ON IRREVERSIBLE CELLS.

BY A. E. TAYLOR.

The present paper is a continuation of the work of Bancroft¹ on single-liquid polarizable cells, with especial reference to the effect of the negative ion on the potential difference between an electrode and the electrolyte in which it is immersed. The electromotive force of a cell, having for electrodes any two of the metals Mg, Zn, Cd, Sn, Pb, or Bi in solutions of chlorides, bromides, iodides, sulphates, nitrates or acetates, does not seem to be in any way a function of the negative ion. When, however, mercury serves as one electrode a variation with the negative ion always appears. Measurements were made with zinc and cadmium in combination with mercury in chloride, bromide, iodide, nitrate, sulphate and acetate solutions. The results obtained were compared with the values given by Paschen² for the single potential differences entering into these same cells. The measurements of Paschen show in every case a variation with the negative ion for the single potential difference. That these variations do not appear in the electromotive forces of the cells in which two of the metals Mg, Zn, Cd, Sn, Pb or Bi are used as electrodes, is explained by the fact that for each negative ion the term due to it has the same numerical value and the same sign for each metal, but varying for the different ions. So, in the electromotive force, which is the sum of the two potential differences taken in opposite directions, this term due to the negative ion disappears. With mercury, however, the value of the term seems to be the same as with the other metals mentioned but with opposite sign. In consequence of this difference in sign, there appears in the electromotive force of a cell, in which mercury is one of the electrodes, a term due to the negative ion and having a value equal to

¹Zeit. phys. Chem., **12**, 289 (1893); Physical Review, **3**, 250 (1896).

²Wied. Ann., **43**, 590 (1891).

twice that appearing in the single potential differences. With platinum the numerical value of this term is no longer the same. The behavior of copper, in this respect thus becomes a matter of interest, and the first part of this paper is given to an investigation of cells composed of Zn, Cd, Hg and Cu in solutions of chlorides, iodides and sulphates.

The cadmium first used was taken from the University museum and later some pure cadmium was obtained from Eimer and Amend. Measurements made with the various cadmium electrodes on the cell, Cd|chloride|Hg all agreed very well among themselves, and further agreed with the measurements of Bancroft on the same cell. Two sticks of pure copper, previously used by Prof. Bancroft in electrical measurements, served as copper electrodes. The mercury used was purified according to the method given by Ostwald in his *Physiko-chemische Messungen*, p. 100, and gave extremely satisfactory results. Impure mercury was repeatedly shaken with dilute sulphuric acid to which was added a few drops of potassium bichromate, and after being carefully washed with distilled water, was allowed to run in a fine stream through a long column of ten per cent. nitric acid. This last process was repeated several times. The pure mercury finally obtained retained a perfectly bright surface during a period of several months, in fact until it was all used. Especial care was exercised in the preparation of the potassium salts used. The potassium chloride had been prepared by being six times precipitated from a concentrated solution of the salt by hydrochloric acid gas, and had been previously used to determine the constant of a conductivity cell. It had also been compared with potassium chloride used by Dr. Kortright in conductivity work, and in both cases the same constant was obtained for the cell. The sulphate first used probably contained a trace of some other salt for it gave low values; but on being recrystallized several times very satisfactory results were obtained.

The determinations of the electromotive force were made with a small Lippmann's electrometer according to the well known compensation method of Poggendorff. A Latimer Clark cell served as a normal element. This cell was compared from time to time with another Clark cell, and the two were always found to agree within

at least a millivolt. Two Leclanché's having a combined electromotive force of about 2.6 volts were used as a working cell. These cells were very constant, although they slowly changed to the extent of about three or four per cent. The value of the Clark in terms of the Leclanché was determined two or three times a day.

The single-liquid cells measured were made up in little vials of about twenty-five millimeters in diameter and seventy-five millimeters in height. These vials were provided with paraffined corks into which the electrodes were tightly fitted. In case that mercury was used as one of the electrodes, a glass tube, into which a platinum wire had been fused, passed down through the electrolyte and made connection with the mercury. Great care was taken to keep the cells perfectly clean, as slight impurities have a very marked effect. Whenever the cells were made up they were first very carefully washed for a long time with distilled water; and each time, the electrodes were carefully scraped or cut with a sharp knife to ensure a bright clean surface, then washed with distilled water and wiped with filter paper to remove any loose particles of metal. The bottles used for the solutions were first thoroughly washed with distilled water and then boiled out with steam.

In all cases the maximum reading of the electromotive force of the cell was taken, for all the cells measured were found to increase rather quickly to a maximum, which remained constant for a time. Most of the cells reached a maximum reading in about an hour, while some of the cells, especially the sulphate cells, might require two or three hours. In a few cases the maximum was reached in fifteen or twenty minutes. However, the time for any particular cell was not in the least constant. Throughout this whole paper twentieth normal solutions are always used when no concentration is specified.

