THE CHEMICAL POTENTIAL OF THE METALS.

By Wilder D. Bancroft.

IN a previous paper[1] I have communicated the numerical values of the electromotive force of certain cells, consisting of two metals and a single solution. It is now desirable to consider the relation between these single-liquid polarizable cells and the corresponding constant reversible cells of the Daniell type. According to the theory of Nernst, the potential difference between a metal and a solution of a salt of that metal is given by the expression[2]

$$\pi = \frac{RT}{ne} \log \frac{P}{p} \times 10^{-4} \text{ volts},$$

where π is the potential difference, n the valency of the kation, p its partial osmotic pressure, e the quantity of electricity transported by a gram-equivalent, and P the solution pressure of the electrode metal. The electromotive force of a cell of the Daniell type $M_1 | p_1 M_1 X | p_2 M_2 X | M_2$ will be the algebraic sum of the two potential differences between the metals and the solutions, plus the difference of potential between the solutions. I leave out of account a possible potential difference between the metals, as this term is negligible so far as our present knowledge goes. The electromotive force of this type of cell will be

$$\pi = \frac{RT}{ne}\left(\log \frac{PM_1}{PM_2} + \log \frac{p_2}{p_1}\right) \times 10^{-4} + z \text{ volts},$$

where z represents the difference of potential between the solutions, and the valency of the metals M_1 and M_2 is the same. If the wandering velocities of the ions M_1 and M_2 are nearly equal,

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[1] Zeitschr. f. ph. Chem., 12, 289, 1893. Through a misprint on p. 290, the correction for Pb|Hg in NaI, and Bi|Hg in NaCl, reads 0.25 and 0.75 volts, instead of 0.025 and 0.075 volts respectively.

[2] Ibid., 4, 148, 1889.

and p_1 and p_2 be made so, the value of z approaches zero, while the term $\log \frac{p_2}{p_1}$ drops out entirely. The electromotive force of the cell, $M_1 | pM_1X | pM_2X | M_2$, is given very nearly by the expression

$$\pi = \frac{RT}{ne} \log \frac{PM_1}{PM_2} \times 10^{-4} \text{ volts},$$

and is independent of the absolute concentration of the salts M_1X and M_2X. Let us take as a concrete case the cell $Zn|ZnSO_4|CuSO_4|Cu$, and let the concentrations of the zinc and copper sulfates always be equal. It has been found experimentally that the electromotive force of this cell is independent of the absolute concentration.[1] Suppose that instead of diluting the two solutions with pure water, we add a solution of K_2SO_4. According to Nernst's theory, this will have no influence on the electromotive force, except in so far as it affects the dissociation of the two sulfates, and thereby the concentrations of the Zn and Cu ions. If the dilution be carried far enough, we shall come at last, without change of electromotive force, to the cell with neither zinc nor copper sulfate, to the cell $Zn|0\,ZnSO_4 + x\,K_2SO_4|0\,CuSO_4 + x\,K_2SO_4|Cu$, which is the same as the cell $Zn|x\,K_2SO_4|Cu$. In other words, the one-liquid, non-reversible cells are the limiting cases of the two-liquid, reversible cells in which the concentrations and wandering velocities of the reversible ions are equal, the dissociation being assumed to be complete. This last clause is necessary; for if the percentage dissociations of the zinc sulfate and copper sulfate were different, equal concentrations of the two sulfates would not correspond to equal concentrations of zinc and copper ions, and this would affect the potential difference between the solutions. The concentration of the K_2SO_4 should have no effect, and it was shown in my previous paper[2] that this was the case. It is clear that in measurements made with two-liquid, reversible cells, there are two sources of error besides those due to the surface conditions of the electrodes. These are differences of concentration and differences of wandering velocities.

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[1] Wright, Phil. Mag. (5), 13, 265, 1882.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Tables II., V.

The effects of these two errors are that the terms $\log \frac{p_2}{p_1}$ and z do not disappear. The determinations made with single-liquid cells are free from these sources of error; but the difficulties due to polarization are so great that the variations are apt to be much larger than in measurements made with two-liquid, reversible cells. In Table I. are some of the results obtained with the two styles of cells. In the first four columns are the measurements of Paschen,[1] myself, Overbeck and Edler,[2] Ostwald,[3] all made with single-liquid cells. In the next three are the figures of Wright and Thompson,[4] Neumann,[5] Braun,[6] with reversible cells. In the eighth are the data of Magnanini,[7] and in the ninth those of Regnauld,[8] the former being for polarizable, the latter for non-polarizable cells.

