are not included as they are obviously in error.

By virtue of the second consideration mentioned above, we have that d is as much greater than c, as e is greater than f, or d — c = e — f. Now, subtracting (7) from (8), we get (d — f) — (c — e) = 0.1199 volt; and from these two equations we obtain that d is 0.0600 volt greater than c.

Consider next combination (9); its observed voltage at 25° is 0.0600 volt; the authors, Expt. No. 8.

(9) Hg—HgCl 1.0*M* HCl—4.1*M* KCl—0.1*M* HCl HgCl—Hg; 0.0600 volt,
$\xleftarrow{c}$ $\xrightarrow{r_1}$ $\xleftarrow{s_1}$ $\xrightarrow{d}$

and since from (7) and (8) the value of d is 0.0600 volt greater than c, it follows that the resultant effect of r_1 and s_1 is zero; that is to say, the values of r_1 and s_1 are equal. Now the values of r_1 and s_1 can only be equal provided that each is equal to zero. This follows from the consideration that if they were different from zero, the amount by which the one would differ from zero would not be equal to the amount by which the other would differ from zero, because the 1.0 *M* HCl would give rise to a greater contact potential difference than would the 0.1 *M* HCl, and consequently we would not get 0.0600 volt as the observed voltage of combination (9).

Since the value of r_1 is zero, we can immediately get the values of $r_2 \ldots r_6$, from which we see that the contact potential differences *xM* KCl — 1.0 *M* HCl at 25° are as follows:

Contact p. d.	r_6	r_5	r_4	r_3	r_2	r_1
Conc. of KCl	0.1	1.0	1.75	2.5	3.5	4.1
Volt	0.0592	0.0238	0.0145	0.0090	0.0031	zero

These values are represented graphically in Fig. 2, where the values calculated by Planck's formula are also given.

We proceed in a similar manner to get the contact potential differences *xM* KCl — 0.1 *M* HCl by taking as our basic system of combinations, one whose first three members are given by (10), (11) and (12), the observed voltages for 25° being:

(10) Hg—HgCl 1.0*M* KCl—4.1*M* KCl—0.1*M* HCl HgCl—Hg; 0.0520 volt
$\xleftarrow{a}$ $\xleftarrow{q_1}$ $\xleftarrow{s_1}$ $\xrightarrow{d}$

(11) Hg—HgCl 0.1*M* KCl—3.5*M* KCl—0.1*M* HCl HgCl—Hg; 0.0514 volt
$\xleftarrow{a}$ $\xleftarrow{q_2}$ $\xleftarrow{s_2}$ $\xrightarrow{d}$

(12) Hg—HgCl 1.0*M* KCl—2.5*M* KCl—0.1*M* HCl HgCl—Hg; 0.0498 volt
$\xleftarrow{a}$ $\xleftarrow{q_3}$ $\xleftarrow{s_3}$ $\xrightarrow{d}$

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[1] *Am. Chem. J.*, **46**, 618 (1912).

[2] *Ibid.*, **50**, 396 (1913). Loomis and Meacham, THIS JOURNAL, **38**, 2312 (1916) claim that Myers and Acree's value of 0.3998 should be 0.4002.

The other combinations of the system we will specify by saying that combination (13) q_4s_4 shall correspond to a 1.75 *M* KCl salt bridge; (14) q_5s_5 to 1.0 *M* KCl; (15) to 0.5 *M* KCl; (16) q_6s_6 to 0.1 *M* KCl; the observed voltages of these combinations being, respectively, 0.0474, 0.0446, 0.0406 and 0.0254 volt; see Expts. Nos. 9 to 15.

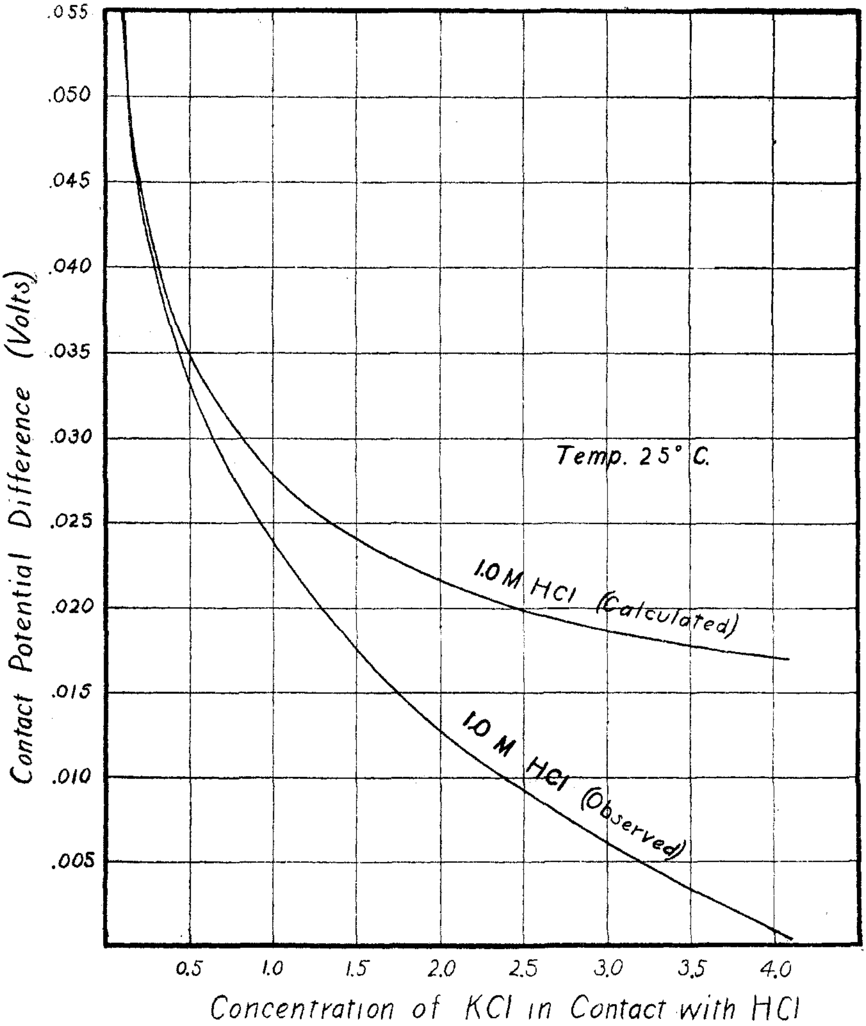

Fig. 2.

By subtracting (11) from (10), (12) from (10), etc., and remembering that d is the positive pole of each of the combinations (10) to (16), inclusive, we get that $s_2 = 0.0006 + s_1 - (q_2 - q_1)$; $s_3 = 0.0022 + s_1 - (q_3 - q_1)$, and so on for s_4, s_5, and s_6. Now the value of s_1 is zero as already shown, so that we have by making use of the values already assigned to the differences ($q_2 - q_1$), ($q_3 - q_1$), etc., that the contact potential differences xM KCl — 0.1 M HCl at 25° are as follows:

Contact p. d.	s_6	s_5	s_4	s_3	s_2	s_1
Conc. of KCl	0.1	1.0	1.75	2.5	3.5	4.1
Volt	0.0270	0.0076	0.0047	0.0022	0.0006	zero

These values are given graphically in Fig. 3, where the values calculated by Planck's formula are also given.

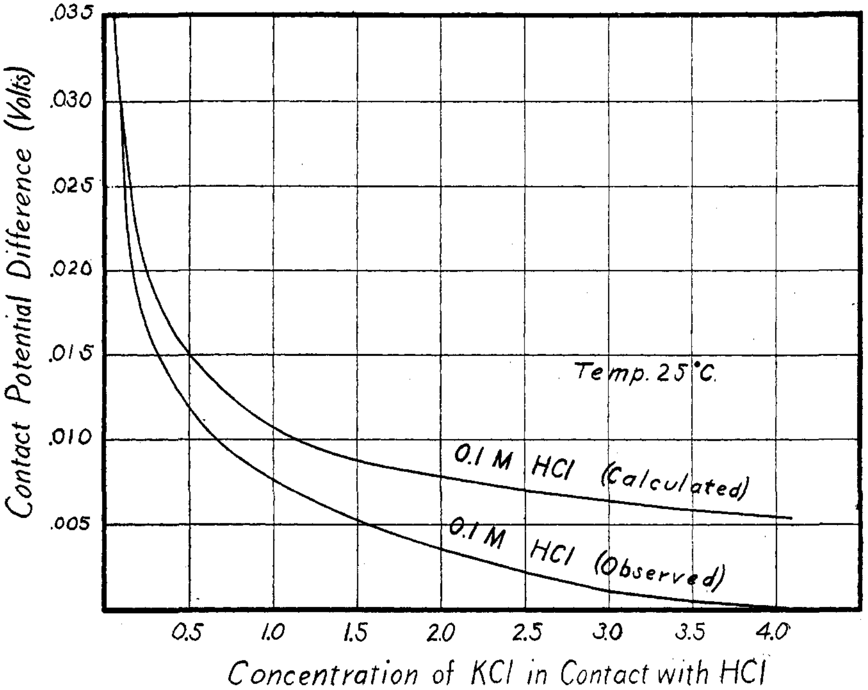

Fig. 3.

