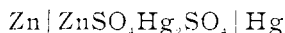# THE TRANSFERENCE NUMBER OF HYDROGEN

BY DOUGLAS MCINTOSH

Transference numbers are usually determined according to the method of Hittorf[1] by electrolyzing a solution and measuring the change of concentration at the anode or cathode. This method is applicable in all cases; but the experimental errors are large. The method of Helmholtz is not applicable in all cases; but seems to have very distinct advantages wherever it can be used.

When two cells of the type

$$Zn \mid ZnSO_4Hg_2SO_4 \mid Hg$$

are connected, mercury to mercury, the effect of their action is to bring the two zinc sulfate solutions to the same concentration. Helmholtz[2] has shown that the electromotive force of such a 'concentration cell without diffusion' can be expressed in terms of the concentrations of the cells, together with the relation obtaining between concentration and vapor pressure; he has shown, further, that the electromotive forces of the allied 'concentration cells with diffusion' can be computed from the same quantities, together with the transference number of the anion of the dissolved electrolyte; and, finally, that the ratio of these two electromotive forces, at any same temperature, is this transference number. His reasoning is essentially as follows:

Let ψ denote the free energy of a solution containing m_1 mass-units of water and m_2 of salt; and let the relative mass $m_1/m_2 = h$ of the water be known as the dilution-value of the solution. We seek the rate of change, with changing concentra-

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[1] Ostwald. Lehrbuch, II, 594.
[2] Ges. Abh. I, 840; II, 979.

tion, of the electromotive force π of a cell containing this solution,— *i. e.* the derivative $d\pi/dh$; that it may be integrated between the two dilution-values of the concentration cell. To find this function, the work-equivalents imparted in the reversible electrolytic addition of unit mass of salt to the solution must be equated with the corresponding change $\partial\psi/\partial m_2$ of the free energy of the latter, and the resulting expression be differentiated with respect to h.

Writing f for the free energy of that mass, of the solution, that contains unit mass of salt,— whereby f becomes a function of h alone for the isothermal changes here considered, — we have as initial equation

$$\psi = m_2 f, \tag{1}$$

whence

$$\frac{\partial\psi}{\partial m_2} = f(h) + m_2 \frac{df}{dh} \frac{\partial h}{\partial m_2}$$

$$= f - h \frac{df}{dh},$$

since $h = m_1/m_2$, and therefore $\partial h/\partial m_2 = -h/m_2$. Now, when q mass-units of salt are brought into solution by unit current in unit time, the quantity of electric work-equivalents added to the solution in the dissolving of unit mass of salt is $-\pi/q$. So

$$\pi = -q\left(f - h \frac{df}{dh}\right),$$

whence

$$\frac{d\pi}{dh} = qh \frac{d^2f}{dh^2}, \tag{2}$$

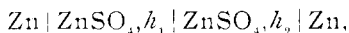or, for the electromotive force between two cells having the dilution values h_1 (dilute) and h_2 (concentrated),

$$\pi_1 - \pi_2 = q\int_{h_2}^{h_1} h \frac{d^2}{dh^2} f(h) \cdot dh. \tag{2a}$$

Helmholtz evaluates this integral, in terms of the vapor pressures of the two solutions, by showing that

$$\frac{d^2f}{dh^2} = v \frac{dp}{dh},$$

and then expressing p and v, the pressure and the specific volume of the vapor, as functions of h. Here the volume is, of course, regarded as a function $v[p(h)]$.

The above concentration cell, when arranged to act with diffusion, would be

$$Zn \mid ZnSO_4, h_1 \mid ZnSO_4, h_2 \mid Zn,$$

in the working of which the migration velocities u and v of the cation and the anion must be considered. When an equivalent of metal dissolves in one side of this cell, with passage of the quantity of electricity E, the quantity $E\dfrac{u}{u+v}$ migrates to the other side, leaving an increase of $E\dfrac{v}{u+v}$. This same quantity of the cation is lost by the other side: for one equivalent of metal falls out there and $E\dfrac{u}{u+v}$ arrives by migration. Of the anion, the quantity $E\dfrac{v}{u+v}$ migrates of necessity from the second side to the first, to balance the increase of the cation at the latter place. An addition of electric work-equivalents to either solution is, therefore, accompanied by an addition of $\dfrac{v}{u+v}$ mass-units of salt where 1 was added in the case previously considered; so this electric work, $\pi_1 - \pi_2$ for unit quantity, assumes a $\dfrac{v}{u+v}$-fold value, and in place of equation (2a) we must write

$$\pi_1 - \pi_2 = \frac{v}{u+v}\int_{h_2}^{h_1} h\,\frac{d^2}{dh^2} f(h) \cdot dh. \tag{2b}$$

It is apparent, therefore, that the ratio of the two electromotive forces (2b) and (2a) is the quantity $v/(u+v)$, the transference number of the anion. So far as I can see at present there are but two tacit assumptions involved in this equation. The first is that the solute shall be non-volatile under the conditions of the experiment. The second is that the transference number of the anion is the same in the two solutions.

