

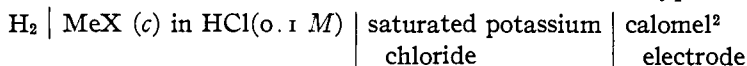
[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE HYDROGEN AND CHLORINE ION ACTIVITIES OF SOLUTIONS OF POTASSIUM CHLORIDE IN 0.1 MOLAL HYDROCHLORIC ACID.

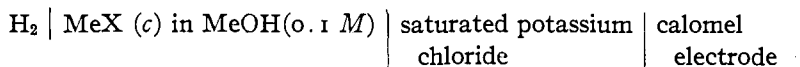
BY HERBERT S. HARNED.

Received July 1, 1916.

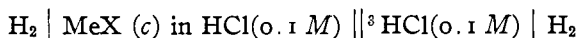
In a recent communication,¹ measurements of cells of the type



and

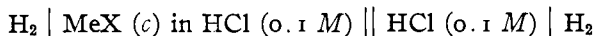


showed that the hydrogen ion activity of the acid and the hydroxyl ion activity of the base were increased by the addition of neutral salts. Further, the evidence obtained with the acid and salt solutions showed that the increase in hydrogen ion activity on the addition of salts differed little, if at all, for the different salts used. At that time a plot was predicted which was thought to give the change in electromotive force of the hydrogen electrode with the change of salt concentration in the acid. Such a change in electromotive force is obviously equal to the electromotive forces of the cells



at different salt concentrations (c). From these, if the hydrogen ion activity of the acid is known, the hydrogen ion activity of the acid-salt solutions can be computed.

The most important difficulty previously encountered in obtaining the electromotive forces of the cells



consisted in the elimination of the liquid potentials set up between the saturated potassium chloride solution and the solutions of the salt in the acid. Saturated potassium chloride, many times recommended for the elimination of liquid potentials, was shown to give different potentials against solutions of different concentrations of the same salt, and against the same concentrations of different salts. A similar series of measurements had been made by Poma⁴ who used a saturated ammonium nitrate solution for the elimination of the liquid potentials. If Poma's results are compared with those mentioned above, it is clear that the liquid

¹ THIS JOURNAL, 37, 2460 (1915).

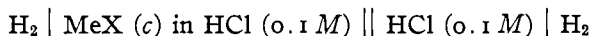
² This symbolizes a series of cells containing salt at a series of concentrations (c).

³ The double bar means that the liquid potential has been eliminated.

⁴ *Z. physik. Chem.*, 87, 197 (1914); 88, 671 (1914).

potentials produced between the solutions of the salts in the acid and the ammonium nitrate solution are greater than those produced when potassium chloride is used. The important point is that neither potassium chloride or ammonium nitrate eliminates these liquid potentials.

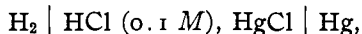
For this reason it is desirable to determine the electromotive forces of the cells



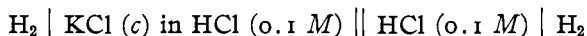
by the use of a method which is free from these liquid potential difficulties. In this paper such a procedure has been adopted.

The Method of this Communication.

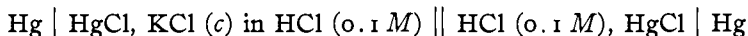
If potassium chloride be added to the hydrochloric acid in the cell



a change in electromotive force will occur. The total effect will be due to the sum of the variations of the two electrodes. Any change in the hydrogen ion activity or the chlorine ion activity will be registered at the hydrogen electrode and the calomel electrode, respectively. This total change in electromotive force will be equal to the sum of the changes in electromotive forces of the cells

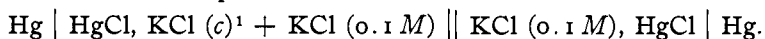


and



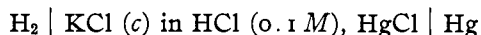
when the concentration of the potassium chloride is the same.