TABLE I.[9]

Electrodes.	Electrolyte.	Paschen.	W. D. B.	O. & E.	Ostwald.	W. & T.	Neumann.	Braun.	Magnanini.	$D = 100$. Regnauld.
ZnCd	Chlorides	0.296	0.333	0.368	0.360	0.330	0.329	0.334	0.32	0.235
ZnCd	Bromides	0.293	0.333	0.364	0.340	0.315	—	0.256	0.30	0.235
ZnCd	Iodides	0.298	0.331	0.365	0.304	0.322	—	0.262	0.20	0.235
ZnCd	Sulfates	0.35	0.334	0.430	0.401	0.360	0.362	0.33–37	0.36	0.307
ZnCd	Nitrates	—	0.332	0.446	0.411	0.352	0.352	0.27–37	0.38	0.235
ZnCd	Acetates	—	0.332	—	0.373	—	—	0.336	—	—
ZnPb	Chlorides	0.512	0.526	0.561	0.610	* 0.591	* 0.598	—	0.51	—
ZnPb	Bromides	0.525	0.528	0.541	0.599	0.571	—	—	0.45	—
ZnPb	Iodides	0.545	[1]0.527	0.558	0.587	0.455	—	—	0.38	—
ZnPb	Sulfates	0.525	0.527	0.502	0.592	* 0.50–55	—	—	0.51	—
ZnPb	Nitrates	—	0.526	0.589	0.598	0.585	0.589	0.44	0.51	—
ZnPb	Acetates	—	[1]0.527	—	0.638	0.607	0.601	0.54–58	—	—
CdPb	Chlorides	0.216	0.195	0.192	0.249	* 0.260	* 0.269	—	—	—
CdPb	Bromides	0.232	0.194	0.181	0.259	0.256	—	—	—	—
CdPb	Iodides	0.247	[1]0.194	0.188	0.256	0.24	—	—	—	—
CdPb	Sulfates	0.18	0.194	0.17	0.191	* 0.13–17	—	0.18–22	—	—
CdPb	Nitrates	—	0.193	0.243	0.187	0.233	0.237	0.240	—	—
CdPb	Acetates	—	[1]0.194	—	0.265	—	—	—	—	—

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[1] Wied. Ann., 43, 590, 1891.

[2] Ibid., 42, 209, 1891.

[3] Zeitschr. f. ph. Chem., 1, 583, 1887.

[4] Phil. Mag. (5), 19, 1, 1885.

[5] Zeitschr. f. ph. Chem., 14, 193, 1894.

[6] Wied. Ann., 16, 575, 1882.

[7] Rend. Acc. Linc., 6, 182, 1890.

[8] Wiedemann Electrizität (2. Aufl.), 1, 792.

[9] Values marked [1] are calculated from the other experiments and are not direct observations.

The agreement is not so striking as one might wish; but it is sufficient. The values marked with a star are not properly comparable, because the two solutions were not of the same concentration. Nernst's formula for the cells we have been discussing is

$$\pi = \frac{R\tau}{n\epsilon} \log \frac{Pm_1}{Pm_2} \times 10^{-4} \text{ volts.}$$

It is, therefore, necessary to consider the nature of $\log P$. Nernst has not made any direct statement, so far as I know, about a possible connection between $\log P$ and the negative ion of the salt solution. Ostwald[1] and his pupils look upon $\log P$ as a function of the electrode metal and the temperature only, and hold that it is independent of the nature of the negative ion. If this be so, we ought to find that all cells of the type $M_1|pM_1X|pM_2X|M_2$, should have the same value so long as M_1 and M_2 remained the same and that a change in X should have no effect, barring secondary disturbances such as differences of wandering velocities, of dissociation, etc. In the non-reversible cells $M_1|RX|M_2$, where these disturbing influences are eliminated, this should be even more noticeably true. That this is the case for certain metals, I have already shown.[2] The results of other investigators, as given in Table I., show this same thing, though not quite so clearly. The values for Zn|Cd in solutions of chlorides, bromides, and iodides are found to be identical by Paschen, by Overbeck and Edler, and by Regnauld, though the three sets differ hopelessly in absolute value. Braun makes the bromides and iodides the same, and puts the chlorides, sulfates, and nitrates in a group together.

There is not the same agreement among the reversible cells in which Pb forms one of the electrodes; but this is due in part to the insolubility of the lead salts. With the polarizable cells things are much clearer, though the discrepancies between the values found by different observers complicates matters very much. Ostwald finds practically the same value for Zn|Pb in all solutions except acetates. Paschen makes the bromides and sulfates the same, while Overbeck and Edler find the chlorides and iodides

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[1] Lehrbuch, II., 855.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Table III.

identical. On the whole we may say that the theory of Nernst has predicted the facts with great accuracy thus far. If, however, the single-liquid cells are the limiting cases of the two-solution reversible cells, and if $\log P$ is a function of the electrodes and temperature only, the electromotive force should always be independent of the nature of the negative ion of the salt solution. That this is not so will be seen from Table II.

TABLE II.

Electrodes.	Electrolytes.	Paschen.	W. D. B.	O. & E.	Ostwald.	W. & T.
ZnHg	Chlorides	1.112	1.151	1.121	1.173	1.12–26
ZnHg	Bromides	0.983	0.991	0.996	1.036	0.972
ZnHg	Iodides	0.846	0.847	0.830	0.841	0.801
ZnHg	Sulfates	1.300	1.302	1.302	1.484	1.46–51
ZnHg	Nitrates	—	1.200	1.330	1.422	1.499
ZnHg	Acetates	—	1.228	—	1.451	—
CdHg	Chlorides	0.816	0.818	0.755	0.813	0.812
CdHg	Bromides	0.690	0.659	0.632	0.696	—
CdHg	Iodides	0.548	0.515	0.465	0.535	—
CdHg	Sulfates	0.968	0.969	0.962	1.083	—
CdHg	Nitrates	—	0.867	0.884	1.011	—
CdHg	Acetates	—	0.898	—	1.078	—