In arriving at the foregoing values for the contact potential differences given in Figs. 2 and 3, we have made use of two assumptions: first, that the values we have used for the differences ($q_2 - q_1$), etc., where q_2 is the contact potential difference between 1.0 M KCl and 3.5 M KCl, and q_1 that between 1.0 M KCl and 4.1 M KCl, are sensibly true; secondly, that the combinations represented by Hg — HgCl xM HCl — xM HCl — H_2 (1 Atmos.) Pt change their pole potential differences by the same amount, but in an opposite direction, as we vary x.

It now becomes necessary to substantiate these assumptions, and this is done by seeing if the values of the pole potential differences which we get by employing the contact potential differences just found, satisfy every combination in which they are used in conjunction with said contact potential differences.

If this criterion is met, then our assumptions are correct and we are justified in accepting both the values for the pole potential differences and for the contact potential differences. We will now show that such is the case.

Let us first derive the values for the 6 pole potential differences that we have already designated by *a*, *b*, *c*, *d*, *e*, and *f*.

(*a*) The value of the pole potential difference Hg — HgCl 1.0 *M* KCl at 18° is taken as the standard as adopted by Ostwald[1] with the value —0.5600 volt.[2] Its temperature coefficient according to various observers is: Chrutschoff and Sisnikoff,[3] 0.00068; Coggeshall,[4] 0.000675; Richards,[5] 0.00061. Taking the two nearest agreeing values of the temperature coefficients we get 0.5648 volt as the value of the normal calomel cell at 25°, and this is the value that we have selected. Incidentally we might mention that this value of 0.5648 volt taken together with the values of the other pole potential differences which result from it gives better agreement than does either the value 0.5646 or 0.5650 volt, when we take account of all the various combinations Nos. 1 to 30, inclusive.

(*b*) The value of the pole potential difference Hg — HgCl 0.1 *M* KCl is found in terms of our standard calomel cell by means of combination (17) to be 0.6168 volt at 25° by solving for *b*:

$$(17)\ \mathrm{Hg}\underset{\xleftarrow{0.5648}}{\text{—}}\mathrm{HgCl}\ 1.0M\ \mathrm{KCl}\underset{\text{none}}{\text{—}}1.0M\ \mathrm{KCl}\underset{\xrightarrow{0.0004}}{\text{—}}0.1M\ \mathrm{KCl}\ \mathrm{HgCl}\underset{\xrightarrow{b}}{\text{—}}\mathrm{Hg};\ 0.0524\ \text{volt}$$

The value of 0.0524 volt for (17) is the authors' value (Expt. No. 16). Lewis[6] claims that the value is 0.0530 volt, but gives no details of his measurements. There is further evidence in support of our value of 0.0524. Sauer[7] found the value of (17) at 18° to be 0.0514 volt; the temperature coefficient of the 1.0 *M* KCl cell is 0.00066[8] and that of the 0.1 *M*

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[1] *Z. physik. Chem.*, 35, 333 (1900).

[2] Since the plus or minus sign attached to the value of a pole potential difference is simply to indicate the electromotive force of the electrolyte against the electrode, and leads to confusion when one is dealing with the component potential differences of a combination, it is preferable to make use of arrows to indicate the direction in which the positive current tends to flow by virtue of the particular potential difference involved.

[3] *Compt. rend.*, 108, 941 (1889).

[4] *Z. physik. Chem.*, 17, 62 (1895).

[5] *Ibid.*, 24, 39 (1897).

[6] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909); Lewis and Sebastian, *Ibid.*, 39, 2255 (1917).

[7] *Z. physik. Chem.*, 47, 176 (1904). The authors obtained for (17) at 15° the value 0.0509 ± 0.0002 as the result of 9 determinations; applying the same temperature coefficients as used with Sauer's data, we get 0.0522 for 25°.

[8] See preceding paragraph.

KCl cell is 0.00079,[1] whence the value of (17) for 25° is 0.0523 volt.

(*c*) The value of the pole potential difference Hg — HgCl 1.0 *M* HCl at 25° is next found by solving combination (18) for *c* to be 0.5567 volt:

$$(18)\ \underset{\overset{0.5648}{\longleftarrow}}{\text{Hg—HgCl}}\ 1.0M\ \text{KCl}\underset{\text{none}}{\text{—}}1.0M\ \text{KCl}\underset{\overset{0.0238}{\longleftarrow}}{\text{—}}1.0M\ \text{HCl}\ \underset{\overset{c}{\longrightarrow}}{\text{HgCl—Hg}};\ 0.0319\ \text{volt}$$

The value of 0.0319 volt for (18) is the authors' value (Expt. No. 5).

(*d*) The value of the pole potential difference Hg — HgCl 0.1 *M* HCl is found upon solving combination (19) for *d* to be 0.6168 volt at 25°:

$$(19)\ \underset{\overset{0.5648}{\longleftarrow}}{\text{Hg—HgCl}}\ 1.0M\ \text{KCl}\underset{\overset{0.0004}{\longrightarrow}}{\text{—}}0.1M\ \text{KCl}\underset{\overset{0.0270}{\longleftarrow}}{\text{—}}0.1M\ \text{HCl}\ \underset{\overset{d}{\longrightarrow}}{\text{HgCl—Hg}};\ 0.0254\ \text{volt}$$

The value of 0.0254 is the authors' value (Expt. No. 15).

From the fact that the value of *d* from (19) is 0.0600 volt greater than the value of *c* from (18) it follows that our earlier assumption in regard to combinations (7) and (8) whereby we were led to assign a value to *d* which is 0.0600 volt greater than *c* is correct.

(*e*) The value of the pole potential difference PtH_2 (1 Atmos.) — 1.0 *M* HCl is seen from combination (7) to be 0.2777 volt at 25° since the value of *c* from (18) is 0.5568 volt.

(*f*) The value of the pole potential difference PtH_2 (1 Atmos.) — 0.1 *M* HCl is seen from combination (8) to be 0.2179 volt at 25° since the value of *d* from (19) is 0.6168 volt.

Summarizing the values *a* to *f* for the pole potential differences, we have then for the temperature of 25° the following figures which are probably reliable to ±0.0002 volt:[2]

	Volt.		Volt.
Hg—HgCl 1.0 *M* KCl..........	0.5648	Hg—HgCl 0.1 *M* KCl.........	0.6168
Hg—HgCl 1.0 *M* HCl..........	0.5567	Hg—HgCl 0.1 *M* HCl.........	0.6168
PtH_2(1 Atmos.) — 1.0 *M* HCl...	0.2777	PtH_2(1 Atmos.) — 0.1 *M* HCl..	0.2179

It is obvious that the values which we have just derived for the various pole and contact potential differences satisfy combinations Nos. (1) to (19), inclusive;[3] let us now further show that they also sensibly fit when

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[1] Richards, *Loc. cit.*

[2] On the other hand, Cumming (*Trans. Faraday Soc.*, **8**, 92 (1912)) has given it as his opinion with respect to values of this kind that a reliability of ±0.0002 volt for the individual potential differences is not warrantable. He says: "A critical review of the present data of our knowledge of electromotive-force work indicates, in my opinion, that no electrode potential difference or diffusion potential is known separately with a greater accuracy than about one millivolt. In many cases it is possible to measure the total potential with certainty to 0.1 millivolt, if not even closer. The problem is, of course, solved if either potential can be estimated accurately, and experiments with this aim are at present in progress."

[3] Combination (5) is the same as (18), while (16) is the same as (19); this duplication of numbering is simply to facilitate reference between the discussion of the combinations and the experimental detail.

applied to the other combinations for which we have experimental data, namely, combinations Nos. (20) to (30), inclusive.

