

# On the Contact Potential.

By

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## 1. INTRODUCTION.

When a galvanic cell is constructed out of two half cells, the measurable value of the E. M. F. is the algebraic sum of the potential differences of these two single electrodes and the contact potential which develops at the junction of the two unlike solutions. Thus, whenever the necessity occurs to determine the E. M. F. of one of these single electrodes, it is a matter of first importance to know the value of the contact potential. In general, however, it is impossible to determine the value of the contact potential experimentally, because, by nature, it cannot be measured separately. And, so long as the measurement of the contact potential is impossible, the E. M. F. of the single electrode cannot be determined.

In order to remove this difficulty which lies in the course of E. M. F. measurements of single electrodes, many investigators<sup>1</sup> have deduced theoretical expressions for the calculation of the value of a contact potential. But since the use of these expressions is limited to some special cases of the concentration of solutions and the composition of ions, they are of not much avail in practice.

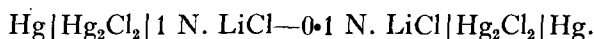
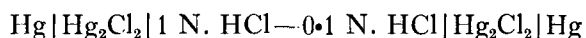
Now, if some method of the conjunction of cells were devised by which no contact potential should develop, the above stated difficulty

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<sup>1</sup> W. Nernst, *Zs. physik. Chem.*, **2**, 613 (1888); *Ibid.*, **4**, 129 (1889); M. Planck, *Wied. Ann.*, **40**, 561 (1890); P. Henderson, *Zs. physik. Chem.*, **59**, 118 (1907); *Ibid.*, **63**, 325 (1908); G. N. Lewis and L. W. Sargent, *J. Amer. Chem. Soc.*, **31**, 363 (1909).

would be swept away. An important guide to the devise of such method of conjunction was given by the theory of W. Nernst<sup>1</sup>, that the contact potential is due to the unequal migration of ions, and on his suggestion, S. Bugarszky<sup>2</sup> devised the following method: if an electrolyte, for example potassium nitrate, is added in high and uniform concentration throughout the entire cell, the current in the cell is carried mainly by the added electrolyte, so that the measurable E. M. F. consists only of the electrode potential differences of the two single electrodes. This is a very appropriate devise for the purpose of eliminating the contact potential. But as the addition of such an electrolyte would bring about some changes in the properties of the original electrode solutions, it is not always a sound method in experimental works.

Another method of eliminating a contact potential, devised by O. F. Tower<sup>3</sup>, consists in the interposition of concentrated ammonium nitrate or potassium chloride solution at the junction of the two electrode solutions. This method has been pursued by many investigators. A. C. Cumming<sup>4</sup> used concentrated solutions of potassium nitrate, ammonium nitrate, or potassium chloride as the connecting solution of the cells of the following type:



He concluded that a concentrated ammonium nitrate solution brought the best result. R. Abegg and A. C. Cumming<sup>5</sup> also found that the ammonium nitrate solution interposed between the two electrode solutions gives a satisfactory result in the case of silver nitrate concentration cells. N. Bjerrum<sup>6</sup> who used a potassium chloride solution

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<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Zs. anorg. Chem.*, **14**, 145 (1897)

<sup>3</sup> *Zs. physik. Chem.*, **20**, 198 (1896).

<sup>4</sup> *Trans. Faraday Soc.*, **2**, 213 (1906).

<sup>5</sup> *Zs. Elektrochem.*, **13**, 18 (1907).

<sup>6</sup> *Zs. physik. Chem.*, **53**, 428 (1905); *Zs. Elektrochem.*, **17**, 58, (1911); *Ibid.*, **17**, 389 (1911).

of various concentrations as a connecting solution, concluded that a saturated potassium chloride solution eliminates not all the contact potentials. He deduced an empirical rule which has thenceforth been adopted in general in the investigation of the physiological solutions; that is, when the saturated and half-saturated solutions of potassium chloride are used as the connecting solution in succession, and if there be no difference in the E. M. F. between them, then the elimination of the contact potential is complete. But if there be a difference, it is equal to the amount of the contact potential still unremoved.

At the present day, following the suggestion of W. Ostwald,<sup>1</sup> it is customary to use a concentrated potassium chloride solution as the connecting solution in almost all investigations of galvanic cells, and it is generally considered that the contact potential can be eliminated in this way. And in fact the elimination seems almost complete when the electrode solutions are very dilute.

The mechanism of the elimination is, however, quite obscure, and we can only say that the concentrated solution of ammonium nitrate or of potassium chloride has the property of eliminating the contact potential. But as the solutions, which are recognized to be effective for the elimination of the contact potential, are concentrated solutions of potassium chloride or of ammonium nitrate, we may draw the following conclusion: a salt solution by which the contact potential is completely eliminated, must possess the following conditions:

- 1) Equal mobilities of the cation and anion.
- 2) The high solubility of the salt, namely, its concentration be far greater than that of electrode solutions.

Potassium chloride nearly fulfils the first condition, and ammonium nitrate the second.

On the other hand, H. A. Fales and W. C. Vosburgh<sup>2</sup> determined

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<sup>1</sup> Ostwald und Luther, *Physiko-chemische Messungen*, 2. Auf., S. 386.