The variation in passing from a chloride to an iodide solution is about 0.3 volts, far more than can be accounted for by any experimental error. This necessitates a reconsideration of the Nernst hypothesis to see where the flaw in the reasoning occurs. The assumption made is that, if a metal be dipped into a solution of one of its salts, the metal will go into solution, and the electrode become charged negatively towards the electrolyte, if the "solution pressure" of the metal is greater than the osmotic pressure of the corresponding ion in the solution. If the latter is greater than the "solution pressure," ions will be precipitated upon the metal which would become positive to the solution. This reasoning is applicable to zinc in a solution of potassium chloride, for instance. The initial concentration of the zinc ions in the solution is zero, and the metal will therefore send off ions until the potential difference corresponding to equilibrium is reached. This will not be the case when we consider mercury in a solution of potassium chloride. There are no mercury ions in solution to precipitate on the metal, and it remains an unanswered problem how the mercury is to become charged positively in respect to the solution. Yet this takes place and the value of the potential difference, as determined by the dropping-mercury electrode method, is a perfectly well defined one. This value should be independent of the nature of the salt solution if Ostwald's assumption about log P is correct. This is not the case. In this connection I may say that the question as to the value of the dropping-mercury electrode as a means of measuring single potential differences does not affect this discussion at all. It is an experimental fact that the sum of the potential differences $M_1|RX$ and $RX|M_2$, as determined by this method is equal to the electromotive force of the cell $M_1|RX|M_2$ and it is immaterial for the present purposes whether the single determinations are wrong by a constant amount, as I am only considering variations in the values. I will now try to show what conclusions may be drawn from the measurements of Paschen[1] on the potential differences between metals and salt solutions not containing the metal of the electrode as ion. He points out himself that the potential difference is not a function of the positive ion of the salt solution. It is not a function of the concentration. Paschen inclines to the opposite view; but I think he is wrong and that his own results as tabulated in Table III. will bear me out. The first column gives the nature and concentration of the solution; the second, third, and fourth the potential differences between the metals, mercury, zinc, and cadmium, and the solution. Mercury is positive towards the solution, zinc and cadmium negative.

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[1] Wied. Ann., 43, 590, 1891.

TABLE III.

Solution.	Sol|Hg	Zn|Sol	Cd|Sol	Solution.	Sol|Hg	Zn|Sol	Cd Sol
HCl = 1 l.	0.560	0.560	0.248	H_2SO_4 = 200 l.	0.825	0.668	0.261
= 10	0.551	0.610	0.272	HBr = 0.272	0.503	0.393	0.175
= 100	0.584	0.643	0.242	= 0.983	0.490	0.423	0.202
KCl = 0.28	0.524	0.525	0.260	= 10	0.493	0.567	0.238
= 1	0.539	0.547	0.249	= 100	0.496	0.610	0.246
= 10	0.553	0.575	0.251	KBr = 0.402	0.474	0.399	0.203
= 100	0.584	0.523	0.240	= 1	0.483	0.441	0.186
NaCl = 0.239	0.562	0.521	0.262	= 10	0.493	0.422	0.167
= 1	0.556	0.512	0.266	= 100	0.505	0.496	0.183
= 10	0.557	0.541	0.268	HI = 10	0.411	0.427	0.117
= 100	0.590	0.557	0.268	= 100	0.417	0.515	0.159
$MgCl_2$ = 0.971	0.546	0.525	0.252	= 1000	0.386	0.584	0.214
= 2	0.547	0.531	0.277	KI = 0.795	0.400	0.250	0.113
= 20	0.548	0.598	0.258	= 1	0.400	0.233	0.113
= 200	0.580	0.516	0.245	= 10	0.412	0.308	0.110
$BaCl_2$ = 0.809	0.562	0.512	0.259	= 100	0.412	0.369	0.120
= 2	0.555	0.554	0.249	= 1000	0.386	0.454	0.199
= 20	0.553	0.583	0.281	K_2SO_4 = 2.152	0.700	0.618	0.287
= 200	0.586	0.566	0.240	= 20	0.720	0.573	0.274
H_2SO_4 = 2	0.835	0.653	0.319	= 200	0.730	0.592	0.252
= 20	0.817	0.668	0.284				

The values for Sol\|Hg are identical for dilutions of 1 l. and 10 l. with the exception of KCl, KBr, K_2SO_4, and H_2SO_4; the variations for K_2SO_4 and H_2SO_4 are in opposite directions and certainly due to experimental error. There is no reason to assume that KCl is different in behavior, theoretically, from NaCl or $BaCl_2$, and we must conclude that this discrepancy is also accidental. In passing from dilutions of 10 l. to those of 100 l. there is a distinct increase in potential difference between mercury and chloride solutions. With the other solutions the change is either non-existent or much less marked. On the other hand, cadmium shows this behavior only with HI and KI solutions, zinc with HCl, NaCl, HBr, KBr, HI, and KI solutions. The solutions of HBr, KBr, HI, and KI are not the ones where mercury shows a marked change of value with increasing dilution, so that there is no qualitative regularity in the phenomena. As there is also no quantitative connection to be detected between the change of concentration and the change of potential difference, and as the experimental error is very large in the case of determinations with dilute solutions, I see no reason to assume that there is any change of potential difference, at any rate within wide ranges of concentration.[1] I am led to this conclusion the more strongly because, if we admit with Paschen that the potential difference increases with increasing dilution, we must admit that the electromotive force of the cell Cd|KCl|Hg is a function of the concentration, and I have already shown that this is not the case.[2]

Paschen has pointed out that these potential differences are functions of the metal forming the electrode and of the anion. This can hardly be accounted for on the Ostwald-Nernst hypothesis. If the potential difference between Hg and KCl or KBr solutions are due to the amount of mercury as ion which has gone into solution, we must say that the amount varies as we change from KCl to KBr, or, in other words, that the negative ion has an effect. This is quite apart from the difficulty of accounting for the sign of the potential difference. I do not see that the relative solubilities of mercurous chloride and bromide can be used to help out matters, because we do not have a saturated solution at all, and the difference in the electromotive forces is more likely to be connected with the difference of solubility as cause than as effect.