The equation of Helmholtz has been tested experimentally by Moser.[1] With $ZnSO_4 100H_2O$ and $ZnSO_4 800H_2O$, the ratio of the electromotive forces was 0.64, while Hittorf found 0.636 by the direct method, and Kohlrausch obtained 0.65. With $ZnCl_2 100H_2O$ and $ZnCl_2 750 H_2O$ the ratio was 0.71, while Hittorf found 0.70. These two instances suffice to show the accuracy of the method, and it is rather surprising that it has not been used more frequently when one considers that two measurements of the electromotive force are all that are necessary and that it is not even essential to know the concentrations of the solutions.

Practically all the work on the transference numbers of the acids has been done by Hittorf. Large and unexpected variations occur for small changes of concentration and these must be due, in part, to experimental error. While it has been proved for many electrolytes that the transference numbers change with the concentration, it is very improbable that the variations can ever be as large as some of the data for the acids would lead one to suppose. The experiments of Nernst and Loeb[2] — perhaps the most carefully performed research on this subject — show that, with many substances, the transference number changes very little with the concentration; as can be seen from the following table for silver nitrate :

Table I

Temp	Conc	$\dfrac{v'}{u + v}$	Temp	Conc	$\dfrac{v'}{u + v}$
20°	0.1043	0.528	0°	0.025	0.538
26	0.0521	0.524	26	0.0105	0.524
26	0.025	0.522	26	0.0105	0.521

At the suggestion of Prof. Bancroft I have attempted to determine the transference numbers for hydrogen in different

[1] Sitzungsber. Akad. Wiss. Wien, **92**, 652 (1885); **94**, 115, (1885).
[2] Zeit. phys. Chem. **2**, 948 (1888).

acids by the Helmholtz method, using gas electrodes. A gas
cell consisting of hydrogen over two concentrations of acid is
apparently quite similar to the concentration cells studied ex-
perimentally by Moser. Platinum strips touch the surface of
the acid and form a hydrogen electrode after being saturated
with hydrogen. This is really a hydrogen electrode because it
has been shown experimentally that the electromotive force does
not change when the platinum is replaced by another conductor
having the property of occluding hydrogen. That the hydrogen
electrode in an aqueous solution of an acid is completely rever-
sible has been shown by Le Blanc.[1] We should therefore expect
that the ratio of the electromotive forces of the cells $\mathrm{Pt_H} \mid c_1\mathrm{HCl}$
$c_2\mathrm{HCl} \mid \mathrm{Pt_H}$ and $\mathrm{Pt_H} \mid c_1\mathrm{HCl} \mid \mathrm{Hg_2Cl_2Hg} \mid \mathrm{Hg_2Cl_2}c_2\mathrm{HCl} \mid \mathrm{Pt_H}$ should
give the transference number for the anion. This arrangement
is open to the criticism that hydrochloric acid is a volatile solute
and that the Helmholtz formula does not necessarily apply to
this case. To this objection there are two answers to be made.
With dilute solutions, the partial pressure of hydrochloric acid
can certainly be considered as practically though not theoretically
zero. If the formula is inapplicable to this case, entirely differ-
ent results should be obtained when sulphuric acid and mercu-
rous sulphate are substituted for hydrochloric acid and mercurous
chloride.

Apparatus. — The apparatus used was similar to that of
Peirce[2] and of Smale.[3] The glass cylinders used for holding the
various gases were from 30 cm to 40 cm long and about 3 cm
in diameter. Several electrodes were used in each cylinder and
were kept in place by elastic bands. To set up the apparatus,
the lower end of the cylinder was placed in a beaker containing
the electrolyte; the air was removed by suction and then the gas
was passed in by means of a bent tube ending in a capillary
point and reaching to the top of the cylinder.

The connections between the electrolytes in the cells with
diffusion were made by siphons plugged with filter paper, or by

[1] Zeit. phys. Chem. **12**, 333 (1893).
[2] Wied. Ann. **8**, 98 (1879).
[3] Zeit. phys. Chem. **14**, 577 (1894).

means of moistened yarn — the latter method proving very satis-
factory.