Taking these up in detail, we have

$$(20)\ \mathrm{Hg}\underset{\overset{0.6168}{\longleftarrow}}{-}\mathrm{HgCl}\ 0.1\,M\ \mathrm{KCl}\underset{\text{none}}{-}0.1\,M\ \mathrm{KCl}\underset{\overset{0.0270}{\longleftarrow}}{-}0.1\,M\ \mathrm{HCl}\ \mathrm{HgCl}\underset{\overset{0.6168}{\longrightarrow}}{-}\mathrm{Hg}$$

Calculated: 0.0270. Observed: Bjerrum,[1] 0.0278; Meyers and Acree,[2] 0.0278; the authors, 0.0270 (Expt. No. 17). There is evidence that the value of Meyers and Acree is high by 0.0009 volt, because when they used the same 0.1 *M* KCl cell in (27) they obtained 0.4012 volt, which shows that their 0.1 *M* KCl cell was 0.0016 volt high, while when they used their 0.1 *M* HCl cell in (8) they obtained 0.3998 volt, which shows that this cell was 0.0008 volt high, therefore, their observed value for (20) is 0.0008 volt high, which gives us 0.0270 volt as the value for (20) when we make the indicated correction.

$$(21)\ \mathrm{Hg}\underset{\overset{0.5648}{\longleftarrow}}{-}\mathrm{HgCl}\ 1.0\,M\ \mathrm{KCl}\underset{\overset{0.0002}{\longleftarrow}}{-}4.1\,M\ \mathrm{KCl}\underset{\text{none}}{-}0.1\,M\ \mathrm{HCl}\underset{\overset{0.2179}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}.$$

Calculated: 0.3471. Observed: the authors, 0.3473 (Expt. No. 18); Harned,[3] 0.3494. As Harned does not report using more than one calomel electrode, there is some question as to the accuracy of his value 0.3494.

$$(22)\ \mathrm{Hg}\underset{\overset{0.5648}{\longleftarrow}}{-}\mathrm{HgCl}\ 1.0\,M\ \mathrm{KCl}\underset{\text{none}}{-}1.0\,M\ \mathrm{KCl}\underset{\overset{0.0076}{\longleftarrow}}{-}0.1\,M\ \mathrm{HCl}\underset{\overset{0.2179}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}$$

Calculated: 0.3545. Observed: the authors, 0.3550 (Expt. No. 19).

$$(23)\ \mathrm{Hg}\underset{\overset{0.5648}{\longleftarrow}}{-}\mathrm{HgCl}\ 1.0\,M\ \mathrm{KCl}\underset{\overset{0.0004}{\longrightarrow}}{-}0.1\,M\ \mathrm{KCl}\underset{\overset{0.0270}{\longleftarrow}}{-}0.1\,M\ \mathrm{HCl}\underset{\overset{0.2179}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}$$

Calculated: 0.3735. Observed; the authors, 0.3735 (Expt. No. 20).

$$(24)\ \mathrm{Hg}\underset{\overset{0.6168}{\longleftarrow}}{-}\mathrm{HgCl}\ 0.1\,M\ \mathrm{KCl}\underset{\overset{0.0006}{\longleftarrow}}{-}4.1\,M\ \mathrm{KCl}\underset{\text{none}}{-}1.01\,M\ \mathrm{HCl}\underset{\overset{0.2779}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}$$

Calculated: 0.3395. Observed: Loomis and Acree,[4] 0.3423.

$$(25)\ \mathrm{Hg}\underset{\overset{0.6168}{\longleftarrow}}{-}\mathrm{HgCl}\ 0.1\,M\ \mathrm{KCl}\underset{\overset{0.0006}{\longleftarrow}}{-}3.5\,M\ \mathrm{KCl}\underset{\overset{0.0031}{\longleftarrow}}{-}1.0\,M\ \mathrm{HCl}\underset{\overset{0.2777}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}$$

Calculated: 0.3428. Observed: the authors, 0.3427 (Expt. No. 21).

$$(26)\ \mathrm{Hg}\underset{\overset{0.6168}{\longleftarrow}}{-}\mathrm{HgCl}\ 0.1\,M\ \mathrm{KCl}\underset{\text{none}}{-}0.1\,M\ \mathrm{KCl}\underset{\overset{0.0592}{\longleftarrow}}{-}1.0\,M\ \mathrm{HCl}\underset{\overset{0.2777}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}$$

Calculated: 0.3983. Observed: the authors, 0.3975 (Expt. No. 22).

$$(27)\ \mathrm{Hg}\underset{\overset{0.6168}{\longleftarrow}}{-}\mathrm{HgCl}\ 0.1\,M\ \mathrm{KCl}\underset{\overset{0.0006}{\longleftarrow}}{-}4.1\,M\ \mathrm{KCl}\underset{\text{none}}{-}0.1\,M\ \mathrm{HCl}\underset{\overset{0.2179}{\longrightarrow}}{-}\mathrm{H_2}\ (1\ \text{Atmos.})\ \mathrm{Pt}$$

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[1] *Z. Elektrochem.*, **17**, 61 (1911).

[2] *Am. Chem. J.*, **50**, 411 (1913).

[3] THIS JOURNAL, **37**, 2475 (1915).

[4] *Am. Chem. J.*, **46**, 615 (1912).

Calculated: 0.3995. Observed: Bjerrum,[1] 0.4102; Loomis and Acree,[2] 0.4000; Myers and Acree,[3] 0.4012; Harned.[2] 0.4004; the authors, 0.3995 (Expt. No. 23).

(28) Hg—HgCl 0.1 *M* KCl—0.1 *M* KCl—0.1 *M* HCl—H_2 (1 Atmos.) Pt

$\overset{0.6168}{\longleftarrow}$ none $\overset{0.0270}{\longleftarrow}$ $\overset{0.2179}{\longrightarrow}$

Calculated: 0.4259. Observed: Bjerrum,[2] 0.4270; Loomis and Acree,[2] 0.4266; Myers and Acree,[2] 0.4269; Harned,[2] 0.4274, the authors values ranging from 0.4272 to 0.4257 (Expt. No. 24).

The agreement among the various investigators in regard to combinations (27) and (28) is far from satisfactory, and more work should be done on these two combinations, because of the importance which they have played in dealing with the contact potential difference between 0.1 *M* KCl and 0.1 *M* HCl. It is to be noticed that the difference between the calculated value of (28) and the calculated value of (27) is 0.0264 volt. If now we take the difference between the observed values of the various investigators, thereby eliminating any error due to their 0.1 *M* KCl cells, we get: Bjerrum, 0.0258; Loomis and Acree, 0.0265; Myers and Acree, 0.0257; Harned, 0.0270; average, 0.0263 volt, which is further corroborative evidence that the value of the contact potential difference between 0.1 *M* KCl and 0.1 *M* HCl is sensibly 0.0270 volt and not 0.0282 as given by Planck's formula.

(29) Hg—HgCl 1.0 *M* HCl—3.5 *M* KCl—0.1 *M* HCl—H_2 (1 Atmos.) Pt

$\overset{0.5567}{\longleftarrow}$ $\overset{0.0031}{\longrightarrow}$ $\overset{0.0006}{\longleftarrow}$ $\overset{0.2179}{\longrightarrow}$

Calculated: 0.3363. Observed: the authors, 0.3364 (Expt. No. 25).

(30) Hg—HgCl 1.0 *M* HCl—0.1 *M* KCl—0.1 *M* HCl—H_2 (1 Atmos.) Pt

$\overset{0.5567}{\longleftarrow}$ $\overset{0.0592}{\longrightarrow}$ $\overset{0.0270}{\longleftarrow}$ $\overset{0.2179}{\longrightarrow}$

Calculated: 0.3065. Observed: the authors, 0.3056 (Expt. No. 26). In view of the two large contact potential differences involved in this combination, the agreement between the calculated and observed values of (30) can be considered as very satisfactory.

It is to be pointed out with reference to combinations (20) to (30) that they are not strictly independent new equations, and hence it may be argued that they only corroborate the consistency of the various values which have been assigned to the pole potential differences, *a* to *f* and the contact potential differences $q_1 \ldots q_6$, $r_1 \ldots r_6$, and $s_1 \ldots s_6$ from a consideration of combinations (1) to (19), but that they do not in reality establish the validity of these assigned values.