The cells first measured were potassium chloride cells in which Cu, Hg and Cd served as electrodes.

The cells are all measured in volts, the value of the standard Clark being taken as 1.434 volts at 15°C. Each value represents a different cell, a series of readings being taken, and the maximum which remains constant being given. The cells are always written,

TABLE I.

—n/20 K Cl—

Electrodes	Cd Hg	Cu Hg	Cd Cu
	0.821	0.255	0.546
	0.814	0.251	0.568
	0.815	0.254	0.566
	0.812	0.254	0.568
	0.813		0.568
	0.818		0.561
			0.557
Averages ---	0.815	0.253	0.565

e. g., $\text{Cd} \left| \frac{n}{20} \text{KCl} \right| \text{Hg}$, so that the current in the cell runs from left to right, the anode thus being written first. A list of measurements is given rather than a simple average, in order that the variation of the various cells may be seen. A greater accuracy than 0.01 volts is not claimed for the results, although it seems probable that the accuracy is somewhat greater than that. It will be seen that the cells obey very well Poggendorff's law, in that the value of the cell $\text{Cd} \left| \text{Hg} \right|$ is very nearly equal to the sum of the values given for the two cells $\text{Cd} \left| \text{KCl} \right| \text{Cu}$ and $\text{Cu} \left| \text{KCl} \right| \text{Hg}$. It would seem therefore that the averages give values which differ but a few millivolts from the true values of the cells measured. At any rate the maximum variation observed would have little or no effect upon the general facts observed.

The sulphate cells in table II were measured.

The values of these cells were much harder to determine than the corresponding ones for the chloride cells. The slightest impurity has a very large effect. A great many measurements were made with a sulphate solution, which I supposed to be pure. The results, however, did not agree very well among themselves, nor would they add up according to Poggendorff's law. The cell $\text{Cd} \left| \text{Hg} \right|$ was not equal to the sum of the two cells $\text{Cd} \left| \text{Cu} \right|$ and $\text{Cu} \left| \text{Hg} \right|$. The salt was thereupon purified by repeated crystallization and satisfactory measurements were obtained. A very slight amount of sulphuric

TABLE II.

—11 / 20 K₂SO₄—

Elec- trodes	Cd Cu		Cu Hg		Cd Hg		Zn Cu (W.D.B.) Zn Cd		Zn Hg ¹	
	0.740		0.309		1.037		1.053			
	0.734		0.314		1.037		1.065			
	0.725		0.303		1.029		1.076			
	0.725		0.292		1.033		1.071			
	0.725		0.300		1.034		1.054			
	0.731		0.300		1.038		1.049			
	0.716		0.318		1.042		1.048			
	0.722				1.020		1.077			
							1.068			
							1.056			
							1.046			
							1.065			
							1.072			
							1.044			
							1.055			
Averages	0.727		0.306		1.034		1.061		0.334	1.367

acid was found to raise the value of the sulphate cells very considerably. The sulphate solutions used showed no trace of acid, when tested with a drop of phenol phthalein indicator, for the solution immediately turned red when a drop of very dilute potassium hydrate solution was added.

The following table for Cd, Zn, and Hg in halogen and sulphate solutions is given by Bancroft :

TABLE III.

Electrodes	K Cl	K Br	K I	K ₂ SO ₄
Zn Hg	1.151	0.991	0.847	1.302
Cd Hg	0.818	0.659	0.515	0.969
Difference	0.333	0.332	0.332	0.333
Zn Cd	0.333	0.333	0.331	0.334

The value 0.818 volts for Cd | KCl | Hg agrees very closely with the value 0.815 volts which I obtained. For the cell Cd | KI

¹Calculated from Zn | Cu + Cu | Hg, or from Cd | Hg + Zn | Cd.

|Hg I obtained 0.514 volts. My values for the sulphate cells do not agree at all with those obtained by Bancroft ; but in view of the special care taken with these cells, it seems probable that his values are too low. I obtained lower values than Bancroft with the first impure sulphate solution used. The electromotive force, 1.367 volts which is given for the cell $\text{Zn} | \text{K}_2\text{SO}_4 | \text{Hg}$ was not directly observed by me, but was calculated by the method indicated. The value given by several investigators is about 1.300 volts, but I think that the true value is probably higher. The cell is a very difficult one to measure, for it seems to polarize almost immediately. I observed about the same electromotive force 1.3 volts myself, but the cell did not remain constant at all and in a minute or two had fallen in value considerably, so that the true value must of necessity be higher than that first observed, and is probably not very different from the one calculated. Aside from the cell just mentioned, the cell $\text{Zn} | \text{K}_2\text{SO}_4 | \text{Cu}$ was the most unsatisfactory one measured, in that the variations are very large ; but from a large number of observations a fairly accurate mean value seems to be obtained.