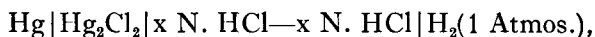
<sup>2</sup> *J. Amer. Chem. Soc.*, **40**, 1291 (1918).

the values of several important single electrodes and contact potentials on the following assumptions :

1) The value of the contact potential which develops at the junction of 1 N. KCl and 4.1 N., 3.5 N., 2.5 N., 1.75 N., or 0.1 N. KCl, is correctly expressed by Nernst's formula :

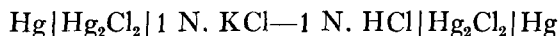
$$E = RT \frac{u-v}{u+v} \log \frac{C_1}{C_2}$$

2) In the cell of the type



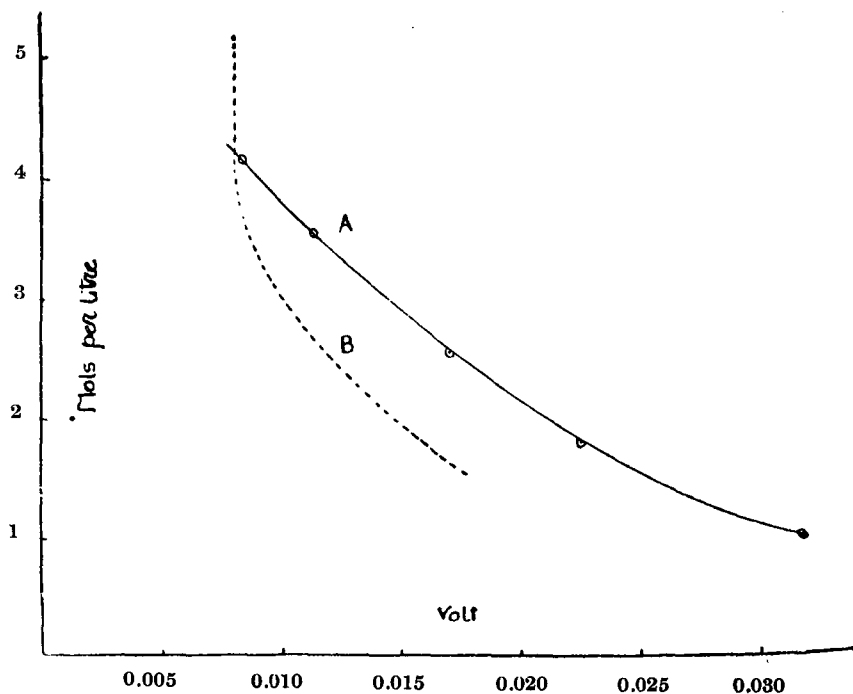
as  $x$  is varied, the electrode potential difference at each electrode changes by the same amount, but in the opposite direction.

Among their investigations there is a series of experiments in which the combination of the type

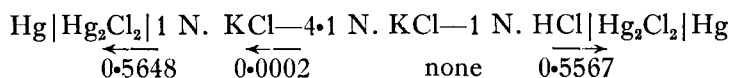


was studied with the interposition of potassium chloride solutions of various concentrations. If we plot the result referring to a rectangular

Fig. 1



coordinate, taking the measured E. M. F. as the abscissa and the concentration of potassium chloride as the ordinate, we obtain the curve A as shown in Fig. 1. According to Fales and Vosburgh, when 4.1 N. KCl is used as a connecting solution, the result is as follows :



and the observed E. M. F. = 0.0083.

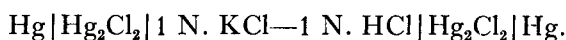
As far as the result is concerned the elimination is almost complete. If, however, the potassium chloride solution only is active in the elimination, the value of the E. M. F. of the cell must remain constant before and behind the concentration of 4.1 N. In other words, the curve must become gradually parallel to the axis of the ordinate before the concentration reaches 4.1 N., as is diagrammatically shown by the curve B.

As to the connecting solution, the more concentrated it is, compared with the electrode solutions, the better seems to be the elimination, and then, if once the contact potential has been eliminated at a certain concentration, no change will take place on the E. M. F. of the cell by further increase of the concentration. If this consideration is justified, no existence of the contact potential at the junction, 4.1 N. KCl—1 N. HCl, must be due to the accidental fact that the curves A and B intersect each other at the point where the concentration of potassium chloride is 4.1 N.

Looking over the literature of cells, it can be inferred that in case of a comparatively high concentration of electrode solutions, it is especially necessary to use a still more concentrated one as the connecting solution. Moreover, as has been stated above, it is desirable to use a salt solution in which the mobilities of the cation and anion are equal.

On the suggestion of Prof. Y. Osaka, the author took up the present investigation to study this problem under the above-stated consideration.

For the cell, the following combination was selected.



The reasons why such combination was selected are three.

1) If electrode solutions were more dilute, as the elimination of the contact potential might be practically complete by a concentrated solution of potassium chloride, we will not be able to know the advantage of using the special connecting solution.

2) The potassium chloride-calomel cell is one of the best known electrodes of its nature.

3) The hydrochloric acid-calomel cell, which contains an electrolyte with ions of very different mobilities, would develop a great contact potential. So it would be advantageous for comparing various connecting solutions.

## 2. EXPERIMENTAL.

### *Apparatus for E. M. F. Measurement.*

All measurements were carried out in an oil thermostat at 25.0°C. The oil used in the thermostat was a transparent machine oil with a boiling point of about 290°C. The E. M. F. was determined by the zero-method with a Leeds and Northrup potentiometer and a D'Arsonval galvanometer.

### *Standard Cell.*

In the preparation of cadmium elements, special attention must be paid to the quality of the mercurous sulphate. According to G. A. Hulett<sup>1</sup>, the best mercurous sulphate is obtained by electrolysis of sulphuric acid (6 : 1) with a current density of 0.5 amp., using platinum as the cathode and mercury as the anode. The product is then washed with a saturated cadmium sulphate solution until no trace of acid can be detected.

Two cadmium elements which were made up of the mercurous sulphate thus prepared, are designated as No. 1 and No. 2. For the

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<sup>1</sup> Zs. physik. Chem., **49**, 483 (1904).

purpose of comparison four more cadmium elements were made up, two of which were prepared with mercurous sulphate of Merck (No. 3 and No. 4) and the other two with the ordinary commercial stuff (No. 5 and No. 6).