If the ion activities of 0.1 *M* potassium chloride and 0.1 *M* hydrochloric acid are the same, then the electromotive forces of the last series of these cells would equal the electromotive forces of the cells

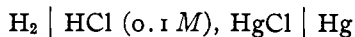


In this communication the following procedure has been adopted:

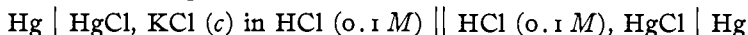
(1) The electromotive forces of the cells



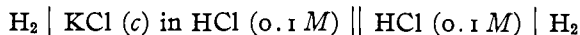
have been measured. From these, the drops in electromotive forces of the cell



on the addition of potassium chloride of different concentrations to the acid have been computed. The electromotive forces of the cells

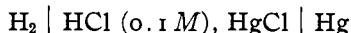


have then been calculated by subtracting the electromotive forces of the cells



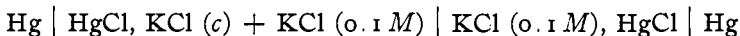
¹ Thus, as will be seen later, a concentration of 0.06 *M* salt in 0.1 *M* hydrochloric acid is compared with 0.16 *M* salt.

obtained from the plot X of the earlier communication from the drops in electromotive forces of the cell

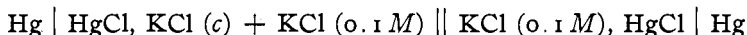


on the addition of potassium chloride.

(2) The electromotive forces of the cells

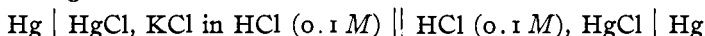


have been measured, and from these the electromotive forces of the cells

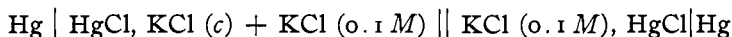


have been obtained by eliminating the liquid potential by means of a suitable formula.

(3) Having obtained the electromotive forces of the cells



and



by the above methods, we are in a position to test the contentions made in the previous article. The last part of this paper will contain a discussion of the values thus obtained and the calculation of the hydrogen and chlorine ion activities of the acid-salt solutions from these values.

Measurements.

1. Cells, $\text{H}_2 \mid \text{KCl (c) in HCl (0.1 M)}, \text{HgCl} \mid \text{Hg}$.—A cell in the form of an H-tube was used, one limb of which contained the calomel electrode, the other the hydrogen electrode. Precautions were taken to separate thoroughly the two limbs of the apparatus, and in no case here recorded did the hydrogen electrode take on a gray coating of mercury. Carefully purified chemicals were employed. Before making up the cell, the calomel paste was washed by decantation six or seven

TABLE I.

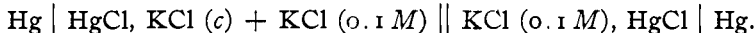
Mols salt per l.	No.	Barometric pressure.	E. M. F. (obs.).	Correction for pressure of H_2 .	Corrected E. M. F.
0.000	No. 1	769.0	0.39915	0.00022	0.39937
0.000	No. 2	765.0	0.39905	0.00029	0.39934
0.060	No. 3	764.5	0.38881	0.00030	0.38911
0.060	No. 4	767.0	0.38889	0.00026	0.38915
0.100		759.5	0.38370	0.00040	0.38410
0.120		765.0	0.38112	0.00029	0.38141
0.200		763.0	0.37439	0.00033	0.37472
0.240		758.0	0.37100	0.00042	0.37142
0.400		764.0	0.36231	0.00031	0.36262
0.600		765.0	0.35360	0.00029	0.35389
0.900		765.0	0.34404	0.00029	0.34433
1.200		765.0	0.33602	0.00029	0.33631
1.800		765.0	0.32268	0.00029	0.32297
2.400		764.5	0.31110	0.00030	0.31140
3.000		765.0	0.30021	0.00029	0.30050

times with the solution to be introduced in the cell and the mixture was allowed to stand three days at 25° before being used. Finally, the cells were kept in a thermostat for a period of two to four days until further shaking of the calomel electrode caused a variation of less than 0.05 of a millivolt over a period of twenty-four hours. All measurements were carried out at 25° with a maximum variation of 0.03°.

Table I shows the values obtained.

The correction of the pressure of the hydrogen was computed by the formula $(RT/2F) \ln 1/p$ as in the previous communication. The corrected electromotive force is what the electromotive force of the cell would be if the pressure of the hydrogen in the cell was one atmosphere¹ at 25°. No. 1 and No. 2 are two completely different cells. No. 3 and No. 4 represent readings taken at the beginning and the end of a twenty-four hour run.