Bancroft found cells of this kind to vary in no case with the concentration. My measurements confirm his results with the cell $\text{Cd} | \text{KCl} | \text{Hg}$ and further I found the same thing to hold true of the cell $\text{Cu} | \text{KCl} | \text{Hg}$.

TABLE IV.

Electrodes	Electrolyte	Concentration	E. M. F.
Cd Hg	K Cl	n / 10	0.818
Cd Hg	K Cl	n / 100	0.817
Cd Hg	K Cl	n / 1000	0.819
Cu Hg	K Cl	n / 20	0.252
Cu Hg	K Cl	n / 400	0.253
Cu Hg	K Cl	n / 4000	0.251

The same thing holds true of all the cells as far as tried, so that two points with regard to these cells may be considered as fairly well settled ; the concentration has no effect, and in every case the negative ion of the salt solution has an effect on the electromotive force of the cell.

Now these inconstant cells correspond somewhat closely to the values obtained from the two liquid reversible cells of the Daniell's type, as was first mentioned by Oberbeck and Edler, and further confirmed by the measurements of Bancroft. It would seem, therefore that these one-liquid cells might be considered as limiting cases of the two-liquid reversible cells. According to Nernst the potential difference between a metal and a solution of a salt of that metal is given by the formula¹

$$\pi = \frac{RT}{nc} \log \frac{P}{p} \times 10^{-1} \text{volts}$$

where π is the potential difference, n the valence of the cation, and p its partial osmotic pressure in the solution, P the solution pressure of the electrode metal and e the quantity of electricity carried by one gram equivalent. The electromotive force, E , of a cell $M_1 | p_1 M_1 X | p_2 M_2 X | M_2$, of the Daniell's type will be given by the expression

$$E = \frac{RT}{nc} \left(\log \frac{P_1}{P_2} + \log \frac{p_2}{p_1} \right) \times 10^{-1} + Z \text{ volts}$$

where Z denotes a possible potential difference between the two solutions; and the valence of the two electrode metals is taken as being the same. Now if we take the two solutions of the same concentration, then the values of p_2 and p_1 are equal, if the salts are wholly or equally dissociated, and the term p_2/p_1 disappears. The electromotive force of the cell then becomes independent of the absolute concentration, if the term Z becomes negligible as is the case when the migration velocities of the ions M_1 and M_2 are equal. Under these conditions the electromotive force of the cell $Zn | ZnSO_4 | CuSO_4 | Cu$ has been found to be independent of the absolute concentration of the zinc and copper sulphates.²

Bancroft looks upon the one liquid polarizable cells as limiting cases of this cell. If both solutions in the cell are diluted with water, the electromotive force remains unchanged. Now according to Nernst's views, if we dilute with potassium sulphate solution instead of water the electromotive force would also be unchanged,

¹Zeit. phys. Chem. **4**, 148 (1889).

²Wright, Phil. Mag., [5], **13**, 265 (1882).

except as it is affected by any change of dissociation of the two sulphates. By increasing the amount of potassium sulphate we should finally reach the limit where the concentration of the zinc sulphate and the copper sulphate would be zero or, in other words, the cell $M_1|K_2SO_4|M_2$. Thus the one liquid polarizable cell $M_1|RX|M_2$ may be looked upon as the limiting case of the reversible two liquid cell $M_1|\rho M_1X|\rho M_2X|M_2$. The term Z is thereby eliminated and the migration velocities of the ions no longer have an effect on the cell. The difficulty of measurement brought about by polarization much more than counterbalances the slight error introduced in the term Z , and in the term $\log(\rho_2/\rho_1)$. Table V gives some of the results obtained for both polarizable and reversible cells.

Most of these figures are taken from the tables given by Bancroft.¹ In the first four columns are measurements on single-liquid polarizable cells by Paschen², Bancroft¹, Oberbeck and Edler³, and Ostwald.⁴ The measurements of Ostwald are with free acids and give higher values. The next three columns are for reversible cells by Wright and Thompson⁵, Neumann⁶ and Braun⁷ and in the last column several measurements by myself. The agreement is not good, but points to the fact that the irreversible cells are limiting cases of the reversible cells. This will be seen best in the cases where there is no insoluble salt formed in the reversible cells, that is, where the concentration is the same on both sides.

The $Zn|Cd$, $Cd|Cu$ sulphate and $Zn|Cu$ sulphate cells differ very little whether polarizable or reversible.

Ostwald,⁸ however, seems to consider these polarizable cells as having no definite electromotive force, and to depend upon the concentration of the ions of the electrode metal which have gone into

¹Proc. Am. Acad. **31**, 96 (1894); Physical Review **2**, 250 (1895).

²Wied. Ann. **43**, 590 (1891).

³Ibid. **42**, 209 (1891).

⁴Zeit. phys. Chem. **1**, 583 (1887).

⁵Phil. Mag. [5] **19**, 1 (1885).

⁶Zeit. phys. Chem. **14**, 193 (1894).