The following table represents the values of these cadmium elements compared with Fritz Köhler Weston normal element No. 325 (0.10183 volt).

Number of element	Measured soon after preparation	Measured after two months
1	1.01825	1.01825
2	1.01827	1.01827
3	1.01895	1.01835
4	1.01890	1.01857
5	1.0262	1.0268
6	1.0269	1.0271

From this table it may be seen that elements made up of electrolytically prepared mercurous sulphate bring the best result.

Fig. 2

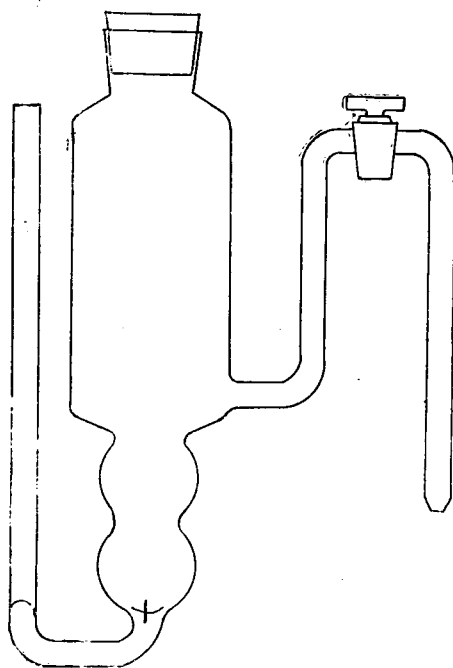
*Calomel Electrode.*

Fig. 2 shows the form of calomel cell used. The advantages of this form of cell are: 1) the form is comparatively simple and it does not need a great quantity of calomel and mercury; 2) the electrode solution can simply be poured into or out of the cell without disturbing the platinum electrode immersed in the mercury.

Though in the ordinary case the cock of the calomel cell is left ungreased, the author, according to W. M.

Clark,<sup>1</sup> obtained a good result by greasing the narrow part of the socket and the wide part of the key to make it turn easily and to prevent the creeping out of the salt.

All vessels as well as the calomel cell, used in the experiments, were treated successively with a chromic acid mixture for three days, a strong solution of potassium hydroxide for a day, a nitric acid for twelve hours, and finally washed thoroughly with water.

#### *Materials.*

Normal hydrochloric acid solution:— Redistilled hydrochloric acid was diluted to a proper degree and standardized with sodium carbonate of Merck. Its concentration was such that, according to Prof. Y. Osaka,<sup>2</sup> it becomes just one normal at 25°C. All the other standard solutions were prepared in the same way.

Normal potassium chloride solution:— Potassium chloride recrystallized three times was fused in a platinum crucible and the proper quantity of it was dissolved.

Potassium nitrate:— After a recrystallization, it was dried at 160°C.

Lithium chloride:— Commercial lithium chloride was precipitated as lithium carbonate. It was then dissolved in pure hydrochloric acid, and as much as possible of the excess of the acid was expelled on a water bath. When it was cooled, lithium chloride crystallized out. These crystals, after being separated from the mother liquor by means of a centrifugal separator, were again dissolved in water. It was again evaporated and cooled—such treatment was repeated several times, and finally a lithium chloride containing no trace of acid was obtained.

Calomel:— Freshly distilled mercury was dissolved in distilled nitric acid of specific gravity 1.2, an excess of mercury being present, then the solution was diluted and it was poured into a dilute solution

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<sup>1</sup> The Determination of Hydrogen Ions, p. 131.

<sup>2</sup> These Memoirs, 4, 113 (1920).



of distilled hydrochloric acid. The precipitated calomel was well washed with water by successive decantations, then with that solution with which it was to be used in a calomel cell. Finally it was shaken with the same solution in a shaking machine for two days.

*Connecting Solutions.*

As has already been pointed out, it is most desirable to use, as the connecting solution, a very concentrated solution of a salt having a cation and an anion the mobilities of which are just equal. Now, as the connecting solution of the first kind, a mixed solution of potassium chloride and potassium nitrate was selected; the mobilities of the ions which are contained in this mixed solution at 25°C. are as follows:

$$K^+ \quad 74.63 \quad Cl^- \quad 75.50 \quad NO_3^- \quad 70.70$$

Now let  $x$  be the percentage of the chlorine ion of the whole anion, then for the solution in which the average value of the mobilities of the anions is equal to the mobility of the cation, we have

$$74.63 \times 100 = 75.50x + 70.70(100 - x)$$

By solving the equation we have for the percentages of the two salts

$$KCl : KNO_3 = 81.87 \text{ mols} : 18.13 \text{ mols.}$$

The mixed solution of this proportion used in the present investigation were as follows:

No. 1.	KCl	3.848	}	mols per litre.
	KNO <sub>3</sub>	0.852		
No. 2.	KCl	2.574	}	" " "
	KNO <sub>3</sub>	0.568		
No. 3.	KCl	1.283	}	" " "
	KNO <sub>3</sub>	0.284		

The connecting solution of the second kind was a mixed solution of ammonium nitrate and lithium chloride. Their proportion was calculated in the same way as in the case of the first kind. The mobilities of the ions are

$$Li^+ \quad 39.78 \quad NH_4^+ \quad 74.70 \quad Cl^- \quad 75.50$$

$$NO_3^- \quad 70.70$$

Let  $x$  be the percentage of the ammonium ion of the whole cation, or that of the nitrate ion of the whole anion, then

$$74.70x + 39.78(100-x) = 75.50(100-x) + 70.70x$$

By the determination of  $x$ , the required proportion will be obtained, which is

$$\text{NH}_4\text{NO}_3 : \text{LiCl} = 89.93 \text{ mols} : 10.07 \text{ mols.}$$

Of the solution of this kind, a solution of comparatively higher concentration can be obtained. The solutions used in the present investigation were

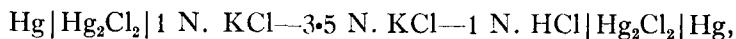
No. 4.	NH <sub>4</sub> NO <sub>3</sub>	8.39	} mols per litre.
	LiCl	0.94	
No. 5.	NH <sub>4</sub> NO <sub>3</sub>	5.59	} " " "
	LiCl	0.63	
No. 6.	NH <sub>4</sub> NO <sub>3</sub>	4.20	} " " "
	LiCl	0.47	
No. 7.	NH <sub>4</sub> NO <sub>3</sub>	2.10	} " " "
	LiCl	0.24	

In the above calculations it was assumed that as all the salts concerned were uni-uni binary, they dissociate in a mixed solution to the same degree.