There are no experimental data, so far as I know, on potential differences at the contact surface of reversible electrodes except some measurements by Neumann,[3] and these do not establish the point they were intended to prove owing to an unfortunate choice of solutions. He measured the potential difference between thallium and solutions of thallium salts. Most of the salts were salts of organic acids, and Ostwald[4] had already found that when

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[1] This will not hold true till the concentration of the salt becomes zero; else we should get in all cases the same potential difference, that of the metal against pure water, which is not true. There will certainly be a minimum concentration beyond which the dissolved substance will not have the properties of matter in mass, and the potential difference will then be a function of the concentration.

[2] Zeitschr f. ph. Chem., 12, 295, 1893, Table V.

[3] Ibid., 14, 225, 1894.

[4] Ibid., 1, 605, 1887,

the negative ion was an organic radical its nature was immaterial. To settle this question one should take negative ions which show marked differences with non-reversible electrodes, such as chlorides, bromides, and iodides. As the negative ion has a very marked influence in these last-named cases, and as there is no reason to suppose that the haloid salts form a class by themselves, the simplest assumption is that the negative ion always has an effect, and that in the cases in which this does not appear, such as the organic radicals, we are measuring something else which is the same in all the cases. Le Blanc[1] found something similar in his studies on polarization, where, beyond a certain point, he obtained the value for the primary decomposition of water.

There are certain quantitative relations connected with the change of the negative ion which deserve to be brought out, and in Table IV. are given the most probable values for the potential differences of the metals Hg, Zn, and Cd in solutions of chlorides, bromides, and iodides; while in Table V. are the corresponding

TABLE IV.

Solution.	Zn|Sol	Cd|Sol	Sol|Hg
Chlorides	0.589	0.255	0.562
Bromides	0.507	0.174	0.483
Iodides	0.436	0.104	0.410

TABLE V.

Solution.	Zn|Sol|Hg	Cd|Sol|Hg
Chlorides	1.151	0.817
Bromides	0.990	0.657
Iodides	0.846	0.514
Sulfates	1.302	0.969

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[1] Zeitschr. f. ph. Chem., 8, 315, 1891.

values for the single-liquid non-reversible cells with Zn and Hg, Cd and Hg as electrodes.[1]

We notice that the numerical change in passing from a chloride to a bromide or iodide solution is the same for these three metals and that the sign is the same for zinc and cadmium as is shown in Table VI. This enables us to formulate matters a little more clearly. The potential difference between a metal and a salt solution is the sum of two terms, one due to the metal and the solvent, the other to the negative ion. For certain metals in certain solutions, the term due to the negative ion is independent, numerically, of the nature of the metal considered. For instance, the potential difference Zn|KCl, Zn|KBr, Cd|KCl, Cd|KBr, Hg|KCl, and Hg|KBr will be $A+a$, $A+b$, $B+a$, $B+b$, $C-a$, and $C-b$. The electromotive forces of the cells Zn|KCl|Cd and Zn|KBr|Cd will be $E_1=A+a-B-a$ and $E_2=A+b-B-b$, whence we see that $E_1=E_2$, which had already been found experimentally. For Zn|KCl|Hg and Zn|KBr|Hg we shall have $E_1=A+a-C+a$ and $E_2=A+b-C+b$, and E_1 will not be equal to E_2. By means of the data in my first paper on this subject,[2] we can now extend our generalization and make it more precise. With the metals, Mg, Zn, Cd, Sn, Pb, and Bi in solutions of chlorides, bromides, iodides, sulfates, nitrates, acetates, carbonates, and oxalates, the term due to the negative ion is not a function of the electrode. There is not much doubt but that the alkaline metals, the metals of the alkaline earths, and the metals of the iron group belong in this

TABLE VI.

Solution.	Zn	Cd	Hg
KCl−KBr	0.082	0.081	−0.079
KBr−KI	0.071	0.070	−0.073
KCl−KI.	0.153	0.150	−0.152

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[1] There is certainly an error in the relative positions of Sn and Pb as shown by my determinations, and I do not therefore give any data for them in Table V.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Table III.

series. Oswald's measurements show that most organic acids may be added to the above list of solutions. With mercury the numerical value of the term due to the negative ion is the same as with the previous metals, but the sign is opposite. With platinum the numerical value is no longer the same. In which of these three groups copper, silver, gold, and the other metals belong I cannot say, though silver is probably like mercury. The results in Tables IV.–VI. open up a whole series of problems to be settled by future investigators. The values for the differences of the terms for any two negative ions have to be determined with accuracy; the behavior of the metals Cu, Ag, etc., must be examined. The work of Magnanini[1] shows that other relations hold when the dissolved salt is an oxidizing or reducing agent, and that the value Zn|RX|Cd, for instance, is independent of the metals only when RX is not an oxidizing agent. It is also well known that in cases where the electrode metal cannot exist in the solution as ion, the general relations already pointed out do not hold. From the results of Negbaur[2] and of Jones[3] we must conclude that the term which I have represented by *A*, *B*, *C*, etc., varies with the nature of the solvent. The amount of this variation is entirely unknown as yet, and it is equally impossible to say beforehand how a change in the solvent will affect the term due to the negative ion.