⁷Wied. Ann. **16**, 575 (1882).

⁸Lehrbuch, 2d Ed. **2**, 815-816.

TABLE V.

Electrodes	Electrolytes	Paschen	W. D. B.	O. & E.	Ostwald	W. & T.	Neumann	Braun	A. E. T.
Zn Cd	Chloride	0.296	0.333	0.368	0.360	0.330	0.329	0.334	
Zn Cd	Bromide	0.293	0.333	0.364	0.340	0.315		0.256	
Zn Cd	Iodide	0.298	0.331	0.365	0.304	0.322		0.262	
Zn Cd	Sulphate	0.350	0.334	0.430	0.401	0.360	0.362	0.33-37	
Zn Pb	Chloride	0.512	0.526	0.561	0.610	0.591	0.598		
Zn Pb	Bromide	0.525	0.528	0.541	0.599	0.571			
Zn Pb	Iodide	0.545	0.527	0.558	0.587	0.455			
Zn Pb	Sulphate	0.525	0.527	0.502	0.592	0.50-55			
Cd Pb	Chloride	0.216	0.195	0.192	0.249		0.269		
Cd Pb	Sulphate	0.18	0.194	0.17	0.191				
Cd Cu	Sulphate				0.672	0.752	0.747	0.740	0.728
Zn Cu	Sulphate				1.07	1.11	1.109	1.1	1.061
Zn Hg	Chloride	1.112	1.151		1.173	1.12-26			
Zn Hg	Bromide	0.983	0.991		1.036	0.972			
Zn Hg	Iodide	0.846	0.847		0.841	0.801			
Zn Hg	Sulphate	1.300	1.302		1.484	1.46-51			
Cd Hg	Chloride	0.816	0.818	0.755	0.813	0.812			0.815
Cd Hg	Bromide	0.670	0.659	0.632	0.696				
Cd Hg	Iodide	0.548	0.515	0.465	0.535				0.514
Cd Hg	Sulphate	0.968	0.969	0.962	1.083				1.034

the solution. This concentration might vary greatly with circumstances. Warburg¹ has shown, especially in certain cases, that air dissolved in the electrolyte will cause the electrode metals to go into solution, and that there may be observed a potential difference between a metal immersed in an electrolyte free from air and the same metal immersed in the same electrolyte containing dissolved air. So, it is usually said that these cells have no definite electromotive force as the concentration of the ions would vary with the amount of air dissolved or some other disturbing influence. However, I do not think it to be actually the case that a definite value cannot be obtained for these cells, as the measurements given seem to show a perfectly definite value. In general, the measurements of Oberbeck and Edler on the polarizable cells agree fairly well with those of Bancroft, though in some cases there are rather large variations. I think that these discrepancies between the measurements of different men are better explained in other ways. It is a well known fact that slight impurities in the electrodes used will alter the electromotive force very greatly. Further, it seems to be essential that the electrolytes used should be absolutely pure, that is, free from the salt of any other acid, more especially in the cases where the negative ion appears to have an effect. With sulphates the presence of any impurity is especially noticeable, and a glance at the table will show that the largest differences are with the sulphates. With the bromides I found that the addition of a slight amount of chloride raised the value, but that the effect of impurity was not as great as with the sulphate.

Bancroft gives a long list of measurements with the cell $\text{Cd}|\text{KCl}|\text{Hg}$, and the variations are comparatively small. With this cell, especially, there is no doubt about its having a perfectly definite value, since everyone finds nearly the same value for it. Take for instance the cells Zn/Cd where the E. M. F. is independent of the negative ion of the electrolyte. The values of Oberbeck and Edler for the chloride, bromide and iodide are regularly 0.03 volts higher than those of Bancroft. Among themselves the results of each investigator agree within four millivolts. Now, this is not what one

¹Wied. Ann. **38**, 321 (1889).

would expect if the air dissolved in the electrolyte explained the differences, but it is exactly what would be expected if the electrodes used by the two were not exactly alike. Bancroft obtained measurements which seem to be constant, and they conform surprisingly well to Poggendorff's law. All the results given in the above table for zinc and cadmium with mercury vary but little.

I think that the action of oxygen on the electrodes does sometimes explain the variations of the individual investigator. Warburg finds that with zinc and copper the effect of air is especially large and somewhat variable. It was exactly with Zn|Cu cells that I found the largest variations for any particular cell, as is well shown by my Zn|K₂SO₄|Cu cell. Further the values for reversible cells, given by different investigators do not agree any too well, and here slight impurities in the materials used is the only explanation, if care has been used in the measurements.

So, it seems to me, that the fact of variations, in some cases rather large, does not in the least show that these polarizable cells have no definite electromotive force, when the difficulties of measurement are taken into account; and further until recently all the measurements have been made with a galvanometer, which is ill suited for polarizable cells.