#### *Method of Junction.*

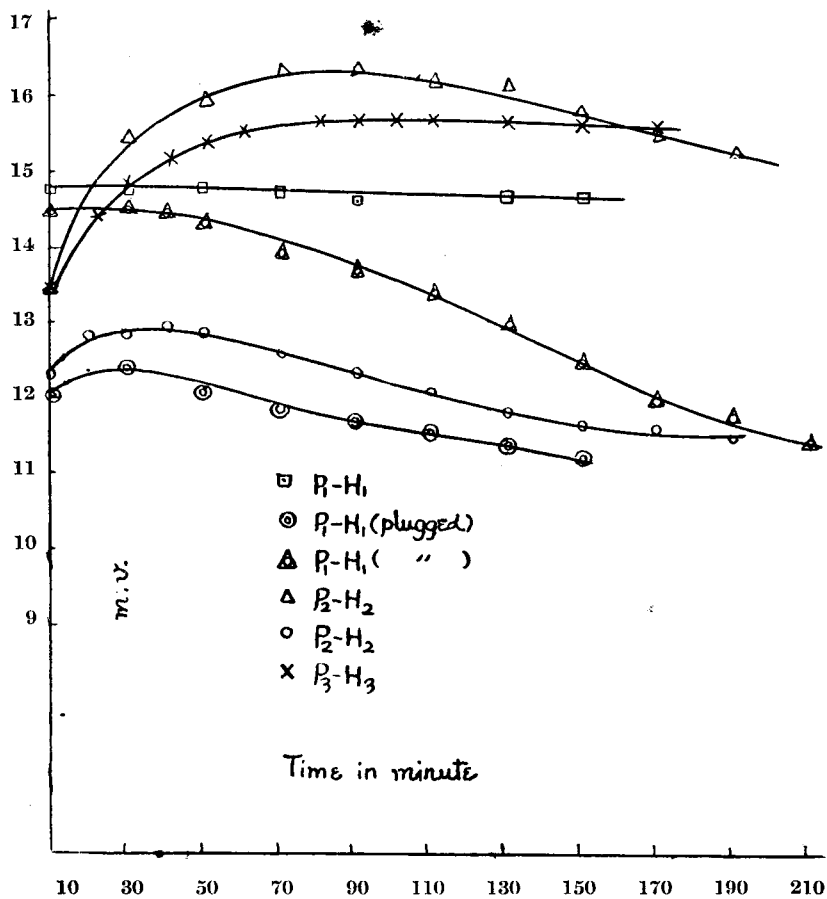
One of the greatest difficulties which we encounter in the course of E. M. F. determination of a galvanic cell with contact potentials is the time effect, that is, the variation of the E. M. F. due to lapse of time. This variation comes from the concentration change of the solutions at their junctions owing to the mechanical mixing and the diffusion which take place at the interface of the two solutions. In the combination of the cells which were used in the present investigation, this effect was considerable.

Fig. 3 shows how the E. M. F. varies with the time in the combination of the type



where P and H denote calomel cells of 1 N. KCl and 1 N. HCl

Fig. 3



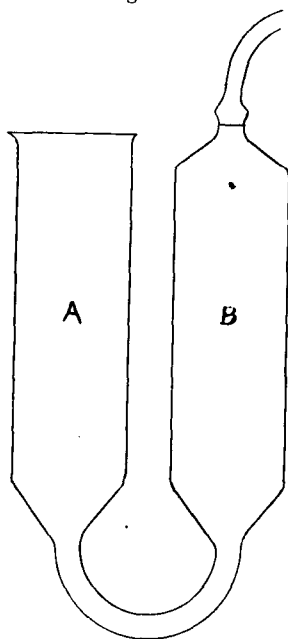
respectively. The first measurement of E. M. F. was taken at exactly ten minutes after the moment when the junctions were made by dipping the side tubes of the component cells into the 3.5 N. potassium chloride solution contained in a small beaker, and successive observations were made every ten or twenty minutes.

This diagram shows that the time effects are very different from one another even when the same electrodes were used. And it may also be seen from it that though the ends of the side tubes were plugged with wooden cones to prevent as far as possible the mechanical flow,

the time effect is still different in each measurement. Clark,<sup>1</sup> in his book, pointed out the necessity of recording the time elapsing after the formation of the liquid junction as a part of the data of the E. M. F., but the above experiments show that such record seems to be of no practical use for finding the true value.

To get around these difficulties there have been several attempts to make a reproducible liquid junction by preventing the mechanical mixing and diffusion. One of the simplest devices is the sandfilling method of Bjerrum,<sup>2</sup> but it seems it does not always give a satisfactory result. The best device both in theory and in practice is the method of making a sharp boundary at the interface of the two unlike

Fig. 4



solutions. G. N. Lewis and F. F. Rupert,<sup>3</sup> Lewis, Brighton and Sebastian,<sup>4</sup> and A. B. Lamb and A. T. Larson<sup>5</sup> devised clever methods which are found to be much more reproducible than the junctions usually made, but these methods seem to be somewhat too complicated for general use.