If we consider the cell $Zn|ZnCl_2|ZnBr_2|Zn$, the two solutions being assumed to be of the same concentration and dissociation and the wandering velocity of the bromine ion being further assumed to be identical with that of the chlorine ion, we should expect an electromotive force of 0.080 volts. This has not been taken into account by Goodwin[4] in his determinations of the solubilities of silver chloride, bromide, and iodide. Goodwin determined the electromotive force of the cells

$$Ag|AgNO_3|AgCl + KCl|Ag,\ Ag|AgNO_3|AgBr + KBr|Ag,\ Ag|AgNO_3|AgI + KI|Ag.$$

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[1] Rend. Acc. Linc., 6, 182, 1890.

[2] Wied. Ann., 47, 27, 1892.

[3] Zeitschr. f. ph. Chem., 14, 346, 1894.

[4] Ibid., 13, 645, 1894. It is only fair to Mr. Goodwin and to myself to say that I have pointed out to him privately the objections I made to his results in order that he might correct them himself if he felt so inclined. He thinks, however, that it would be better for me to make my comments in print, and I have accordingly done so.

From the observed electromotive forces the solubilities were calculated by the formula $S = \sqrt{\frac{p_1 p_2}{\phi}}$, where $\log \phi = \frac{E}{C}$. In this equation s is the solubility, p_1 the concentration of the Ag ions in the nitrate solutions, p_2 the concentration of the Cl, Br, or I ions in the corresponding solutions, E is the electromotive force of the cells, and C the integration constant which is equal at 25° to 0.0256. It is more than probable that a correction should be applied for a possible difference of $\log P$ in nitrate and chloride solutions, but as this value is not accurately determined, I will first calculate the solubilities on the assumption that $\log P_{NO_3} = \log P_{Cl}$.[1] We find from Table VI. $\log P_{Cl} - \log P_{Br} = 0.080$ and $\log P_{Cl} - \log P_I = 0.152$ volts. These values are to be subtracted from the electromotive forces observed in the cells with AgBr and AgI, in order to get the term E called for by the formula. In Tables VII.–IX. I give the results of these calculations. In the first column are the values for p_1; in the second those for p_2; in the third the observed electromotive forces; in the fourth the solubilities as calculated by Goodwin; in the fifth the solubilities as calculated by myself under the assumption that $\log P_{NO_3} = \log P_{Cl}$; and in the sixth the values if one assumes further that $\log P_{NO_3} - \log P_{Cl} = 0.03$ volts. I also give the solubilities found by Kohlrausch and Rose,[2] and by Holleman[3] with the conductivity method.

It will be seen that the second column of solubilities agrees much better with the results obtained by other investigators than the solubilities calculated by Goodwin. The solubilities in the last column do not show so good an agreement; but I do not feel sure that this proves that the formula by which they are calculated is wrong. It seems to me quite as probable that these figures represent the actual solubilities in the cells examined by Goodwin, but not the real solubilities of AgCl, AgBr, AgI. The solubilities of AgCl and AgBr are much changed by contin-

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[1] I use the term $\log P_{Cl}$ to denote the value of $\log P$ for a given metal when in a chloride solution. $\log P_M$ denotes $\log P$ for the metal M without reference to any particular solution, and is a purely abstract conception having no numerical value as yet.

[2] Zeitschr. f. ph. Chem., 12, 324, 1893.

[3] Ibid., 12, 125, 1893.

TABLE VII.[1]

Conc. Ag ions = p_1.	Conc. Cl ions = p_2.	E.M.F.	Calc. S_1	Calc. S_2	Calc. S_3
0.0813	0.0861	0.451	1.24×10^{-5}	1.25×10^{-5}	2.25×10^{-5}
0.0813	0.0861	0.449	1.28×10^{-5}	1.30×10^{-5}	2.34×10^{-5}
0.04295	0.04455	0.418	1.25×10^{-5}	1.25×10^{-5}	2.24×10^{-5}
0.04295	0.04455	0.419	1.23×10^{-5}	1.22×10^{-5}	2.20×10^{-5}
Solubility. AgCl at 25° Average . .			1.25×10^{-5}	1.25×10^{-5}	2.26×10^{-5}
Kohlrausch & Rose			1.44×10^{-5}	at 25°	
Holleman			1.81×10^{-5}	at 25°	

TABLE VIII.