We will consider again Nernst's formula for the reversible cells,

$$\pi = \frac{RT}{ne} \left(\log \frac{P_1}{P_2} + \log \frac{p_2}{p_1} \right) \times 10^{-4} \text{ volts,}$$

and the particular case where $p_2 = p_1$

$$\pi = \frac{RT}{ne} \left(\log \frac{P_1}{P_2} \right) \times 10^{-4} \text{ volts,}$$

and see how well it predicts the facts for the polarizable cells we have been considering. We have found the cells to be independent of the concentration, as the formula would indicate. Ostwald¹ and LeBlanc² state definitely that $\log P$, the solution pressure of the electrode metal, depends solely upon the metal and the temperature, and is independent of the negative ion of the solution. This being the case we would expect the electromotive force to depend solely on

¹Lehrbuch, 2d Ed. 2, 855.

²Elektrochemie, 184.

the electrode metals and to be independent of the salt in which they are immersed; and this Bancroft found to be true when mercury was not used as an electrode. The figures given by him in the first part of Table V are a striking confirmation of this fact. But when we consider the cells in which mercury or copper serve as one of the electrodes, then this is not true in the least, and the negative ion of the salt solution seems to have a very definite effect, for in the cells $\text{Zn}|\text{Hg}$ and $\text{Cd}|\text{Hg}$ there is always observed an increase of electromotive force of 0.3 volts in passing from the iodide to the chloride cell, and about 0.16 volts in passing from the iodide to the bromide. These values seem to be perfectly well defined, and are surely not due to experimental error.

Let us now further consider the value of the solution pressure and inquire into the single potential difference between a metal and a solution. The assumption of Nernst is that, when a metal is immersed in a solution of a salt of the metal, if the solution pressure of the metal be greater than the osmotic pressure of the metal ions in the solution, then positive metal ions will go from the electrode into the solution and the electrode thus become negatively charged to the solution. If, however, the osmotic pressure of the ions in the solution is greater than the solution pressure, then metal ions will be precipitated from the solution on the metal, thus charging the electrode positively to the solution. What happens when we consider cadmium and mercury in salts of the alkali metals and the single potential differences arising therefrom? The solution pressure of cadmium is large and we would expect the cadmium to be charged negatively to the solution, and this is actually found to be the case when the single potential differences are measured by the method of the dropping mercury electrodes. But with mercury or copper the metal is found to be positive to the solution. How does this come about? There are no mercury ions in potassium sulphate to be precipitated on the mercury. Yet we may assume with Warburg that oxygen contained in the electrolyte dissolves up some mercury. Then we can say that the mercury ions are precipitated on the mercury again, if their osmotic pressure has become greater than the solution pressure of the mercury. It does not, however, seem entirely correct to assume that mercury goes into

solution only to be again precipitated, and by this precipitation the mercury become positively charged. The following equations express the reaction,

or in other words, in the presence of mercury, oxygen unites with water to form two hydroxyl ions.

However this may be, the single potential differences measured by the dropping mercury electrodes do make cadmium negative and mercury positive to solutions of potassium salts just as to salts of the electrode metals. It is also interesting to see if the single potential differences vary with the nature of the negative ion in any or all cases. If the assumption of Ostwald with regard to the solution pressure be true, then there would be no variation. The method of dropping mercury electrodes does not give very accurate results, but it is sufficiently accurate to point out the facts desired. The values $\text{M}_1|\text{RX}$ and $\text{RX}|\text{M}_2$ do give when added the value for the cell $\text{M}_1|\text{RX}|\text{M}_2$. Values found for Zn, Cd and Hg by Paschen¹ and for Cu by Ostwald² are given in Table VI.

Ostwald made measurements on a large number of metals and acids and came to the conclusion that the halogen acids differ from the oxygen acids, the latter forming a group by themselves. With the more dilute acids this is very noticeable. Zn|Hg shows with most oxygen acids a value of approximately 1.4 volts, hydrochloric acid 1.2 volts, hydrobromic acid 1.0 volt and hydriodic acid 0.8 volts. In most cases the numbers with increasing dilution tend toward the negative side. Whether the influence of dilution is great or small depends upon the metal and upon the acid. Zn, Fe and Bi show the greatest changes, while Cd, Pb, Cu, Ag and Hg show comparatively little change. In all cases dilution has no great effect with the organic acids.

Paschen made measurements between metals and salt solutions not containing the electrode metal as ion. His conclusion is that the potential difference depends upon the anion and not on the cation

¹Wied. Ann. **43**, 590 (1891).

²Zeit. phys. Chem. **1**, 601 (1887).

TABLE VI.