The fact that combinations (20) to (30) are not independent new equations does not of itself prevent the assigned values for the pole potential

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[1] *Z. physik. Chem.*, **53**, 430 (1905).

[2] *Loc. cit.*

[3] *Am. Chem. J.*, 50, 409 (1913).

differences and the contact potential differences from being valid; it simply indicates the possibility of there being another set of values which would be consistent among themselves and at the same time would satisfy all the equations. If future work should show that such a set of values exists it would then be a question as to which set, the new set or the set now derived by the authors, is nearer the truth.

On the other hand, it is obvious that any set of values which is not consistent is not valid. Apropos of this, it has already been pointed out earlier in this article that if in the combinations therein considered, we use as values for contact potential differences the values given by Planck's formula, it leads to results for any given pole potential difference that are not consistent;[1] consequently Planck's formula is not valid, at least for the cases considered in this research. The extent to which the formula is in error is represented by the difference between the respective graphs of Figs. 2 and 3.

Experimental.

Water Bath and Potentiometer.—All the electromotive-force measurements were made at the temperature of 25.0 ± 0.01° by immersing the cells in a water bath controlled by a mercury thermostat. The null method was employed and the voltages determined by means of a Leeds and Northrup potentiometer and a D'Arsonval galvanometer, which latter had a sensitivity of 280 megohms, a period of 2.5 seconds, and a total resistance of 444 ohms. As primary standard of potential difference a Weston standard cell was used which had been calibrated by the U. S. Bureau of Standards, and rechecked by us against another Weston cell.

At the start of the investigation a certain erratic behavior was encountered in the action of the galvanometer. This occurred when the potentiometer was being finally adjusted by means of the revolvable drum to give the precise value of the e. m. f. being measured. At such times the galvanometer reading would suddenly go entirely off the scale, and it seemed as if this action might be caused by leakage currents in the water bath. The real cause, however, was found to be the contact of the operator's fingers with the metallic band on the lower edge of the revolving drum of the potentiometer. After this trouble had been located, it was

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[1] A further illustration of this inconsistency seems advisable at this point. Putting the values from Planck's formula in combinations Nos. (29) and (30), we have, respectively:

$$\text{(29) Hg}\underset{\overset{\text{a}}{\longleftarrow}}{\text{—}}\text{HgCl 1.0 } M \text{ HCl}\underset{\overset{0.0180}{\longrightarrow}}{\text{—}}\text{3.5 } M \text{ KCl}\underset{\overset{0.0061}{\longleftarrow}}{\text{—}}\text{0.1 } M \text{ HCl}\underset{\overset{\text{f}}{\longrightarrow}}{\text{—}}\text{H}_2 \text{ (1 Atmos.) Pt; 0.3363 volt}$$

$$\text{(30) Hg}\underset{\overset{\text{a}}{\longleftarrow}}{\text{—}}\text{HgCl 1.0 } M \text{ HCl}\underset{\overset{0.0532}{\longrightarrow}}{\text{—}}\text{0.1 } M \text{ KCl}\underset{\overset{0.0282}{\longleftarrow}}{\text{—}}\text{0.1 } M \text{ HCl}\underset{\overset{\text{f}}{\longrightarrow}}{\text{—}}\text{H}_2 \text{ (1 Atmos.) Pt; 0.3056 volt}$$

Solving (29) for a, we have; $a = 0.3482 + f$,

Solving (30) for a, we have; $a = 0.3306 + f$,

values for a which are plainly inconsistent.

not encountered again during the investigation and the constancy of the readings at the final adjustment left nothing to be desired.[1]

New Form of Calomel Cell.—After trying several types of calomel cells, the authors devised the form which is shown in Fig. 4 as embodying certain advantages that are lacking in the usual types. These advantages are: the liquid in the cell can be drawn off without disturbing the mercury; fresh liquid can be added without disturbing the electrode; the cell can be immersed in a water bath without affecting the electrical connections. The lower bulb is filled with mercury, and the upper bulb half-filled with calomel, while the rest of the cell is filled with solution to about the level indicated.

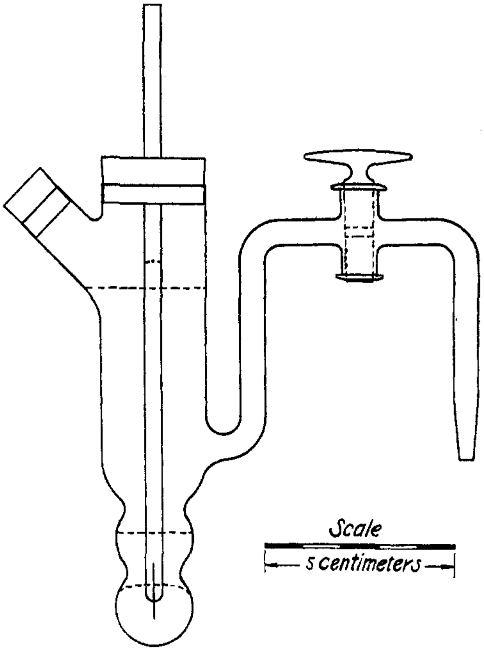

Fig. 4.

Method of Making the Liquid Junctions.—The junctions were made by dipping the ends of the siphon tubes of the component cells into the potassium chloride solution serving as the salt bridge and contained in a small beaker, the cells being so adjusted with reference to the salt bridge that every meniscus was on the same level. To prevent as far as possible the mechanical flow of the one liquid into the other, the ends of the siphon tubes were plugged with wooden tooth-picks or with cones made from sectors of filter paper.

This arrangement stops the mechanical flow but does not stop the diffusion, hence there is a gradual decrease in the value of the contact potential difference with time owing to the mingling of the two liquids.[2] This decrease may amount to a considerable fraction of the value of the contact potential difference involved, so that for combinations having large contact potential differences, the final voltage of the combination

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[1] On the other hand, Lewis, Brighton and Sebastian (THIS JOURNAL, **39**, 2246 (1917)) claim that only an oil bath should be used. Compare also the work of Loomis and Acree (*Am. Chem. J.*, **46**, 593 (1911)) who used an oil bath.

[2] See Lewis, Brighton and Sebastian, *Loc. cit.*, who to overcome this effect make frequent renewals of the liquid junction in a specially designed form of apparatus.

may differ by several millivolts from the initial voltage if much time has elasped in the meanwhile.[1]

The idea occurred to the authors that the diffusion effect might be almost eliminated if instead of using a liquid salt bridge of a given concentration of potassium chloride, there was used a *jelly salt bridge* of agar-agar containing the same concentration of potassium chloride.[2]

The authors accordingly made up an agar-agar salt bridge by dissolving 3 g. of agar-agar in 100 cc. of 0.1 *M* potassium chloride at about 90° and then adjusting the resulting volume to as near 100 cc. as possible after the addition of a few drops of methyl orange. While still warm (40°) the solution was poured into a small U-tube so that about 2 cm. free space remained above the surface of the agar-agar solution. This free space was subsequently filled with 0.1 *M* potassium chloride in one limb of the tube, and 0.1 *M* hydrochloric acid in the other, and the U-tube then used in connection with corresponding calomel cells to study combination (20).

In these measurements of (20), no plugs were used in the ends of the siphon tubes of the calomel cells. The voltages (average) which were observed for combination (20) at 25° are given herewith; these values, while they show quite clearly the slowing down of the diffusion due to the agar-agar, also show that the diffusion still continues, a fact which was further demonstrated by an advancing zone of pink color due to the methyl orange changing color as the hydrochloric acid diffused into the potassium chloride of the agar-agar. If these results are plotted it will be noticed that for the first 40 hours, the decrease in the voltage is a linear function of the time.

Voltage of combination (20) using 0.1 *M* KCl agar-agar salt bridge:

Age of bridge in hours	Start	12	42	66	120
Observed voltages (average)	0.0268	0.0259	0.0242	0.0231	0.0223
± Average deviation	0.0010	0.0012	0.0012	0.0012	0.0018

Hydrogen Electrodes.—Platinum electrodes platinized with platinum black were used; the electrodes were of plate form, 2 cm. long by 1 cm. wide by 0.025 cm. thick. Compressed hydrogen was used, and for purification was passed in succession through an alkaline permanganate solution, an alkaline pyrogallate solution, water, cotton-wool, and then through a solution similar to that contained in the electrode vessel.