Conc. Ag ions = p_1.	Conc. Br ions = p_2.	E.M.F.	Calc. S_1	Calc. S_2	Calc. S_3
0.0813	0.0861	0.598	7.1×10^{-7}	33.8×10^{-7}	60.7×10^{-7}
0.0813	0.0861	0.603	6.4×10^{-7}	30.1×10^{-7}	55.0×10^{-7}
0.0813	0.0861	0.597	7.2×10^{-7}	34.4×10^{-7}	61.9×10^{-7}
0.04295	0.04455	0.570	6.4×10^{-7}	30.5×10^{-7}	54.9×10^{-7}
0.04295	0.04455	0.571	6.3×10^{-7}	29.9×10^{-7}	53.8×10^{-7}
0.04295	0.04455	0.570	6.4×10^{-7}	30.5×10^{-7}	54.9×10^{-7}
Solubility. AgBr at 25° Average . .			6.6×10^{-7}	31.5×10^{-7}	56.9×10^{-7}
Kohlrausch & Rose			20.9×10^{-7}	at 25°	
Holleman			30.2×10^{-7}	at 25°	

TABLE IX.

Conc. Ag ions = p_1.	Conc. I ions = p_2.	E.M.F.	Calc. S_1	Calc. S_2	Calc. S_3
0.0813	0.0861	0.815	1.02×10^{-8}	19.9×10^{-8}	35.7×10^{-8}
0.0813	0.0861	0.813	1.06×10^{-8}	20.7×10^{-8}	37.2×10^{-8}
0.0813	0.0861	0.815	1.02×10^{-8}	19.9×10^{-8}	35.7×10^{-8}
0.04295	0.04455	0.787	0.94×10^{-8}	18.0×10^{-8}	32.3×10^{-8}
0.04295	0.04455	0.786	0.96×10^{-8}	18.3×10^{-8}	32.9×10^{-8}
0.04295	0.04455	0.790	0.88×10^{-8}	17.0×10^{-8}	30.5×10^{-8}
Solubility. AgI at 25° Average . .			0.98×10^{-8}	19.0×10^{-8}	34.0×10^{-8}
Kohlrausch & Rose			60.00×10^{-8}	at 18°.0	
Holleman			395.00×10^{-8}	at 28°.4	

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[1] S_1 and S_2 in this table should be identical, as they are calculated from the same data by the same formula; the variations are due to errors in calculation.

ued shaking,[1] and I cannot find that Goodwin has taken this into account at all. I conclude, therefore, that if he had shaken his AgCl and AgBr, he would have found much smaller electromotive forces than those recorded in his paper. He has tried to prove the accuracy of his formula in two ways. Having calculated the solubilities by substituting the experimental data for the electromotive forces in the formula, he reverses the operation, and substituting the solubilities he calculates the electromotive forces. It is true that there is an intervening step, but the principle is the same, also the result. If he had taken the cells $Ag|AgNO_3|AgCl + KCl|Ag$ and $Ag|AgNO_3|AgBr + KBr|Ag$ and substituted directly in these the fallacy of such a test would have been patent. Instead of this he has combined the two cells

$$Ag|AgCl+KCl|AgNO_3|Ag|AgNO_3|AgBr+KBr|Ag$$
$$=Ag|AgCl+KCl|AgBr+KBr|Ag,$$

calculated the electromotive force of the resultant cell, and compared this with the experimental value and with the difference of the mean of the two component cells. Any other formula, which had given fairly constant values for the solubilities, would have stood the test equally satisfactorily. If, instead of taking Goodwin's formula and his value for AgBr, 6.6×10^{-7} reacting weights per liter, one takes, for instance, my first modification of his formula and the corresponding value for AgBr, 31.5×10^{-7} units, one will reproduce his table exactly. One cannot agree with him when he says in regard to this table:[1] "Die Uebereinstimmung der beobachteten mit der berechneten Werten ist eine sehr gute, wie sie ja nicht anders sein konnte, wenn die frühere Formel (25), nach der die Löslichkeiten berechnet wurden, überhaupt richtig war. Sie bestätigt also diese Formel." The other proof is not satisfactory in the light of my experiments. Goodwin determined the solubility of thallium bromide by the electrical and by the analytical methods, the difference between the two being about 10 per cent of the total solubility. This result cannot be compared with the experiments on the solubilities of the silver haloids, because the conditions were not the same.

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[1] Proc. of Am. Acad., 30, 325, 1894.

[2] Zeitschr. f. ph. Chem., 13, 651, 1894.

In the thallium determinations the cell used was of the form $Tl|TlBr+KNO_3|TlBr+KBr|Tl$. There were bromine ions in contact with both electrodes, while with the silver salts the bromine ions came in contact with one electrode.

One other point remains to be considered, whether the potential difference at the surface of a reversible electrode is a function of the concentration at all. The only direct measurements are those of Neumann,[1] which confirm the Nernst theory in every detail. In addition, there are many determinations on two-liquid cells, made chiefly by Ostwald's pupils, and in all these cases there is a most satisfactory agreement between the theory and the facts. On the other hand, there are a few observations by other people which are not so easily reconciled with the theory. In Table X. I give some measurements of Paschen's[2] on cells having zinc and mercury electrodes, and solutions of $ZnSO_4$ and $MgSO_4$ of varying concentrations as electrolyte. The first column gives the nature of the cell; the second, the specific gravity of the electrolyte; the third, the concentration in grams per hundred grams of the solution; the fourth, the electromotive force observed. The values for the concentrations are only approximate because they were not determined by Paschen directly, and I have taken them from Landolt and Börnstein's tables.

TABLE X.