2. Cells, Hg | HgCl, KCl (*c*) + KCl (0.1 *M*) | KCl (0.1 *M*), HgCl | Hg.—It will not be necessary to go into detail in describing these measurements. Let it suffice to say that, if the solutions used in the calomel electrodes in these cells were allowed to stand three or four days at 25° before being introduced, measurements of the cells could be reproduced to within 0.05 of a millivolt. The object of these measurements is to determine the electromotive forces of the cells



Hence, it is necessary to eliminate the liquid potential from the cells in which ion-transference is taking place. To this end a formula, derived by MacInnes² from thermodynamic considerations of the electromotive forces of cells with and without transference, was used. This formula must hold throughout all ranges of concentration. It is

$$E_l = E_t (1 - 1/2n_c)$$

where E_l is the liquid potential, E_t the total electromotive force of the cell, and n_c the cation transference number. The equation of MacInnes gives the same results as would be obtained from the Nernst formula

$$E_l = (n_c - n_a)RT \ln c_1/c_2$$

if the correct activity values for the ions be substituted for the concentrations. Accurate data for the cation transference number of potassium chloride above 0.2 *M* were not available. The value³ 0.495 was used throughout the complete range of concentrations employed.

These results are compiled in Table II. E_t is the electromotive forces of the cells with transference, E_l the liquid potential, and $E_t + E_l$ the electromotive forces of the cells after the liquid potential has been elim-

¹ See Lewis and Randall, *THIS JOURNAL*, 36, 1973 (1914).

² MacInnes, *THIS JOURNAL*, 37, 2301 (1915).

³ Noyes and Falk, *THIS JOURNAL*, 33, 1336 (1911).

inated. Finally, the chlorine ion activities of the potassium chloride solutions have been calculated on the basis that the chlorine ion activity of 0.1 *M* potassium chloride is 0.0730. (This will be referred to later.)

TABLE II.

Conc. of salt (<i>c</i> + 0.1 <i>M</i>).	E_f .	E_f .	$E_f + E_l$.	Activity of the chlorine ion.
0.100	0.00000	0.00000	0.00000	0.0730
0.160	-0.01044	-0.00011	-0.01055	0.1101
0.200	-0.01536	-0.00016	-0.01552	0.1336
0.220	-0.01802	-0.00018	-0.01820	0.1483
0.300	-0.02475	-0.00025	-0.02500	0.1932
0.340	-0.02785	-0.00028	-0.02813	0.2183
0.500	-0.03637	-0.00037	-0.03674	0.3051
0.700	-0.04443	-0.00045	-0.04488	0.4191
1.000	-0.05287	-0.00053	-0.05340	0.5836
1.300	-0.05910	-0.00059	-0.05969	0.7455
1.900	-0.06843	-0.00069	-0.06912	1.0760
2.500	-0.07572	-0.00076	-0.07648	1.4332
3.100	-0.08165	-0.00082	-0.08247	1.8097

3. Comparison of the Cells.—

$\text{Hg} | \text{HgCl}, \text{KCl} (c) + \text{KCl} (0.1 M) || \text{KCl} (0.1 M), \text{HgCl} | \text{Hg}$
and

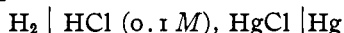
$\text{Hg} | \text{HgCl}, \text{KCl} (c) + \text{HCl} (0.1 M) || \text{HCl} (0.1 M), \text{HgCl} | \text{Hg}.$

The comparison of the above cells can best be understood from Table III.

TABLE III.

Conc. of salt ¹ (<i>c</i>).	(1).	(2).	(3).	(4).
0.060	-0.01022	-0.00010	-0.01012	-0.01055
0.100	-0.01525	-0.00015	-0.01510	-0.01552
0.120	-0.01794	-0.00020	-0.01774	-0.01820
0.200	-0.02463	-0.00030	-0.02433	-0.02500
0.240	-0.02793	-0.00040	-0.02753	-0.02813
0.400	-0.03673	-0.00075	-0.03598	-0.03674
0.600	-0.04546	-0.00125	-0.04421	-0.04488
0.900	-0.05502	-0.00225	-0.05277	-0.05340
1.200	-0.06304	-0.00375	-0.05929	-0.05969
1.800	-0.07638	-0.00775	-0.06863	-0.06912
2.400	-0.08795	-0.01200	-0.07595	-0.07648
3.000	-0.09885	-0.01640	-0.08245	-0.08247

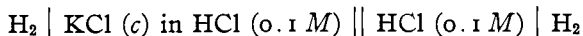
Col. 1 gives the drop in electromotive force of the cell



on the addition of potassium chloride at a concentration of *c* mols per liter.

Col. 2 gives the electromotive forces of the cells

¹ Thus, a concentration of 0.06 *M* salt in 0.1 *M* hydrochloric acid is compared with a concentration of 0.16 *M* salt.