Solution	Zn Sol.	Cd Sol.	Hg Sol.	Cu	Solution	Zn Sol.	Cd Sol.	Hg Sol.	Cu
HCl=1 l.	0.560	0.248	0.560	0.305	HBr=0.272 l.	0.393	0.175	0.503	
=10 l.	0.610	0.272	0.551	0.367	=0.9833 l.	0.423	0.202	0.490	0.316
=100 l.	0.643	0.242	0.548	0.414	=10 l.	0.567	0.238	0.493	0.394
KCl=0.280 l.	0.525	0.260	0.524		=100 l.	0.610	0.246	0.496	0.410
=1 l.	0.547	0.249	0.539		KBr=0.402 l.	0.399	0.203	0.474	
=10 l.	0.575	0.251	0.553		=1 l.	0.441	0.186	0.483	
=100 l.	0.523	0.240	0.584		=10 l.	0.422	0.167	0.493	
NaCl=0.239 l.	0.521	0.262	0.562		=100 l.	0.496	0.183	0.505	
=1 l.	0.512	0.266	0.556		HI=10 l.	0.427	0.117	0.411	0.320
=10 l.	0.541	0.268	0.557		=100 l.	0.515	0.159	0.417	0.301
=100 l.	0.557	0.268	0.590		=1000 l.	0.584	0.214	0.386	
MgCl ₂ =0.971 l.	0.525	0.252	0.546		KI=0.795 l.	0.250	0.113	0.400	
=2 l.	0.531	0.277	0.547		=1 l.	0.233	0.113	0.400	
=20 l.	0.598	0.258	0.548		=10 l.	0.308	0.110	0.412	
=200 l.	0.516	0.245	0.580		=100 l.	0.369	0.120	0.412	
BaCl ₂ =0.809 l.	0.512	0.259	0.562		=1000 l.	0.454	0.199	0.386	
=2 l.	0.554	0.249	0.555		K ₂ SO ₄ =2.152 l.	0.618	0.287	0.700	
=20 l.	0.583	0.281	0.553		=20 l.	0.573	0.274	0.720	
=200 l.	0.566	0.240	0.586		=200 l.	0.592	0.252	0.730	
H ₂ SO ₄ =2 l.	0.653	0.319	0.835		H ₂ SO ₄ =1 l.				0.408
=20 l.	0.668	0.284	0.817		=10 l.				0.369
=200 l.	0.668	0.261	0.825		=100 l.				0.364

in the solution.¹ Especially with like concentrations of salts having the same anion, are the same values obtained. From these measurements of Ostwald and Paschen it is rather difficult to determine whether the potential difference varies with the concentration of the electrolyte or not. The variations are not at all large except in certain cases, and may in general come within the limits of experimental error. Further, if we consider the two cells $\text{Cd}|\text{KCl}|\text{Hg}$ and $\text{Cu}|\text{KCl}|\text{Hg}$ which were found to be invariable over a very wide range of concentration, we may come to one of two conclusions with regard to the single potential differences. Either they do not vary at all with the concentration, or the variation is equal in each case and consequently does not appear in the electromotive force. Bancroft adopted the first view, but later work on my part seems to point to the latter alternative as the more probable of the two.

Further, what do the single potential differences show with regard to the effect of the negative ion? Does the negative ion have an effect simply on mercury and copper, as the measurements on the cells might indicate? From the measurements of Paschen, Bancroft saw that with Cd, Hg and Zn the negative ion always had an effect. Further in passing from the chloride to the iodide a difference of about 0.15 volts, and from the bromide to the iodide a difference of 0.08 volts was to be observed. Now in measuring the $\text{Zn}|\text{Hg}$ or $\text{Cd}|\text{Hg}$ cells a difference of 0.3 volts was noticed between the chloride and iodide cells, and 0.16 volts between the chloride and bromide cells, while $\text{Zn}|\text{Cd}$ was the same for chlorides, bromides and iodides. This showed that the effect of the negative ion was the same on all the metals considered, but that with mercury the sign was different. The numbers assigned by Bancroft as being the most probable values for Zn, Cd and Hg in chlorides bromides and iodides are given in Table VII. In addition to these values, I have calculated from my measurements the values for the sulphates and for copper in chlorides and sulphates, in the following manner:

$\text{Cd} \text{K}_2\text{SO}_4 \text{Hg}$	$=1.035$	$\text{Cd} \text{K}_2\text{SO}_4 \text{Cu}$	$=0.728$
$\text{Cd} \text{K}_2\text{Cl} \text{Hg}$	$=0.815$	$\text{Cd} \text{K}_2\text{SO}_4$	$=0.365$
$2(\text{SO}_4-\text{Cl})$	$=0.220$	$\text{SO}_4 \text{Cu}$	$=0.363$
SO_4-Cl	$=0.110$		

¹Wied. Ann. **43**, 570, 608 (1891).

$$\text{Cu}|\text{KCl}|\text{Hg} = 0.252$$

$$\text{Cl}|\text{Hg} = 0.562$$

$$\text{Cu}|\text{Cl} = 0.310$$

TABLE VII.