Electrodens.	Electrolyte.	Density.	Per cent in grams.	E.M.F.
ZnHg	$MgSO_4$	1.042	4.0	1.194
ZnHg	$MgSO_4$	1.040	4.0	1.236
ZnHg	$MgSO_4$	1.040	4.0	1.186
ZnHg	$ZnSO_4$	1.433	32.9	1.249
ZnHg	$ZnSO_4$	1.409	31.5	1.252
ZnHg	$ZnSO_4$	1.403	31.1	1.309
ZnHg	$ZnSO_4$	1.402	31.1	1.327
ZnHg	$ZnSO_4$	1.400	31.0	1.236
ZnHg	$ZnSO_4$	1.315	25.5	1.310
ZnHg	$ZnSO_4$	1.305	25.0	1.238

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[1] Zeitschr. f. ph. Chem., 14, 225, 1894.

[2] Wied. Ann., 43, 570, 1891.

These figures lose a good deal of their value owing to the considerable variation in the determinations for the same solutions, and because the range of concentrations is too limited; but two things are very noticeable in spite of this. In the cells Zn|$ZnSO_4$|Hg, the electromotive force does not decrease with increasing concentration of zinc sulfate, as it should according to the theory. The cells Zn|$MgSO_4$|Hg, have the same value as the cells Zn|$ZnSO_4$|Hg, or a smaller one, while the theory demands a larger one. The same thing is seen, though in a less satisfactory manner, in the experiments of Damien.[1] He used zinc and copper as electrodes, and his results are given in Table XI. The first column shows the electrolyte; the second, the specific gravity of the solution; the third, the percentage composition; the fourth, the electromotive force when ordinary zinc was used; the fifth, the corresponding values when the electrode was amalgamated.

TABLE XI.

ZnCu Electrodes.

Electrolyte.	Density at 15°.	Per cent in grams.	E.M.F.	Amalg. Zn E.M.F.
K_2SO_4	1.036	4.5	1.035	1.067
Na_2SO_4	1.038	*10.0	1.012	1.037
$(H_4N)_2SO_4$ . .	1.075	13.1	1.012	1.019
$MgSO_4$	1.035	*5.8	1.047	1.059
$Al_2(SO_4)_3$ . . .	1.135	5.8	1.050	1.062
$ZnSO_4$	1.064	*9.2	1.004	1.047
KCl	1.077	12.0	0.788	0.802
NaCl	1.061	8.5	0.805	0.810
NH_4Cl	1.039	13.0	0.845	0.850
$BaCl_2$	1.110	12.0	0.782	0.820
$CaCl_2$	1.212	23.0	0.743	0.751
$ZnCl_2$	1.384	37.5	0.746	0.752

Values with a * refer to hydrated salt.

As will be noticed, there are marked variations even in cases where no one claims that there should be any, such as between

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[1] Ann. chim. phys. (6), 6, 289, 1885. The reference to Vol. V. in Wied. Elektrizität I, 734, also in Beibl. 10, 185, is a misprint.

ammonium sulfate and potassium sulfate solutions, between calcium chloride and ammonium chloride. This weakens the conclusions which one would like to draw from these experiments; but, making allowance for a large experimental error, it is still very curious that $Zn|ZnSO_4|Hg$ should give so nearly the same value as the cells with indifferent sulfates, and that zinc chloride should be indistinguishable electrically from calcium chloride. The experiments of Hockin and Taylor[1] may be interpreted either way. They found that the combination of zinc and another metal in sulfuric acid gave a higher electromotive force than the same two metals in a saturated solution of zinc sulfate. This is not so convincing as if they had used potassium sulfate instead of sulfuric acid, because in all except dilute solutions free acids do give a higher value than the corresponding salts. The reason for this variation is unknown. When it comes to the absolute values in the zinc sulfate solution, matters are no better. In some of the metals, notably cadmium and mercury, the zinc sulfate appears to give the same value as any other sulfate; with others there is a qualitative agreement with Nernst's theory. The same remarks hold true of the work of Lindeck.[2] I have not access to the original paper of Wolff, and the review of it[3] is two meager to be of much assistance. He investigated, among other things, the effect of changing the concentration of the zinc sulfate in a one-liquid cell. His results are given in Table XII. The first column

TABLE XII.

	Density.	E.M.F.
$Zn\|ZnSO_4\|Cu$	1.438–1.001	0.965–1.066
$Zn\|ZnSO_4\|CuO$	1.427–1.003	1.008–1.015
$Zn\|ZnSO_4\|Fe$	1.427–1.003	0.378–0.385
$Zn\|ZnSO_4\|Pb$	1.427–1.003	0.456–0.587
$Zn\|ZnCl_2\|Cu$	1.637–1.003	0.734–0.930
$Zn\|ZnCl_2\|Fe$	1.917–1.003	0.385–0.390
$Zn\|Zn(NO_3)_2\|Cu$	1.496–1.004	0.669–0.698

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[1] J. Tel. Eng., 8, 282, 1879.

[2] Wied. Ann., 35, 311, 1888.

[3] Beibl., 12, 700, 1888.

shows the electrodes and the electrolyte; the second, the concentrations of the latter in specific gravities; the third, the corresponding electromotive forces.