In the present experiment, a connecting vessel as shown in Fig. 4 was used. At first, the connecting solution is sucked up into the tube B and the side tubes of the component cells are introduced into the tube A to the same level. After the apparatus has attained the temperature of 25° C., the pinch cock on the rubber tubing is opened and the connecting solution is al-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Bjerrum, *Loc. cit.*; G. N. Lewis, T. B. Brighton and R. L. Sebastian, *J. Amer. Chem. Soc.*, **39**, 3245 (1917); C. N. Myers and S. F. Acree, *Amer. Chem. J.*, **50**, 396 (1913).

<sup>3</sup> *J. Amer. Chem. Soc.*, **33**, 299 (1911).

<sup>4</sup> *Loc. cit.*

<sup>5</sup> *J. Amer. Chem. Soc.*, **42**, 229 (1920).

lowed to rise slowly in A. Taking the moment when the side tubes come in contact with connecting solution as the starting point, successive observations are made as quickly as possible. The data obtained in this way are plotted on a time-E. M. F. diagram and the curve obtained by connecting these points is extended and the point of intersection of this curve and the E. M. F. -axis is sought for. This point may represent the E. M. F. at the moment of contact.

The reasons why such a method was used are as follows : as the influence of the diffusion on the E. M. F. may be traced by a very smooth curve on the time-E. M. F. diagram, if the utmost care is taken to prevent the mechanical mixing, we should be able to eliminate the diffusion effect by means of this method. Moreover, even if a mechanical mixing occurs more or less at first, as the mixed boundary, by nature, becomes the diffused boundary in course of time, by this method we should also be able to reduce the mechanical mixing effect.

An example of the results obtained by means of this method is given in the following table :

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl (P <sub>1</sub> —3.5 N. KCl—1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg(H <sub>1</sub> )
Time elapsing after making the contact		E. M. F. (volt)		
The first measurement.				
m	s			
0	20	0.0121		
1	40	0.01245		
2	40	0.0129		
3	30	0.0132		
4	20	0.0134		
5	00	0.0136		
6	20	0.0137		
7	30	0.0139		
9	00	0.0141		
The second measurement.				
m	s			
0	30	0.0115		
1	40	0.0120		
2	30	0.0124		
3	40	0.01275		
4	50	0.0129		
5	40	0.0130		
6	20	0.0131		
7	50	0.01325		
8	40	0.0133		

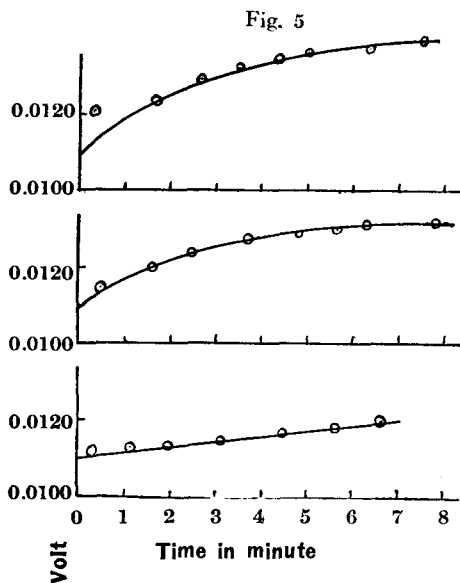
Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl (P <sub>1</sub> )—3.5 N. KCl—1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg·H <sub>1</sub>
Time elapsing after making the contact			E. M. F. (volt)	

The third measurement.

m	s	E. M. F. (volt)
0	20	0.0112
1	10	0.0113
2	00	0.0113
3	10	0.01145
4	30	0.01165
5	40	0.0118
6	40	0.01195

From these data, the required E. M. F. may be obtained graphically as shown in Fig. 5. The mean value thus found is  $0.0110 \pm 0.00000$  volt.

In the following experiment this method of forming a junction was used. By means of this method, however, we cannot always expect



such a fair coincidence of the results as above cited. For example, the following data were obtained in the measurement of the combination P<sub>1</sub>—H<sub>3</sub>.

0.0108  
0.0112  
0.0111  
0.0113

Such inconstancy in data may spring from the following facts:

1) We are often uncertain two or three seconds in the determination of the starting point—the moment of contact. When the inclination of the curve is small against the horizontal axis, the error will be negligible, but when the inclination is large, the error will be more or less appreciable.

2) Though the utmost care is taken in making the liquid junction, more or less mechanical mixing is unavoidable. As has been

already stated, the mixed boundary becomes the diffused boundary in course of time, so the data of the initial part of the measurement—the part affected by the mixed boundary—were discarded. This effect of mixed boundary seems to cease within one minute when two solutions are brought together very gently. In some cases, however, it is very difficult to determine to what extent we may discard the data.

3) Calomel cells, when repeatedly used, produce polarization and give inconstant results; for example the results of the successive measurements of the combination P<sub>1</sub>—H<sub>3</sub> are

0.0108,  
0.0119,  
0.0125.

According to the author's experience, a calomel cell once used must be let stand for an hour at least.

*Preliminary experiment.*

To examine the reproducibility of the contact potential at the liquid junction, a combination of the type

<sup>200</sup>Hg|Hg<sub>2</sub>Cl<sub>2</sub>|1 N. KCl—3.5 N. KCl—1 N. HCl|Hg<sub>2</sub>Cl<sub>2</sub>|Hg  
was measured. The results are represented in the following table. Each datum is the mean value of three or four measurements.

calomel cells used	E. M. F.
P <sub>1</sub> —H <sub>1</sub>	0.0110
P <sub>1</sub> —H <sub>2</sub>	0.0111
P <sub>1</sub> —H <sub>3</sub>	0.0111
P <sub>2</sub> —H <sub>1</sub>	0.0111
P <sub>2</sub> —H <sub>2</sub>	0.0113
P <sub>2</sub> —H <sub>3</sub>	0.0110
P <sub>3</sub> —H <sub>1</sub>	0.0115
P <sub>3</sub> —H <sub>3</sub>	0.0115
Mean	0.0112±0.00021

The result of this cell obtained by Fales and Vosburgh is 0.0114 volt.