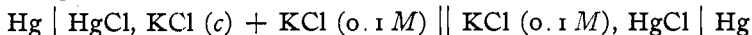
as obtained from the plot X of the previous communication.

Col. 3 gives the electromotive forces of the cells



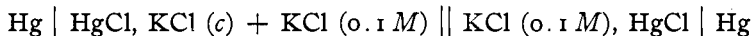
obtained by subtracting the values in Col. 2 from those in Col. 1.

Col. 4 gives the electromotive forces of the cells

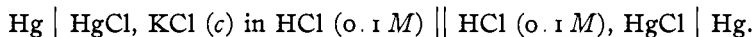


obtained from $E_i + E_i$ in Table II.

Now, as has been stated under the discussion of the general method here employed, if the activity of the chlorine ion in 0.1 *M* hydrochloric acid is equal to the activity of the chlorine ion in 0.1 *M* potassium chloride, then the values for the cells in Cols. 3 and 4 should be identical. As can readily be seen, there is a striking agreement between the values obtained even up to a salt concentration of 3 *M*. The widest deviation between the two series of results is 0.00076 volt at a salt concentration of 0.400 *M*. Furthermore, it is to be noticed that at every concentration of salt, the electromotive force of the cell

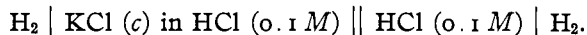


is greater than that of the cell

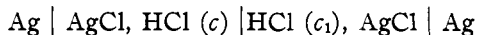


This deviation may be due to two causes; firstly, the X-plot of the previous communication may be faulty; secondly, the ion-activity of the hydrochloric acid may be greater than the ion activity of the potassium chloride at 0.1 *M* concentration. Since the widest deviations occur in the more dilute solutions and since the values in Col. 4 are in every case greater than those in Col. 3, there is great likelihood that the ion activity of the acid is greater than that of the salt.

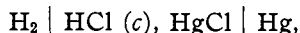
4. Further Discussion of the Results. Final Calculation of the Electromotive Forces of the Cells.—



There is as yet no reliable value for the activity of the hydrogen and chlorine ions in 0.1 *M* hydrochloric acid. From the data obtained by Jahn¹ on the cells



and by Ellis² on the cells



the latter has calculated the activity coefficient³ of 0.1 *M* hydrochloric acid. In this calculation, the assumption was made that at an acid con-

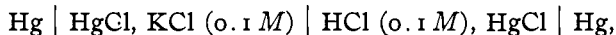
¹ *Z. physik. Chem.*, 33, 545 (1900).

² *THIS JOURNAL*, 38, 737 (1916).

³ The activity coefficient is equal to the activity divided by the concentration.

centration of 0.00167, the activity coefficient equalled the conductance viscosity ratio. Ellis obtained in this manner the value 0.843 for the activity coefficient, which makes the hydrogen ion activity 0.0843. More reliable calculations have been made by Ellis on the activity coefficient of 0.1 *M* potassium chloride from the osmotic pressure calculations of Bates¹ and the electromotive force measurements of MacInnes and Parker.² The values 0.732 and 0.727 for the activity coefficients are obtained from these two sources. If we take the ion-activity of 0.1 *M* potassium chloride to be 0.0730, then there is reason to believe that the ion-activity of 0.1 *M* hydrochloric acid is less than 0.0843. Ellis was aware of the provisional nature of this value.

According to the formula of Lewis and Sargent,³ the liquid potential at the surface of a 0.1 *M* potassium chloride solution and a 0.1 *M* hydrochloric acid solution is -0.0284. Recent measurements of the cell



obtained by Lewis and Sebastian,⁴ give the value -0.0284. This argues that there is little, if any, difference between the ion activities of the acid and the salt at this concentration.

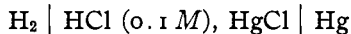
From the results reported in this paper, it is thought that the activity of the ions in 0.1 *M* hydrochloric acid is greater than in 0.1 *M* potassium chloride but only slightly greater. If 0.0730 be accepted to represent the ion-activity of the salt, there is reason to assume that the ion-activity of the acid is 0.0755. The arbitrary nature of this choice is realized; it simply fits in with the large amount of evidence obtained by the author.

The extent of this correction can best be shown by Table IV and the plots in Fig. 1. Table IV contains the following:

(1) Salt concentration (*c*).