In all cases there is a qualitative agreement with the theory; that is, the electromotive force increases with decreasing concentration of zinc sulfate. The quantitative agreement is not so satisfactory. In the second, third, sixth and last cells given in the table the variations are much too small; while, in the other cases, they are too large. The ratio of the strongest solutions to the weakest in the experiments of Wolff lies between 100 and 1000 to 1, which corresponds to a change of electromotive force of 0.05–9 volts owing to the bivalence of zinc. Some experiments which I made with the cell $Cd|CdCl_2|Hg$, the strength of the solution being unknown, gave me 0.815, 0.821, 0.814, average 0.817 volts, the same value which I had already found for the KCl solution.

The simplest way to decide what effect the concentration of the reversible ion, if I may use such a phrase, has on the electromotive force would be to make a series of measurements on reversible electrodes by the dropping-mercury method. I have not been in a position to do this, and I have had to find an easier, though less satisfactory manner of settling the question. Suppose we have electrodes of zinc and copper in a mixture of zinc and copper sulfates, one solution. Increasing the concentration of the zinc sulfate or decreasing the concentration of the copper sulfate must diminish the electromotive force of the cell, and *vice versa* if the reverse operations be performed. Through the courtesy of Professors Trowbridge and Peirce of the Physical Laboratory, I have been able to make the few experiments necessary. As it was only required to find out whether there was any change at all, there was no need of determining the absolute value of the electromotive force. This made the experimental part very easy. I connected the cell with a large external resistance and a galvanometer. I changed the ratio of the two components in the solution and noted the position of the galvanometer needle. I made measurements with the electrodes in pure zinc sulfate solutions, in pure copper sulfate solutions, and in mixtures of these in varying proportions. Under all these different conditions I obtained the same electromotive force, showing that it is a function neither of the relative nor of the absolute concentrations.[1] Although one obtains the same value from the different solutions, they do not behave exactly alike. With solutions of pure copper sulfate or with mixtures containing copper sulfate in any quantity, the maximum value is obtained at once and is very constant. With solutions of pure zinc sulfate or mixtures containing only traces of copper sulfate, the maximum value can be obtained only by vigorous stirring and is very inconstant. There is, of course, nothing surprising about this, as it is what one would have predicted. It is a very curious fact that the Nernst formula, though deduced from apparently erroneous assumptions, should yet give the effect of changes of concentration in a two-liquid cell with such surprising accuracy.

It will be noticed that the electromotive forces of the non-reversible cells have nothing to do with the heats of reaction. This has always been known; but it acquires a new significance, since it has been shown that the non-reversible cells are to be considered, as far as the electromotive forces are concerned, as limiting cases of the reversible two-liquid cells. In the cell $Zn|H_2SO_4|Ag$ there is not much doubt what reaction takes place; but it has nothing to do with determining the electromotive force. An interesting example of this, which also brings up another point, is the cell $Cu|CuSO_4|Pt$. Here the reaction consists in the replacement of copper by copper. What happens experimentally, on closing the circuit, is that copper is dissolved from the copper electrode and precipitated on the platinum until the latter becomes, electrically considered, an electrode of pure copper, when further action becomes impossible.[2] Overbeck[3] made some experiments a few years ago to determine what thickness of copper made a platinum electrode behave like a piece of pure copper. His

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[1] This applies only to electrodes reversible in respect to the kation. I hope to treat the case of electrodes reversible in respect to the anion in another paper.

Since this paper was written I have seen the article of J. Meyer, Wied. Ann., 53, 898, 1894, which confirms my views, though with certain exceptions.

[2] When I performed this experiment I was not aware that a similar one had been described by Gladstone and Tribe, Proc. Roy. Soc., 1876.

[3] Wied. Ann., 31, 337, 1887.

method was to deposit copper on platinum electrolytically, and was open to the objection that it was almost impossible to be certain that the copper was deposited uniformly over the surface of the platinum. By using the cell $Cu|CuSO_4|Pt$, it would seem that this difficulty might be avoided, as the plating is stopped automatically as soon as the minimum thickness is reached. Suppose we balance this cell to some extent by an electromotive force less than its own. There will still be a tendency for copper to be deposited on the platinum; but it cannot be deposited to the thickness corresponding to pure copper, as it must then dissolve up again under the influence of the external electromotive force. It can precipitate only till equilibrium is reached, and we shall have the condition referred to by Gibbs,[1] of a substance present in too small quantities to have the properties of "matter in mass." By making the external electromotive force differ infinitely little from the electromotive force of the cell, it would be possible, theoretically at any rate, to obtain an infinitely thin film of copper. It is to the separation of the ion on the electrode in such small quantities as not to have the properties of matter in mass that is due the gradual change of the polarization instead of having a sudden jump from the initial to the final value.

The main results of this research may be summed up as follows:

1. The potential difference between a metal and an electrolyte is not a function of the concentration of the salt solution nor of the nature of the positive ion except in certain special cases.

2. It is a function of the electrode, of the negative ion, and of the solvent.

3. In aqueous solutions, the potential difference is the sum of the term due to the electrode and the term due to the negative ion in the normal cases.

4. For most metals in most electrolytes the term due to the negative ion has the same numerical value and the same sign.

5. For mercury it has the same numerical value, but the opposite sign; for platinum, neither the same numerical value nor the same sign.

CAMBRIDGE, December, 1895.

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[1] Thermodynamische Studien, p. 393.