<sup>1</sup> The positive current runs through the cell from right to left. This applies to the corresponding parts in the following.

## 3. RESULTS.

## Experiment 1.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—No. 1—	1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. F.		
		P <sub>1</sub> —H <sub>1</sub>			0.0064
		P <sub>1</sub> —H <sub>2</sub>			0.0063
		P <sub>1</sub> —H <sub>3</sub>			0.0061
		P <sub>2</sub> —H <sub>1</sub>			0.0068
		P <sub>2</sub> —H <sub>2</sub>			0.0062
		P <sub>2</sub> —H <sub>3</sub>			0.0069
		P <sub>3</sub> —H <sub>1</sub>			0.0068
		P <sub>3</sub> —H <sub>2</sub>			0.0062
		P <sub>3</sub> —H <sub>3</sub>			0.0070
		mean			0.0065 ± 0.00035

## Experiment 2.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—No. 2—	1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. F.		
		P <sub>1</sub> —H <sub>1</sub>			0.0128
		P <sub>1</sub> —H <sub>2</sub>			0.0129
		P <sub>1</sub> —H <sub>3</sub>			0.0127
		P <sub>2</sub> —H <sub>1</sub>			0.0137
		P <sub>2</sub> —H <sub>2</sub>			0.0128
		P <sub>2</sub> —H <sub>3</sub>			0.0137
		P <sub>3</sub> —H <sub>1</sub>			0.0135
		P <sub>3</sub> —H <sub>2</sub>			0.0125
		P <sub>3</sub> —H <sub>3</sub>			0.0135
		mean			0.0131 ± 0.00047

## Experiment 3.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—No. 3—	1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. F.		
		P <sub>1</sub> —H <sub>1</sub>			0.0257
		P <sub>1</sub> —H <sub>2</sub>			0.0257
		P <sub>1</sub> —H <sub>3</sub>			0.0258
		P <sub>2</sub> —H <sub>1</sub>			0.0265
		P <sub>2</sub> —H <sub>2</sub>			0.0261
		P <sub>2</sub> —H <sub>3</sub>			0.0263
		P <sub>3</sub> —H <sub>1</sub>			0.0255
		P <sub>3</sub> —H <sub>2</sub>			0.0251
		mean			0.0258 ± 0.00045



Experiment 4.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. HCl—No. 4—1 N. KCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used		E. M. F.		
	P <sub>1</sub> —H <sub>1</sub>	0.0031		
	P <sub>1</sub> —H <sub>2</sub>	0.0029		
	P <sub>1</sub> —H <sub>3</sub>	0.0026		
	P <sub>2</sub> —H <sub>1</sub>	0.0023		
	P <sub>2</sub> —H <sub>2</sub>	0.0029		
	P <sub>3</sub> —H <sub>1</sub>	0.0021		
	P <sub>3</sub> —H <sub>2</sub>	0.0022		
	mean	0.0026 ± 0.00039		

Experiment 5.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—No. 5—1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used		E. M. F.		
	P <sub>1</sub> —H <sub>1</sub>	0.0028		
	P <sub>1</sub> —H <sub>2</sub>	0.0028		
	P <sub>2</sub> —H <sub>2</sub>	0.0032		
	P <sub>2</sub> —H <sub>3</sub>	0.0030		
	P <sub>3</sub> —H <sub>1</sub>	0.0027		
	P <sub>3</sub> —H <sub>3</sub>	0.0031		
	mean	0.0029 ± 0.00020		

Experiment 6.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—No. 6—1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used		E. M. F.		
	P <sub>1</sub> —H <sub>1</sub>	0.0086		
	P <sub>1</sub> —H <sub>2</sub>	0.0093		
	P <sub>2</sub> —H <sub>2</sub>	0.0087		
	P <sub>2</sub> —H <sub>3</sub>	0.0087		
	P <sub>3</sub> —H <sub>2</sub>	0.0090		
	P <sub>3</sub> —H <sub>3</sub>	0.0087		
	mean	0.0088 ± 0.00027		

## Experiment 7.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—No. 7—1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used		E. M. F.		
		P <sub>1</sub> —H <sub>1</sub>		0.0201
		P <sub>1</sub> —H <sub>2</sub>		0.0205
		P <sub>2</sub> —H <sub>2</sub>		0.0208
		P <sub>2</sub> —H <sub>3</sub>		0.0206
		P <sub>3</sub> —H <sub>1</sub>		0.0209
		P <sub>3</sub> —H <sub>3</sub>		0.0209
		mean		0.0205 ± 0.00034

## Experiment 8.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—8.39 N. NH <sub>4</sub> NO <sub>3</sub> —1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used		E. M. F.		
		P <sub>1</sub> —H <sub>1</sub>		0.0013
		P <sub>1</sub> —H <sub>2</sub>		0.0021
		P <sub>2</sub> —H <sub>1</sub>		0.0019
		P <sub>2</sub> —H <sub>2</sub>		0.0016
		P <sub>2</sub> —H <sub>3</sub>		0.0019
		P <sub>3</sub> —H <sub>1</sub>		0.0021
		P <sub>3</sub> —H <sub>3</sub>		0.0018
		mean		0.0018 ± 0.00029

## Experiment 9.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	1 N. KCl—6.29 N. NH <sub>4</sub> NO <sub>3</sub> —1 N. HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used		E. M. F.		
		P <sub>1</sub> —H <sub>1</sub>		0.061
		P <sub>2</sub> —H <sub>2</sub>		0.057
		P <sub>2</sub> —H <sub>3</sub>		0.062
		P <sub>3</sub> —H <sub>1</sub>		0.061
		P <sub>3</sub> —H <sub>3</sub>		0.059
		mean		0.060 ± 0.00020

The symbols *a* and *b* in the following tables denote 1/10 N. ZnCl<sub>2</sub> calomel cell and 1/100 N. ZnCl<sub>2</sub> calomel cell respectively.