Correction for Barometric Pressure.—In using hydrogen electrodes in

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[1] The practice throughout this work has been to record the observed values of the various combinations right after the siphon tubes were dipped into the salt bridge, except in those cases where hydrogen electrodes were used, and for such cases the time of standing in contact is given under the experiment. See in particular Expt. No. 24.

[2] This idea was suggested by the experiment for showing the relative speeds of migration of hydrogen ion, hydroxyl ion, and cupric ion, as described by Noyes and Blanchard, THIS JOURNAL, 22, 726 (1900).

conjunction with calomel cells, it is necessary to apply a correction to the observed voltage of the combination because of the fact that the partial pressure of the hydrogen in the hydrogen cell is (usually) less than one atmosphere, which latter pressure is the standard to which measurements of this kind should be invariably referred. The method of making this correction is best described by quoting the words of Harned:[1]

"To each measurement it is necessary to apply the correction $RT/(2F \ln 1/p)$ for the pressure of the hydrogen, where p equals the pressure of the gas in atmospheres. This is less than the atmospheric pressure by the vapor pressure of the solution. At 25°, the vapor pressure of water is 23.5 mm. This, expressed in atmospheres, subtracted from the barometric pressure, gave the value of p which was used in the above formula. Although the vapor pressure of the solutions in the hydrogen electrode were less than that of water, the error introduced by this substitution was less than the error of experiment."

Making the allowance of 23.5 mm. for the vapor pressure of the solution in the hydrogen electrode and plotting the corrections as a function of the observed barometric pressure, we get the graph given herewith in Fig. 5.

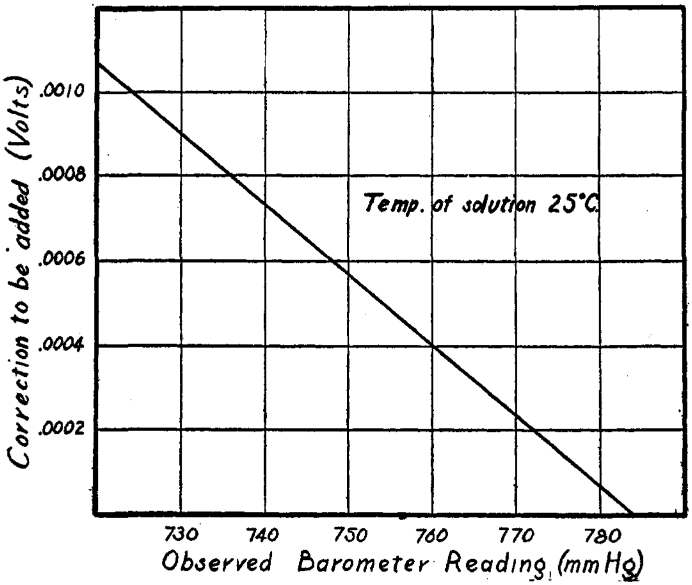

Fig. 5.

Preparation of Materials and Solutions.—The water used in all the work presented in this paper was the ammonia-free portion of the distillate obtained by distilling ordinary distilled water from alkaline perman-

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[1] This Journal, 37, 2465 (1915).

ganate, using a block tin condenser. This water was collected and kept in non-sol bottles which had been thoroughly steamed; it was tested and found to have a concentration of hydrogen ion equal to $10^{-5.8}$ by means of *p*-nitro phenol.[1]

The mercury used in the preparation of the calomel cells was first treated with nitric acid according to the method of Hildebrand,[2] then filtered through a dry towel, then distilled under reduced pressure in a current of air as directed by Hulett.[3]

Three lots of calomel were used: Kahlbaum's, J. T. Baker's, and calomel prepared by the electrolytic process of Ellis.[4] The calomel was put into a 500 cc. non-sol. bottle with about 400 cc. of the appropriate potassium chloride or hydrochloric acid solution to be used in making up the calomel cells, and the calomel and the solution shaken for about two hours in a shaking machine. No difference could be noticed on an average between cells made up with any one of the above lots of calomel.

There were 4 standard solutions employed in making up the various cells used throughout these experiments, namely, 1.0 *M* and 0.1 *M* hydrochloric acid, and 1.0 *M* and 0.1 *M* potassium chloride. The 0.1 *M* hydrochloric acid was prepared by diluting 100 cc. of the 1.0 *M* acid at 20° to 1 liter at 20°. The precise value of the 0.1 *M* acid at 20° was found to be 0.1001 molar by titration against sodium carbonate using methyl orange as the indicator, whence the value of the 1.0 *M* acid at 20° was 1.001 molar.[5] The 1.0 *M* acid was prepared by suitably diluting a stock solution of 6.12 *M* hydrochloric acid which latter itself had been obtained by first diluting a freshly opened lot of conc. hydrochloric acid (J. T. Baker's Analyzed) with about an equal volume of water, distilling, and using the middle portion of the distillate.

The 1.0 *M* potassium chloride was made by weighing out 74.560 g. of the salt and making up to 1 liter at 20°; the 0.1 *M* solution was made by measuring out 100 cc of this 1.0 *M* potassium chloride at 20° and making up to 1 liter at the same temperature. The potassium chloride was prepared by recrystallizing J. T. Baker's Analyzed potassium chloride twice from distilled water and then fusing over a Méker burner. Standard volumetric apparatus was used in all cases and the solutions brought to the proper temperature by immersion in a water bath at 20°.

For the sake of facilitating future comparisons, the specific gravities of the 4 standard solutions were determined for various temperatures by

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[1] See Fales and Nelson, THIS JOURNAL, **37**, 2781 (1915).

[2] THIS JOURNAL, **31**, 933 (1909).

[3] *Z. physik. Chem.*, **33**, 611 (1900).

[4] THIS JOURNAL, **38**, 740 (1916).

[5] In Expts. Nos. 7, 25, and 26 the concentration of the hydrochloric acid used was 1.006 molar. The reason for this is that these particular experiments were performed some time previous to the others.

means of the pycnometer; these values, together with the densities calculated therefrom, and the corresponding molar strengths as calculated from the ratios of the densities, are given herewith:

SPECIFIC GRAVITIES AND DENSITIES OF SOLUTIONS.

(1.0 *M* HCl) 1.022 moles HCl per 1000 g. water.

	15°.	18°.	20°.	25°.	30°.	35°.
Sp. gr. $t°/t°$	1.0202	1.0183	1.0178	1.0177	1.0176	1.0174
Density $t°/4°$	1.0193	1.0169	1.0160	1.0147	1.0132	1.0113
Moles per liter	1.004	1.002	1.001	1.000	0.998	0.996

(0.1 *M* HCl) 0.1003 mole HCl per 1000 g. water.

	15°.	18°.	20°.	25°.	30°.	35°.
Sp. gr. $t°/t°$	1.0041	1.0027	1.0022	1.0019	1.0017	1.0016
Density $t°/4°$	1.0033	1.0013	1.0004	0.9990	0.9974	0.9956
Moles per liter	0.1004	0.1002	0.1001	0.1000	0.0998	0.0996

(1.0 *M* KCl) 1.030 moles KCl per 1000 g. water.

	15°.	18°.	20°.	25°.	30°.	35°.
Sp. gr. $t°/t°$	1.0491	1.0471	1.0463	1.0463	1.0461	1.0456
Density $t°/4°$	1.0482	1.0456	1.0444	1.0432	1.0416	1.0394
Moles per liter	1.004	1.001	1.000	0.999	0.997	0.995

(0.1 *M* KCl) 0.1004 mole KCl per 1000 g. water.

	15°.	18°.	20°.	25°.	30°.	35°.
Sp. gr. $t°/t°$	1.0071	1.0056	1.0050	1.0048	1.0048	1.0048
Density $t°/4°$	1.0062	1.0042	1.0032	1.0018	1.0004	0.9988
Mole per liter	0.1003	0.1001	0.1000	0.0999	0.0997	0.0996

Combinations Measured.—All observations made at the temperature of 25° ± 0.01° and the results expressed in volts. The different kinds of calomel cells used, namely, 1.0 *M* KCl, 0.1 *M* KCl, 1.0 *M* HCl, and 0.1 *M* HCl are, respectively, designated by the capital letters A, B, C and D; the individual cells of each kind are designated by subscripts, thus, A_1, A_2, A_3, etc.

Combination (1).

Expt. No.