Solution	Zn Sol.	Cd Sol.	Sol. Hg	Sol. Cu
Chloride	0.589	0.255	0.562	0.310
Sulphate	0.699	0.365	0.672	0.363
Bromide	0.507	0.174	0.483	
Iodide	0.436	0.104	0.410	

It will be seen that with copper the value due to the negative ion is not the same in value as with Zn, Cd and Hg. It has, however, the same sign as the term for mercury, but a smaller value. In passing from a chloride to a sulphate, with copper there is a difference of but 0.053 volts instead of 0.110 volts, so that when combined with Zn, Cd or Hg the electromotive force always appears to be a function of the negative ion.

The following table will give the values obtained for the single-liquid reversible cells, Zn|Hg, Cd|Hg, Zn|Cd, Zn|Cu, Cd|Cu and Cu|Hg, from actual observation and by calculation from Table VII. The first three series of cells were measured by Bancroft, the last three by myself, as were also the sulphates.

TABLE VIII.

Solution	Zn Hg		Cd Hg		Zn Cd	
	calc.	obs.	calc.	obs.	calc.	obs.
				0.817		
Chloride	1.151	1.151	0.817	0.815	0.334	0.333
Sulphate	1.371		1.037	1.035	0.334	0.334
Iodide	0.846	0.847	0.514	0.515	0.332	0.331
Bromide	0.990	0.991	0.657	0.659	0.333	0.333
Solution	Zn Cu		Cd Cu		Cu Hg	
	calc.	obs.	calc.	obs.	calc.	obs.
Chloride	0.899	0.897	0.565	0.565	0.252	0.252
Sulphate	1.062	1.061	0.728	0.728	0.309	0.306

It is an easy matter to give a formula for these cells if we consider the single potential differences made up of two terms; one due to the metal and the solvent, and the other due to the negative ion. Now we have found that in all cases except with copper the term due to the negative ion is independent of the metal considered. So, for the potential differences $\text{Zn}|\text{K}_2\text{SO}_4$, $\text{Zn}|\text{KCl}$, $\text{Cd}|\text{K}_2\text{SO}_4$, $\text{Cd}|\text{KCl}$, $\text{Hg}|\text{K}_2\text{SO}_4$, $\text{Hg}|\text{KCl}$, $\text{Cu}|\text{K}_2\text{SO}_4$, $\text{Cu}|\text{KCl}$, we may write $A+a$, $A+b$, $B+a$, $B+b$, $C-a$, $C-b$, $D-a$, and $D-b$. We would then have for the cells $\text{Zn}|\text{K}_2\text{SO}_4|\text{Cd}$ and $\text{Zn}|\text{KCl}|\text{Cd}$ the formulæ $A+a-B-a$ or $A-B$, and $A+b-B-b$ or $A-B$ for the electromotive forces; that is, the values of the two cells are equal and independent of the negative ion. For the cells $\text{Cd}|\text{K}_2\text{SO}_4|\text{Hg}$ and $\text{Cd}|\text{KCl}|\text{Hg}$ we should have $B+a-C+a$ or $B-C+2a$, and $B+b-C+b$ or $B-C+2b$. The two values are not equal and a term due to the negative ion comes in, which is twice the value of the term due to the negative ion in the single potential differences. Similarly we should have for $\text{Cu}|\text{K}_2\text{SO}_4|\text{Hg}$ and $\text{Cu}|\text{KCl}|\text{Hg}$, $D-a-C+a$ or $D-C+2a$, and $D-b-C+b$ or $D-C+2b$.

In view of the measurements of Bancroft on Sn, Pb, Bi and Mg combined with Cd or Zn in chlorides, bromides, iodides, sulphates, nitrates, acetates, carbonates and oxalates, in which he found that the electromotive force is a function of the electrode metals and independent of the negative ions, we may conclude that with all of these metals the term due to the negative ion has the same numerical value and the same sign, and consequently disappears when the metals are combined in a one liquid cell. With mercury the values for the various negative ions are the same as with the metals just enumerated but having opposite sign. With copper the term due to the negative ion has the same sign as with mercury, but has a smaller numerical value than the corresponding term with mercury. With platinum the term due to the negative ion has not the same value; and further cells, in which platinum serves as an electrode, vary with the concentration.

Very little work has been done on the measurement of single potential differences with reversible electrodes. Le Blanc¹ made a

¹Zeit. phys. Chem. **12**, 345 (1893).