Experiment 10.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	N/100. ZnCl <sub>2</sub> -3.5 N.KCl-N/10. ZnCl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. E.	
a <sub>1</sub> -b <sub>1</sub>			0.0546	
a <sub>2</sub> -b <sub>2</sub>			0.0555	
a <sub>3</sub> -b <sub>3</sub>			0.0548	
mean			0.0550	

Experiment 11.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	N/100. ZnCl <sub>2</sub> -4.1 N.KCl-N/10. ZnCl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. E.	
a <sub>1</sub> -b <sub>1</sub>			0.0553	
a <sub>1</sub> -b <sub>2</sub>			0.0554	
a <sub>2</sub> -b <sub>1</sub>			0.0557	
a <sub>2</sub> -b <sub>2</sub>			0.0559	
a <sub>2</sub> -b <sub>3</sub>			0.0558	
a <sub>3</sub> -b <sub>2</sub>			0.0557	
a <sub>3</sub> -b <sub>3</sub>			0.0557	
mean			0.0556 ± 0.00022	

Experiment 12.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	N/100. ZnCl <sub>2</sub> -No. 1-N/10. ZnCl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. E.	
a <sub>1</sub> -b <sub>1</sub>			0.0545	
a <sub>1</sub> -b <sub>2</sub>			0.0549	
a <sub>1</sub> -b <sub>3</sub>			0.0552	
a <sub>2</sub> -b <sub>1</sub>			0.0547	
a <sub>2</sub> -b <sub>2</sub>			0.0545	
a <sub>2</sub> -b <sub>3</sub>			0.0550	
a <sub>3</sub> -b <sub>1</sub>			0.0546	
a <sub>3</sub> -b <sub>2</sub>			0.0543	
a <sub>3</sub> -b <sub>3</sub>			0.0546	
mean			0.0547 ± 0.00028	

## Experiment 13.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	N/100. ZnCl <sub>2</sub> -10.18 N. NH <sub>4</sub> NO <sub>3</sub> - N/10. ZnCl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. E.	
a <sub>1</sub> -b <sub>1</sub>			0.0551	
a <sub>1</sub> -b <sub>2</sub>			0.0539	
a <sub>1</sub> -b <sub>3</sub>			0.0550	
a <sub>2</sub> -b <sub>1</sub>			0.0544	
a <sub>2</sub> -b <sub>2</sub>			0.0541	
a <sub>2</sub> -b <sub>3</sub>			0.0544	
a <sub>3</sub> -b <sub>1</sub>			0.0547	
a <sub>3</sub> -b <sub>2</sub>			0.0540	
a <sub>3</sub> -b <sub>3</sub>			0.0543	
mean			0.0544 ± 0.00042	

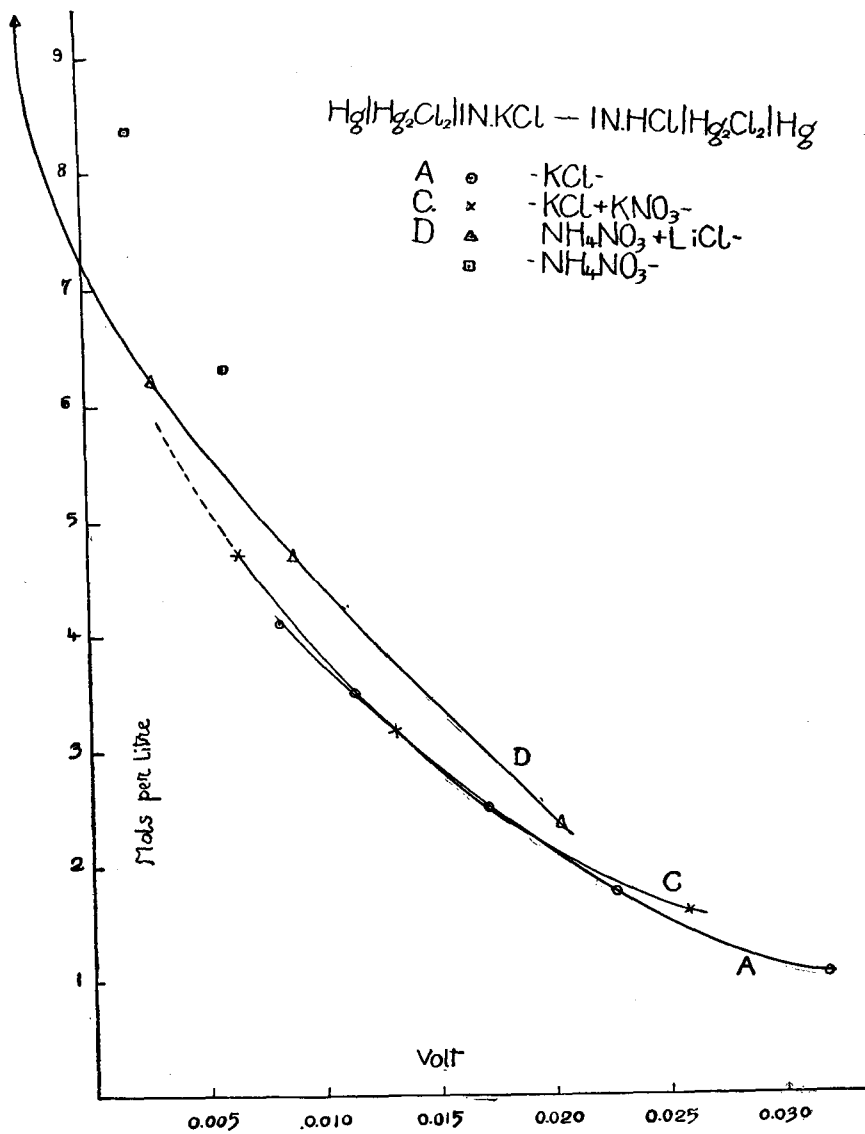
## Experiment 14.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	N/100. ZnCl <sub>2</sub> -6.72 N. NH <sub>4</sub> NO <sub>3</sub> -N/10. ZnCl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. E.	
a <sub>1</sub> -b <sub>1</sub>			0.0553	
a <sub>1</sub> -b <sub>2</sub>			0.0540	
a <sub>1</sub> -b <sub>3</sub>			0.0546	
a <sub>2</sub> -b <sub>1</sub>			0.0545	
a <sub>2</sub> -b <sub>2</sub>			0.0540	
a <sub>2</sub> -b <sub>3</sub>			0.0545	
a <sub>3</sub> -b <sub>1</sub>			0.0547	
a <sub>3</sub> -b <sub>2</sub>			0.0539	
a <sub>3</sub> -b <sub>3</sub>			0.0544	
mean			0.0544 ± 0.00044	