1 Hg—HgCl 1.0 *M* KCl—4.1 *M* KCl—1.0 *M* HCl HgCl—Hg. KCl cells used: A_4, A_5, A_6. HCl cells used: C_1, C_2, C_3. Observed voltages:

A_4C_1	0.0082	A_5C_1	0.0080	A_6C_1	0.0080
A_4C_2	0.0086	A_5C_2	0.0084	A_6C_2	0.0086
A_4C_3	0.0086	A_5C_3	0.0083	A_6C_3	0.0083

Average, 0.0083 ± 0.0002.

Combination (2).

2 Hg—HgCl 1.0 *M* KCl—3.5 *M* KCl—1.0 *M* HCl HgCl—Hg. KCl cells used: A_4, A_5, A_6. HCl cells used: C_1, C_2, C_3. Observed voltages:

A_4C_1	0.0116	A_5C_1	0.0113	A_6C_1	0.0115
A_4C_2	0.0118	A_5C_2	0.0117	A_6C_2	0.0120
A_4C_3	0.0112	A_5C_3	0.0110	A_6C_3	0.0111

Average, 0.0114 ± 0.0003.

After making these measurements of (2), the authors tested cell A_5 against cells B_1 and B_2 by means of (17) getting 0.0526 and 0.0527 (theory 0.0524).

Combination (3).

Expt. No.

3 Hg—HgCl 1.0 *M* KCl—2.5 *M* KCl—1.0 *M* HCl HgCl—Hg. KCl cells used: A_7, A_8, A_9. HCl cells used: C_2, C_4, C_5. Observed voltages:

A_7C_2	0.0176	A_8C_2	0.0174	A_9C_2	0.0172
A_7C_4	0.0169	A_8C_4	0.0171	A_9C_4	0.0169
A_7C_5	0.0171	A_8C_5	0.0176	A_9C_5	0.0174

Average, 0.0172 ± 0.0002.

After making these measurements of (3), the authors tested cells A_7, A_8, and A_9 against cell B_8 by means of (17) getting 0.0527, 0.0522 and 0.0524, respectively (theory 0.0524).

Combination (4).

4 Hg—HgCl 1.0 *M* KCl—1.75 *M* KCl—1.0 *M* HCl HgCl—Hg. KCl cells used: A_7, A_8, A_9. HCl cells used: C_2, C_4, C_5. Observed voltages:

A_7C_2	0.0220	A_8C_2	0.0224	A_9C_2	0.0220
A_7C_4	0.0229	A_8C_4	0.0231	A_9C_4	0.0229
A_7C_5	0.0226	A_8C_5	0.0231	A_9C_5	0.0234

Average, 0.0227 ± 0.0004.

Combination (5) and (18).

5 Hg—HgCl 1.0 *M* KCl—1.0 *M* KCl—1.0 *M* HCl HgCl—Hg. KCl cells used: A_7, A_8, A_9. HCl cells used: C_2, C_4, C_5. Observed voltages:

A_7C_2	0.0316	A_8C_2	0.0318	A_9C_2	0.0316
A_7C_4	0.0320	A_8C_4	0.0319	A_9C_4	0.0321
A_7C_5	0.0319	A_8C_5	0.0319	A_9C_5	0.0320

Average, 0.0319 ± 0.0001.

After making these measurements of (5), cells A_7, A_8, and A_9 were tested against B_7 and B_8 by means of (17) giving:

A_7B_7	0.0527	A_7B_8	0.0525
A_8B_7	0.0523	A_8B_8	0.0522
A_9B_7	0.0521	A_9B_8	0.0520

Average, 0.0523 (theory 0.0524).

Combination (6).

6 Hg—HgCl 1.0 *M* KCl—0.1 *M* KCl—1.0 *M* HCl HgCl—Hg. KCl cells used: A_4, A_5, A_6. HCl cells used: C_1, C_2, C_3. Observed voltages:

A_4C_1	0.0665	A_5C_1	0.0670	A_6C_1	0.0668
A_4C_2	0.0672	A_5C_2	0.0673	A_6C_2	0.0670
A_4C_3	0.0667	A_5C_3	0.0668	A_6C_3	0.0666

Average, 0.0669 ± 0.0002.

Cells A_4, A_5, A_6 were tested against B_5 and B_6 by means of combination (17) giving

A_4B_5	..	A_4B_6	0.0525
A_5B_5	0.0524	A_5B_6	0.0522
A_6B_5	..	A_6B_6	0.0526

Average, 0.0524 (theory, 0.0524).

Combination (7).

7 Hg—HgCl 1.0 *M* HCl—1.0 *M* HCl—H_2 (1 Atmos.) Pt. The combination employed by the authors differed slightly from the above; it was Hg—HgCl

1.006 *M* HCl—1.006 *M* HCl—H_2Pt. Bubbling hydrogen was used, the gas being first passed through a sample of the same 1.006 *M* HCl placed in series. Two hydrogen electrodes were used. Barometer, 760 mm. Observed voltages:

Min.	42.	127.	160.	245.	320.	360.
Electrode No. 1	0.27760	0.27800	0.27807	0.27820	0.27835	0.27835
Electrode No. 2	0.27755	0.27795	0.27805	0.27815	0.27835	0.27837

Correcting to exact molarity and 1 Atmos. H_2 we get 0.27835 + 0.0003 + 0.0004 = 0.2791 volt.

Combination (9).

Expt. No.

8 Hg—HgCl 1.0 *M* HCl—4.1 *M* KCl—0.1 *M* HCl HgCl—Hg. 1.0 *M* HCl cells used: C_4, C_5, C_6. 0.1 *M* HCl cells used: D_1, D_2, D_3. Observed voltages:

D_1C_4	0.0597	D_2C_4	0.0594	D_3C_4	0.0596
D_1C_5	0.0604	D_2C_5	0.0606	D_3C_5	0.0604
D_1C_6	0.0600	D_2C_6	0.0596	D_3C_6	0.0599

Average, 0.0600 ± 0.0003.

Combination (10).

9 Hg—HgCl 1.0 *M* KCl—4.1 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_4, D_5, D_6, D_7. Observed voltages:

A_7D_4	0.0522	A_9D_4	0.0522	$A_{10}D_4$	0.0522
A_7D_5	0.0518	A_9D_5	0.0519	$A_{10}D_5$	0.0518
A_7D_6	0.0520	A_9D_6	0.0521	$A_{10}D_6$	0.0520
A_7D_7	0.0520	A_9D_7	0.0521	$A_{10}D_7$	0.0520

Average, 0.0520 ± 0.0001.

Same KCl cells but another set of HCl cells, D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8	0.0521	A_9D_8	0.0522	$A_{10}D_8$	0.0520
A_7D_9	0.0519	A_9D_9	0.0521	$A_{10}D_9$	0.0519
A_7D_{10}	0.0522	A_9D_{10}	0.0524	$A_{10}D_{10}$	0.0522
A_7D_{11}	0.0518	A_9D_{11}	0.0520	$A_{10}D_{11}$	0.0519

Average, 0.0521 ± 0.0001.

Combination (11).

10 Hg—HgCl 1.0 *M* KCl—3.5 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8	0.0514	A_9D_8	0.0516	$A_{10}D_8$	0.0514
A_7D_9	0.0512	A_9D_9	0.0514	$A_{10}D_9$	0.0512
A_7D_{10}	0.0515	A_9D_{10}	0.0517	$A_{10}D_{10}$	0.0515
A_7D_{11}	0.0512	A_9D_{11}	0.0514	$A_{10}D_{11}$	0.0513

Average, 0.0514 ± 0.0001.

Combination (12).

11 Hg—HgCl 1.0 *M* KCl—2.5 *M* KCl 0.1*M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8	0.0497	A_9D_8	0.0498	$A_{10}D_8$	0.0497
A_7D_9	0.0497	A_9D_9	0.0498	$A_{10}D_9$	0.0497
A_7D_{10}	0.0500	A_9D_{10}	0.0501	$A_{10}D_{10}$	0.0500
A_7D_{11}	0.0496	A_9D_{11}	0.0497	$A_{10}D_{11}$	0.0495

Average, 0.0498 ± 0.0001.

Combination (13).

Expt. No.