(2) The values of Col. A were obtained on the assumption that the ion activities of 0.1 *M* hydrochloric acid equalled the ion-activities of 0.1 *M* potassium chloride. In other words, the electromotive forces of the cells

$\text{Hg} \mid \text{HgCl}, \text{KCl} (c) + \text{KCl} (0.1 M) \parallel \text{KCl} (0.1 M), \text{HgCl} \mid \text{Hg},$
($E_t + E_s$, Table II) were subtracted from the drop in electromotive forces of the cell



on the addition of potassium chloride (Col. 2, Table III). A in Fig. 1 is the plot of these values. Here, the electromotive forces are plotted against the salt concentration (*c*) in gram equivalents per liter.

¹ THIS JOURNAL, 37, 1421 (1915).

² *Ibid.*, 37, 1445 (1915).

³ *Ibid.*, 31, 363 (1909).

⁴ Lewis and Randall, *Ibid.*, 36, 1973 (1914).

(3) The column headed "dotted line" and corresponding to the dotted line in Fig. 1 was obtained as follows:

a. It was assumed that the ion-activity of the acid was 0.0755 and the salt 0.0730.

b. The chlorine ion-activities of the acid-salt mixtures were assumed to be equal to those of the salt solution plus 0.0025 at the different concentrations. This should be a good approximation.

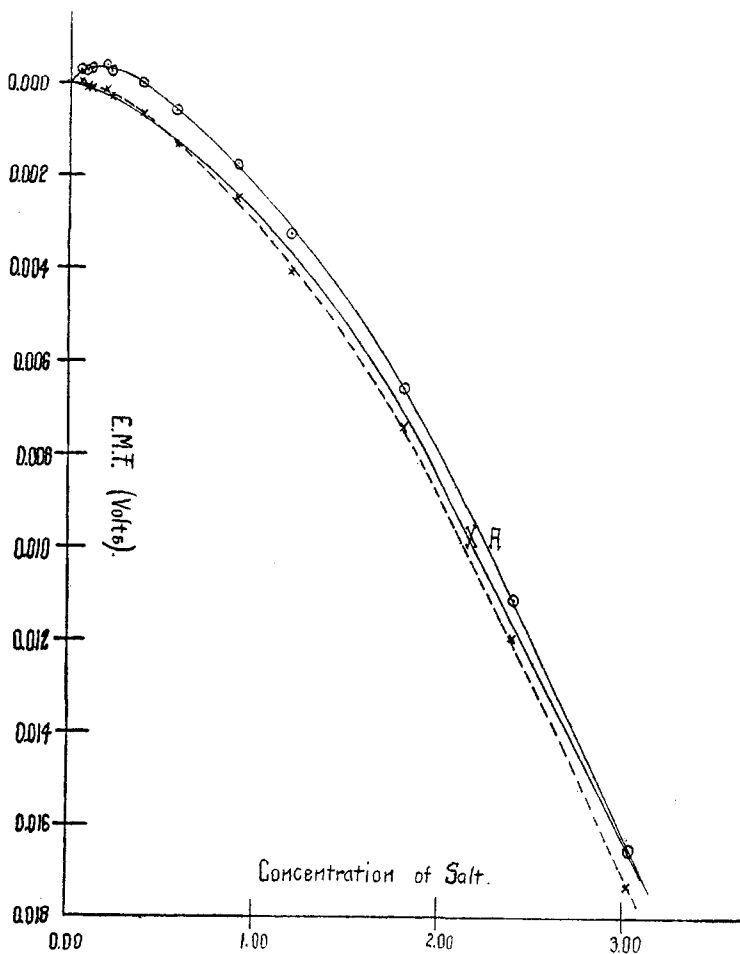
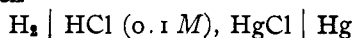


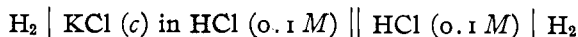
Fig. 1.

c. From this data, the electromotive forces of the cells

$\text{Hg} \mid \text{HgCl}, \text{KCl in HCl (0.1 M)} \parallel \text{HCl (0.1 M)}, \text{HgCl} \mid \text{Hg}$
 were calculated. By subtracting these values from the drops in electro-
 motive force of the cell



on the addition of potassium chloride of concentration (c), the electromotive forces of the cells



are obtained. This gives the final data on the electromotive forces of the last of these cells as obtained from the measurements in this paper.

(4) The Col. X, corresponding to X in Fig. 1, represents the electromotive forces of this last series of cells as obtained from the Plot X of the earlier communication.