## Experiment 15.

Hg	Hg <sub>2</sub> Cl <sub>2</sub>	N/100. ZnCl <sub>2</sub> -No.4-N/10. ZnCl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	Hg
calomel cells used			E. M. E.	
a <sub>1</sub> -b <sub>1</sub>			0.0550	
a <sub>1</sub> -b <sub>2</sub>			0.0542	
a <sub>1</sub> -b <sub>3</sub>			0.0547	
a <sub>2</sub> -b <sub>1</sub>			0.0544	
a <sub>2</sub> -b <sub>2</sub>			0.0543	
a <sub>2</sub> -b <sub>3</sub>			0.0547	
a <sub>3</sub> -b <sub>1</sub>			0.0547	
a <sub>3</sub> -b <sub>2</sub>			0.0540	
a <sub>3</sub> -b <sub>3</sub>			0.0546	
mean			0.0545 ± 0.0003	

Fig. 6



#### 4. DISCUSSION OF RESULTS.

The results of experiments (from 1 to 9) are represented graphically in Fig. 6. In this figure the results achieved by Fales and Vosburgh, in which potassium chloride solutions were used as the connecting solution, are also added.

It was expected at first that if the connecting solution used in the present experiment were ideal, the curve C and D would begin to become parallel to the ordinate at a certain concentration of the connecting solution, and if the values of the half cells,  $1\text{ N. KCl}|\text{Hg}_2\text{Cl}_2|\text{Hg}$  and  $1\text{ N. HCl}|\text{Hg}_2\text{Cl}_2|\text{Hg}$ , were 0.5648 and 0.5567 respectively, the value of the parallel part of the curve would be equal to the difference between the values of these two half cells, namely, 0.0081 volt.

But the result as represented in the figure shows that though the curve C has a slightly greater tendency to be parallel to the ordinate at the upper part than the curve A, the difference caused by the addition of potassium nitrate to potassium chloride is almost negligible. The concentration of the first kind of connecting solution is insufficient for this cell.

As the second kind of connecting solution can be prepared in a more concentrated solution than potassium chloride solution or the first kind of connecting solution, the author expected some good results from it for the present purpose. The curve D is prone to be parallel to the ordinate gradually as the connecting solution is more concentrated, and may be quite parallel to it at about  $-0.0025$ — $-0.003$  volt. (Pure ammonium nitrate solution shows a different result from the second connecting solution as shown in this figure.)

From the curve D it may be seen that if the consideration which has already been stated at the introduction,—that once the contact potential has been eliminated at a certain concentration of the connecting solution, no change will take place on the E. M. F. of the cell, when the concentration is further increased—is justified, the value of

the cell in the present investigation which does not contain the contact potential is  $-0.0025$ — $-0.0030$  volt. This value was determined by Fales and Vosburgh to be  $0.0081$  volt.

The correctness of the value of Fales and Vosburgh depends on their conclusion that the contact potential at the junction,  $4.1$  N. KCl— $1$  N. HCl, is null, and on the values of the calomel cells which they adopted. As to the values of the calomel cells, the author has no materials to discuss now, but as to the conclusion that the contact potential at the junction,  $4.1$  N.KCl— $1$  N. HCl, is null, the author hesitates to accept it from consideration of Nernst's theory of the contact potential. The author, therefore, concludes from the above consideration that the value containing no contact potential of this cell is  $-0.0025$ — $-0.0030$ .

Accordingly the second kind of connecting solution at a comparatively higher concentration is satisfactory for the cell above considered.

Though the author expected the coincidence of the curves C and D, the results were somewhat different. It might come from the error in the assumption that the salts dissociate in the solution in the same degree. But from Fig. 6, it may be expected that if it were possible to prepare the more concentrated solution of the first kind of solution, the curve C would coincide with the curve D after all.

If we use the electrode solution, of which the difference of mobilities between the cation and anion is not so great, and which is comparatively dilute, the cell gives the constant value within  $1$  m. v., using ammonium nitrate, potassium chloride, the first kind of solution or the second kind of solution over a certain concentration, as shown by the experiments (from 10 to 15). In such case, when we use the concentrated solution of potassium chloride or of ammonium nitrate as the connecting solution, we need not use a special solution owing to the perfect elimination of contact potential.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind guidance.