12 Hg—HgCl 1.0 *M* KCl—1.75 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8....	0.0476	A_9D_8..........	0.0477	$A_{10}D_8$.........	0.0475
A_7D_9....	0.0469	A_9D_9..........	0.0470	$A_{10}D_9$.........	0.0469
A_7D_{10}....	0.0473	A_9D_{10}.........	0.0474	$A_{10}D_{10}$.........	0.0473
A_7D_{11}....	0.0477	A_9D_{11}..........	0.0478	$A_{10}D_{11}$.........	0.0477

Average, 0.0474 ± 0.0003.

Combination (14).

13 Hg—HgCl 1.0 *M* KCl—1.0 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8....	0.0447	A_9D_8..........	0.0447	$A_{10}D_8$.........	0.0446
A_7D_9....	0.0447	A_9D_9............	0.0447	$A_{10}D_9$.........	0.0446
A_7D_{10}....	0.0448	A_9D_{10}.........	0.0448	$A_{10}D_{10}$.........	0.0447
A_7D_{11}....	0.0444	A_9D_{11}..........	0.0444	$A_{10}D_{11}$.........	0.0443

Average, 0.0446 ± 0.0001.

Combination (15).

14 Hg—HgCl 1.0 *M* KCl—0.5 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8....	0.0406	A_9D_8..........	0.0406	$A_{10}D_8$.........	0.0404
A_7D_9....	0.0406	A_9D_9..........	0.0407	$A_{10}D_9$.........	0.0405
A_7D_{10}....	0.0409	A_9D_{10}.........	0.0410	$A_{10}D_{10}$.........	0.0408
A_7D_{11}....	0.0402	A_9D_{11}..........	0.0403	$A_{10}D_{11}$.........	0.0401

Average, 0.0406 ± 0.0002.

Combination (16) also (19).

15 Hg—HgCl 1.0 *M* KCl—0.1 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: A_7, A_9, A_{10}. HCl cells used: D_8, D_9, D_{10}, D_{11}. Observed voltages:

A_7D_8....	0.0252	A_9D_8..........	0.0253	$A_{10}D_8$.........	0.0250
A_7D_9....	0.0256	A_9D_9..........	0.0256	$A_{10}D_9$.........	0.0254
A_7D_{10}....	0.0258	A_9D_{10}.........	0.0259	$A_{10}D_{10}$.........	0.0256
A_7D_{11}....	0.0251	A_9D_{11}..........	0.0252	$A_{10}D_{11}$.........	0.0250

Average, 0.0254 ± 0.0003.

Combination (17).

16 Hg—HgCl 1.0 *M* KCl—0.1 *M* KCl—0.1 *M* KCl HgCl—Hg. 1.0 *M* KCl cells used: A_1, A_2, A_3. 0.1 *M* KCl cells used: B_1, B_2, B_3. Observed voltages:

A_1B_1.....	0.0524	A_2B_1..........	0.0524	A_3B_1..........	0.0522
A_1B_2.....	0.0520	A_2B_2..........	0.0525	A_3B_2..........	0.0521
A_1B_3.....	0.0523	A_2B_3..........	0.0523	A_3B_3..........	0.0529

Average, 0.0524 ± 0.0002.

Another set of measurements with different cells:

A_4B_4.....	0.0525	A_5B_4..........	0.0527	A_6B_4..........	0.0525
A_4B_5.....	0.0523	A_5B_5..........	0.0524	A_6B_5..........	0.0524
A_4B_6.....	0.0523	A_5B_6..........	0.0524	A_6B_6..........	0.0524

Average: 0.0524 ± 0.0001.

Some further measurements with different cells:

A_7B_7.....	0.0525	A_8B_7..........	0.0523	A_9B_7..........	0.0526
A_7B_8.....	0.0525	A_8B_8..........	0.0521	A_9B_8..........	0.0525

Average: 0.0524 ± 0.0001.

See also Experiments Nos. 3, 5, 6, and 22 for further values obtained in regard to combination (17).

Combination (20).

Expt. No.

17 Hg—HgCl 0.1 *M* KCl—0.1 *M* KCl—0.1 *M* HCl HgCl—Hg. KCl cells used: B_{10}, B_{11}, B_{13}. HCl cells used: D_{15}, D_{16}, D_{17}, D_{19}. Observed voltages:

$B_{10}D_{15}$...	0.0270	$B_{11}D_{15}$.........	0.0260	$B_{13}D_{15}$.........	0.0222
$B_{10}D_{16}$...	0.0272	$B_{11}D_{16}$.........	0.0279	$B_{13}D_{16}$.........	0.0265
$B_{10}D_{17}$...	0.0278	$B_{11}D_{17}$.........	0.0279	$B_{13}D_{17}$.........	0.0262
$B_{10}D_{19}$...	0.0268	$B_{11}D_{19}$.........	0.0268	$B_{13}D_{19}$.........	0.0270

Average (excluding B_{13}, B_{15}): 0.0270 ± 0.0005.

Why the value of $B_{13}D_{15}$ should be so far different from the other values, it is not possible to account for. It is to be noticed that the average deviation obtained in the case of (20) is the largest average deviation obtained by the authors in all of the combinations measured by them, Expts. Nos. 1 to 26; in other words, combination (20) does not seem to be reproducible with any degree of precision.

Combination (21).

18 Hg—HgCl 1.0 *M* KCl—4.1 *M* KCl—0.1 *M* HCl—H_2 (1 Atmos.) Pt. KCl cells used: A_7, A_9, A_{11}, A_{12}. Hydrogen electrode used: Nos. 2 and 3. Barometer 760 mm. Observed voltages:

	H-electrode No. 2.			H-electrode No. 3.		
Min.	84.	135.	205.	84.	135.	205.
A_7..................	0.3468	0.3468	0.3469	0.3469	0.3469	0.3469
A_9..................	0.3467	0.3468	0.3468	0.3468	0.3467	0.3467
A_{10}.................	0.3469	0.3470	0.3470	0.3470	0.3469	0.3469
A_{11}.................	..	0.3472	0.3471	..	0.3471	0.3469
A_{12}.................	..	0.3474	0.3470	..	0.3472	0.3469

Average for 135 mins., 0.3470 ± 0.0002; for 205 mins., 0.3469 ± 0.0001.

The constancy of the foregoing values shows that there was very little change, if any, in the value of the contact potential differences during the experiment. Correcting to 1 Atmos. H_2, we get 0.3473 volt as the value of (21).

Combination (22).

19 Hg—HgCl 1.0 *M* KCl—1.0 *M* KCl—0.1 *M* HCl—H_2(1 Atmos.) Pt. KCl cells used: A_7, A_9, A_{11}, A_{12}. Hydrogen electrodes used: Nos. 2 and 3. Barometer 754 mm. Observed voltages:

	H-electrode No. 2.			H-electrode No. 3.		
Min.	35.	65.	110.	35.	65.	110.
A_7..................	0.3538	0.3544	0.3546	0.3545	0.3545	0.3545
A_9..................	..	..	0.3545	..	..	0.3545
A_{10}.................	..	..	0.3546	..	..	0.3545
A_{11}.................	..	..	0.3547	..	..	0.3546
A_{12}.................	..	..	0.3546	..	..	0.3546

Average after 110 min., 0.3546 ± 0.0001.

Correcting to 1 Atmos. H_2, we get 0.3550 volt as the value of (22).

Combination (23).

20 Hg—HgCl 1.0 *M* KCl—0.1 *M* KCl—0.1 *M* HCl—H_2 (1Atmos.) Pt. KCl cells used: A_7, A_9, A_{10}, A_{11}, A_{12}. Hydrogen electrodes used: Nos. 2 and 3. Barometer 754 mm. Observed voltages:

	H-electrode No. 2.			H-electrode No. 3.		
Min.	40.	65.	98.	40.	65.	98.
A_7	0.3798	0.3729	0.3730	0.3798	0.3768	0.3732
A_9	..	..	0.3729	..	..	0.3731
A_{10}	..	..	0.3730	..	..	0.3731
A_{11}	..	..	0.3731	..	..	0.3732
A_{12}	..	..	0.3730	..	..	0.3731

Average for 98 min., 0.3731 ± 0.0001.

Correcting to 1 Atmos. H_2, we get 0.3735 volt as the value of (23).

Combination (25).

Expt. No.

21 Hg—HgCl 0.1 *M* KCl—3.5 *M* KCl—1.0 *M* HCl—H_2 (1 Atmos.) Pt. Only one KCl cell used; this was tested, however, by means of combination (27) giving a voltage (corrected to 1 Atmos. H_2) of 0.3998 (theory 0.3996). Hydrogen electrodes saturated with hydrogen before beginning of experiment. Barometer 758 mm. Observed voltages:

Min.	12.	32.	36.	40.
Electrode No. 1	0.3412	0.3425	0.3423	0.3423
Electrode No. 2	0.3416	0.3423	0.3422	0.3421

Average of last three sets of observations: 0.3423 ± 0.0001.