few measurements by determining the decomposition point of certain normal salt solutions. Neumann¹ has made quite a list of measurements on the potential difference between a metal and normal solutions of sulphates, chlorides, acetates and nitrates of these metals. These measurements were made with the aid of a normal mercury-calomel electrode, consisting of mercury in a normal potassium chloride solution to which an excess of calomel was added. Ostwald gives the value 0.560 volts to this normal electrode, and its value has been found to be extremely constant by Coggeshall.² The method of determining the single potential differences was by measuring the electromotive force of a cell composed of the calomel electrode combined with the metal and electrolyte whose potential difference was desired, and subtracting the value 0.560 volts from this. From these single potential differences may be obtained by addition the values for the electromotive force of reversible cells; and the values thus obtained for reversible cells agree very well with the values directly measured. Now let us further consider the single potential differences involved in one or two concrete examples of a cell composed of two metals and two electrolytes *e. g.* $\text{Zn}|\text{ZnSO}_4|\text{Hg}_2\text{Cl}_2\text{KCl}|\text{Hg}$, $\text{Cu}|\text{CuSO}_4|\text{Hg}_2\text{Cl}_2\text{KCl}|\text{Hg}$ and $\text{Zn}|\text{ZnSO}_4|\text{CuSO}_4|\text{Cu}$. We then have in the first case the four potential difference:

A between Zn and the electrolyte ZnSO_4 .

B between ZnSO_4 and KCl .

C between KCl and Hg .

D between Zn and Hg .

This last value *D* is negligible. The value of the cell is then $A+B+C$, similarly for the second cell we have A_1+B_1+C , and for the third $A+B_2-A_1$. By subtracting the second from the first value $A-A_1+(B-B_1)$ is obtained, and this was found experimentally to agree with the formula $A+B_2-A_1$. The assumption is made from the formulæ given by Planck and Nernst that the values *B*, *B₁*, and *B₂* are very small, but I do not know that there are any measurements that make this entirely justifiable. It is easily seen that the only assumption which need be made, that the sum of the first

¹Ibid. **14**, 225 (1894).

²Zeit. phys. Chem. **17**, 62 (1895).

two cells shall give the third, is that $B_2 = B - B_1$. Now if B_2 is small or zero then B and B_1 may have any values provided that they are equal or nearly so. If, however, the values B and B_1 are not so small as to be neglected, the single potential differences of Neumann are incorrect by just such an amount.

The following values are given by Neumann as the absolute potential of the metals in their normal salt solutions.

TABLE IX.

Metal	Sulphate	Chloride	Metal	Sulphate	Chloride
Mg	1.239	1.231	Bi	-0.490	-0.315
Al	1.040	1.015	As		-0.550
Mn	0.815	0.824	Sb		-0.376
Zn	0.524	0.503	Sn		-0.085
Cd	0.162	0.174	Cu	-0.585	
Tl	0.114	0.151	Hg	-0.980	
Fe	0.093	0.087	Ag	-0.974	
Co	-0.019	-0.015	Pd		-1.066
Ni	-0.022	-0.020	Pt		-1.140
Pb		-0.095	Au		-1.356

It will be seen that the sulphates and chlorides do not vary much. As the solutions are all normal, Neumann explains the differences by the fact that the dissociation cannot be assumed to be complete, and consequently the osmotic pressures of the cation can not be assumed to be equal. To prove that on sufficient dilution the apparent effect of the anion will disappear completely, he measured thallium in solutions of tenth, fiftieth and hundredth normal thallium salts. With the hundredth normal solutions the same value within a millivolt was obtained in every case, and further a very satisfactory increase of potential with dilution. The measurements are not as convincing as they might be if the various halogen acids had been used, in which in other cases the largest effect due to the negative ion has been observed. He did measure hydrochloric and hydrofluoric acid salts, but the remaining salts are salts of organic acids; and Ostwald previously found that all the organic acids gave about the same value, and that very near to sulphuric acid. What influence the fluorine ion may have in other cases I do

not know, as I think no other measurements have been made with it.

I made a few measurements on one-liquid cells reversible with respect to one of the electrodes,

TABLE X.

Electrodes	Electrolyte	Concentration	E. M. F.
Cd Hg	Cd Cl ₂	n / 20	0.814
Cd Hg	KCl	n / 20	0.815
Cd Hg	Cd SO ₄	n / 10	1.041
Cd Hg	K ₂ SO ₄	n / 20	1.034
Cu Hg	Cu SO ₄	n / 20	0.309
Cu Hg	Cu SO ₄	n / 10	0.303
Cu Hg	H ₂ SO ₄	n / 20	0.353
Cu Hg	K ₂ SO ₄	n / 20	0.306
Cd Cu	Cd Cl ₂	n / 20	0.565
Cd Cu	KCl	n / 20	0.565

and found that in every case they agreed very nearly with the values obtained from the cells in which potassium salts served as electrolytes. The most natural conclusion to draw is that the single potential differences are the same in corresponding cells, that is, Cd | Cd Cl₂ is the same as Cd | KCl etc. We are practically forced to this if we consider the potential difference at the cathode independent of the concentration or to be practically independent of the nature of the cation, when this is not the same as the electrode metal, as the measurements of Paschen would indicate. However, the values which would thus be obtained for single potential differences at reversible electrodes do not at all agree with those obtained by Neumann, especially in the case of copper. My values for copper are about the same as those obtained by Ostwald for the free acid.

[To be continued.]