(5) The last column represents the difference between the values under "dotted line" and X.

TABLE IV.

Conc. of salt (c).	A.	Dotted line.	X.	Difference.
0.060	0.00033	0.00002	-0.00010	0.00012
0.100	0.00027	-0.00011	-0.00015	0.00004
0.120	0.00026	-0.00017	-0.00020	0.00003
0.200	0.00037	-0.00017	-0.00030	0.00013
0.240	0.00020	-0.00038	-0.00040	0.00002
0.400	0.00001	-0.00065	-0.00075	0.00010
0.600	-0.00058	-0.00128	-0.00125	-0.00003
0.900	-0.00162	-0.00236	-0.00225	-0.00011
1.200	-0.00335	-0.00413	-0.00375	-0.00038
1.800	-0.00726	-0.00808	-0.00775	-0.00033
2.400	-0.01147	-0.01230	-0.01200	-0.00030
3.000	-0.01638	-0.01721	-0.01640	-0.00081

A very close agreement is obtained except at the higher concentrations of salt. In no case is the difference more than 1 millivolt. This may be due to an error in the values obtained in the previous communication. The large increase in the hydrogen ion activity in the more concentrated solutions would tend to diminish the liquid potential between the acid-salt solutions and the solution of saturated potassium chloride there used. This effect would act in such a way as to increase the electromotive force of the cell and thus render the electromotive force decrease of the Plot X too small. We cannot at present be entirely certain of this, for at these high concentrations an error may have been introduced in assuming that the cation transference number of potassium chloride is 0.495 throughout the complete range of concentrations. The evidence offered in this paper would tend to prove that this value varies slightly, if at all. However, if the cation transference number decreases with increasing salt concentration, there will result a smaller difference between the Plot X and the dotted line.

5. The Ion Activities of Solutions of Potassium Chloride in 0.1 M Hydrochloric Acid.—Table V gives these ion activities calculated from the data thus obtained. The hydrogen ion activities are calculated from the electromotive forces in Table IV. Up to a concentration of

0.600 *M* salt, these have been obtained from the values given in Col. X; at salt concentrations higher than this, they have been obtained from the means of the values of Col. X and Col. "dotted line." The chlorine ion activities have been obtained by adding 0.0025 to the values given in Table II. The last column gives the free energy transfer of one gram ion of hydrogen from a solution of 0.1 *M* hydrochloric acid to a solution of 0.1 *M* hydrochloric acid containing potassium chloride at the concentration designated.

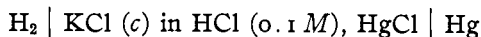
TABLE V.

Conc. of salt (<i>c</i>).	Hydrogen ion activities.	Chlorine ion activities.	Free energy transfer.
0.000	0.0755	0.0755	...
0.060	0.0758	0.1126	-9.65
0.100	0.0759	0.1361	-14.47
0.120	0.0761	0.1508	-19.30
0.200	0.0765	0.1957	-28.95
0.240	0.0767	0.2208	-38.60
0.400	0.0777	0.3076	-72.37
0.600	0.0793	0.4216	-120.6
0.900	0.0826	0.5861	-222.0
1.200	0.0880	0.7480	-382.0
1.800	0.1027	1.0785	-763.3
2.400	0.1211	1.4357	-1172.0
3.000	0.1452	1.8122	-1621.0

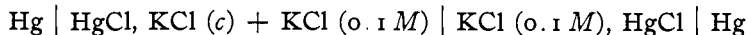
Since an error of 0.00025 volt corresponds to an error of 1% in the ion activity and since there is still an element of guess-work in the calculation of these values, an accuracy of less than 1% is not claimed.

Summary.

1. Measurements of the cells

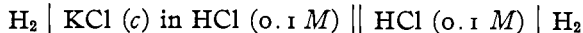


and



up to a concentration of 3 *M* potassium chloride have been made.

2. From these, if the ion activities of 0.1 *M* potassium chloride and 0.1 *M* hydrochloric acid are known, the electromotive forces of the cells



can be calculated.

3. The measurements here recorded, along with those of an earlier communication, indicate that if the ion activity of 0.1 *M* potassium chloride is 0.0730, then the ion activity of 0.1 *M* hydrochloric acid is 0.0755.

4. From these two values, and the measurements of the above cells, the hydrogen and chlorine ion activities of solutions of potassium chloride at different concentrations in 0.1 *M* hydrochloric acid have been computed.