Correcting to 1 Atmos. H_2, we get 0.3427 as the value of (25).

Combination (26).

22 Hg—HgCl 0.1 *M* KCl—0.1 *M* KCl—1.0 *M* HCl—H_2(1 Atmos.) Pt. Same KCl cell used as in Expt. No. 21. Barometer 760 mm. Observed voltages:

Min.	60.	66.	74.	81.
Electrode No. 1	0.3965	0.3967	0.3967	0.3967
Electrode No. 2	0.3972	0.3974	0.3974	0.3974

Average of last three sets of observations: 0.3971 ± 0.0003.

Correcting to 1 Atmos. H_2, we get 0.3975 as the value of (26).

Combination (27).

23 Hg—HgCl 0.1 *M* KCl—4.1 *M* KCl—0.1 *M* HCl—H_2(1 Atmos.) Pt. KCl cells used: B_9, B_{12}, B_{13}. Hydrogen electrodes used: Nos. 1 and 2. Barometer 757 mm. Observed voltages:

	H-electrode No. 1.			H-electrode No. 2.		
Min.	80.	115.	152.	80.	115.	152.
B_9	0.3989	0.3988	0.3990	0.3988	0.3992	0.3990
B_{12}	0.3992	0.3990	0.3991	0.3993	0.3995	0.3989
B_{13}	0.3992	0.3989	0.3991	0.3990	0.3993	0.3987

Average of all observations, 0.3991 ± 0.0002.

Correcting to 1 Atmos. H_2, we get 0.3995 volt as the value of (27). After making these measurements, cells B_9, B_{12}, B_{13} were tested against 1.0 *M* KCl cells A_{13}, A_{14}, A_{16}, by means of combination (17) giving:

$A_{13}B_9$	0.0525	$A_{14}B_9$	0.0524	$A_{16}B_9$	0.0522
$A_{13}B_{12}$	0.0525	$A_{14}B_{12}$	0.0524	$A_{16}B_{12}$	0.0521
$A_{13}B_{13}$	0.0525	$A_{14}B_{13}$	0.0526	$A_{16}B_{13}$	0.0523

Average: 0.0524 ± 0.0001 (theory 0.0524).

Combination (28).

24 Hg—HgCl 0.1 *M* KCl—0.1 *M* KCl—0.1 *M* HCl—H_2(1 Atmos.) Pt. This experiment was run immediately after testing cells B_9, B_{12}, B_{13} in connection

with Expt. No. 23. Cell B_9 was used and hydrogen electrodes Nos. 1 and 2. Cells B_{12} and B_{13} were not used because the results with B_9 showed that it was not possible to get a constant value for combination (28). Barometer 757 mm. Observed voltages:

Min.	5.	15.	27.	43.	59.
Electrode No. 1	0.4268	0.4258	0.4258	0.4256	0.4254
Electrode No. 2	0.4268	0.4251	0.4251	0.4251	0.4249

Correcting to 1 Atmos. H_2 we get for combination (28) values ranging from 0.4272 to 0.4257 volt.

Combination (29).

Expt. No.

25 Hg—HgCl 1.006 *M* HCl—3.5 *M* KCl—0.1 *M* HCl—H_2 (1 Atmos.) Pt. Same 1.006 *M* HCl used as in Expt. No. 7. Hydrogen electrodes used: Nos. 1 and 2. Barometer 760 mm. Observed voltages:

Min.	58.	78.	100.
Electrode No. 1	0.3359	0.3362	0.3362
Electrode No. 2	0.3354	0.3357	0.3355

Average of all observations: 0.3358 ± 0.0003.

Correcting to exact molarity and 1 Atmos. H_2 we get, $0.3358 + 0.0002 + 0.0004 = 0.3364$ volt as the value of (29).

Combination (30).

26 Hg—HgCl 1.006 *M* HCl—0.1 *M* KCl—0.1 *M* HCl—H_2 (1 Atmos.) Pt. Same 1.006 *M* HCl used as in Expt. No. 25. Hydrogen electrodes used: Nos. 1 and 2. Barometer 760 mm. Observed voltages:

Min.	8.	70.	150.	196.	228.
Electrode No. 1	0.3002	0.3041	0.3047	0.3048	0.3047
Electrode No. 2	0.3002	0.3042	0.3050	0.3052	0.3047

Average of last three sets of observations: 0.3049 ± 0.0002.

Correcting to exact molarity and 1 Atmos. H_2, we get $0.3049 + 0.0002 + 0.0004 = 0.3056$ as the value of (30).

Summary.

Planck's formula for the contact potential difference between solutions has been shown to be invalid for the liquid junctions xM KCl — 1.0 *M* HCl and xM KCl — 0.1 *M* HCl, where x ranges from 0.1 to 4.1, and the temperature is 25°.

There is no contact potential difference at 25° between a saturated solution of potassium chloride (4.1 *M*) and hydrochloric acid solutions ranging in concentrations from 0.1 molar to 1.0 molar.

In an electromotive-force combination having a contact potential difference as one of its component electromotive forces, the diffusion across the liquid junction of the one liquid into the other brings about a decrease in the magnitude of the contact potential difference, and this decrease may amount to as much as one-tenth of the initial magnitude of the contact potential difference. For this reason combinations having only very small or zero contact potential differences should be used for precise e. m. f. measurements.

The values of certain important pole potential differences have been ascertained for the temperature of 25° with a precision probably reliable to ±0.0002 volt. These values are:

	Volt.		Volt.
Hg—HgCl 1.0 *M* KCl.........	0.5648	Hg—HgCl 0.1 *M* KCl.........	0.6168
Hg—HgCl 1.0 *M* HCl.........	0.5567	Hg—HgCl 0.1 *M* HCl.........	0.6168
PtH$_2$(1 Atmos.)—1.0 *M* HCl...	0.2777	PtH$_2$(1 Atmos.)—0.1 *M* HCl....	0.2179

NEW YORK, N. Y.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE RATIO OF MESOTHORIUM TO THORIUM.

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Received June 6, 1918.

The thorium series comprises the following substances: Th, Ms$_1$, Ms$_2$, Rt, ThX, Em, A, B, C, D. The first product of thorium called mesothorium-one, Ms$_1$, or simply mesothorium, has a period of 5.5 years and is rayless; it produces mesothorium-two, Ms$_2$, which has a period of 6.14 hours and gives intense beta and gamma rays. Pure Ms$_1$, after an interval of about 3 days, contains the maximum amount of Ms$_2$. The γ-ray activity of mesothorium is, therefore, due to Ms$_2$. Since mesothorium has never been obtained pure, its amount, in a given case, is only determinable by its activity. One milligram of mesothorium is, by convention, a quantity of Ms$_1$ containing the equilibrium amount of Ms$_2$, which has a γ-ray activity equal to that of one mg. of radium, containing the equilibrium amounts of its short-lived products.

The activities of pure thorium compounds and minerals have been studied by Boltwood,[1] McCoy and Ross,[2] Dadourian,[3] and McCoy and Viol,[4] and others. As a result, it has been definitely shown that the α-ray activity of a mineral is proportional to its thorium content, correction being made for any radium and uranium present. This proves that there exists a constant ratio of Ms to Th. The object of the work here reported was the determination of this ratio. In anticipation, it may be stated that we found that "one milligram of mesothorium" is in equilibrium with 19.0×10^6 mg. of thorium in minerals. In other words, one g. of thorium contains 0.524×10^{-6} milligrams of mesothorium, a "milligram of mesothorium" being defined as above.

In the uranium series, it was early shown by Boltwood,[5] McCoy,[6]

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[1] *Am. J. Sci.*, **21**, 409 (1906).

[2] *Ibid.*, **21**, 433 (1906); THIS JOURNAL, **29**, 1709 (1907).

[3] *Am. J. Sci.*, **21**, 427 (1906).

[4] *Phil. Mag.*, **25**, 333 (1913).

[5] *Nature*, **70**, 80 (1904); *Phil. Mag.*, **9**, 599 (1905).

[6] *Ber.*, **37**, 2641 (1904); THIS JOURNAL, **27**, 391 (1905).