The electrodes were of platinum and had a surface of about
2 cm² and making them somewhat larger or smaller had no per-
ceptible effect on the electromotive force.   Platinum wires were
welded to the electrodes and fastened to copper wires. These latter
were adjusted in small glass tubes so that only platinum came in
contact with the gas and the electrolyte.   Since variable and
unsatisfactory results were obtained with unplatinized elec-
trodes, they were platinized[1] by making them cathodes in a
platinic chloride solution to which a little lead acetate had been
added, the current being furnished by an accumulator.   Since
platinum black absorbs both chlorine and platinic chloride, the
electrodes were then made cathodes in a solution of sulphuric
acid, the current passing for about an hour.   The electrodes
were kept in boiling water for several hours until no two showed
a difference of potential when connected with a galvanometer.
They were left in boiling water until needed, so as to prevent
absorption of oxygen.   If burned off in the blast-lamp they ab-
sorb much less gas and do not prove so constant.

Gold electrodes were also tried and proved to be much like
unplatinized platinum.   On covering them with a thick coating
of palladium black, from a palladium chloride solution, they were
much improved, but still inferior to the platinum electrodes,
although Böttger[2] found them very satisfactory.   The measure-
ments were therefore made entirely with platinum electrodes.

The measurements were made by the Poggendorff compen-
sation method, using either a Lippmann upright electrometer
or a galvanometer as the zero instrument.   With the electrom-
eter, measurements could be made to 0.0005 V and with the
galvanometer to half of this, an accuracy quite sufficient in view
of the other sources of error.   Two resistance boxes of 1100 and
10,000 ohms were used and the various resistances were checked.
As working element a Leclanché cell proved very satisfactory.

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[1] Lummer and Kurlbaum. Verh. phys. Ges. Berlin, **14,** 56 (1895); Kohl-
rausch. Wied. Ann. **60,** 315 (1897).

[2] Zeit. phys. Chem. **24,** 253 (1897).

It gave an electromotive force of about 1.51 V and varied but 0.03 V in several months. It was compared before each set of measurements with a standard Clark that agreed exactly with one from the Imperial German Institute. Its value was taken as $1.4336 - (15 - t)0.0011$ V. A cupron cell of 0.7 V was also available as working element. It was checked against a cell[1] $Cu \mid CuSO_4 Hg_2SO_4 \mid Hg$, this latter being in turn compared with a Clark cell. The electromotive force of the copper-mercury standard cell was taken as 0.361 V at 17°. All measurements were made at the ordinary temperature, about 18° C.

Hydrogen electrodes. — The hydrogen was made from pure zinc and sulphuric acid, and freed from impurities by passing through potassium permanganate, potassium hydroxide and water. This gives the same results as electrolytically prepared hydrogen.[2] The hydrogen was stored in a large balloon flask over water that had been freed from air by boiling.

The acids used were bought as chemically pure and were all found to be free from impurities excepting the hydrobromic acid and the hydriodic acid, the first of which contained free bromine and the second free iodine. These two acids were purified by distillation in a current of hydrogen. The solutions were made up to the given concentrations with a possible error of about one-fourth of one percent, greater accuracy than this being superfluous.

Since the measurements varied from time to time, a large number of observations were made and each value given in the following table is the mean of a series. The maximum variation was about 0.0015 V. In Table II are given the results for hydrogen concentration cells with diffusion, the electrolytes being hydrochloric, hydrobromic, hydriodic, sulphuric and oxalic acids. Under column I are given the concentrations expressed in liters per reacting weights; under II the values found by Smale[3] and under III my own determinations.

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[1] Jour. Phys. Chem. **2**, 185 (1898).
[2] Glaser. Zeit. Elektrochemie, **15**, 355 (1898).
[3] Zeit. phys. Chem. **14**, 577 (1894).

Table II

Hydrogen concentration cells with diffusion

I Conc	II Smale	III Found	I Conc	II Smale	III Found
Hydrochloric acid			Sulphuric acid		
1 : 10	0 0186	0.0183	1 : 10	0.0108	0.0092
1 : 100	0.0338	0.0350	1 : 100	0.0172	0.0187
1 : 1000	0.0549	0.0544	1 : 1000	0.0259	0.0289
10 : 100	0.0170	0.0183	10 : 100	0.0097	0.0097
10 : 1000	0.0359	0.0360	10 : 1000	0.0172	0.0193
100 : 1000	0.0210	0.0216	100 : 1000	0.0081	0.0102
Hydrobromic acid			Oxalic acid		
1 : 10	0.0194	0.0196	1 : 10	....	0.0060
1 : 100	0.0367	0.0364	1 : 100	....	0.0126
1 : 1000	0.0606	0.0571	1 : 1000	....	0.0230
10 : 100	0.0192	0.0204	10 : 100	....	0.0084
10 : 1000	0.0409	0.0417	10 : 1000	....	0.0135
100 : 1000	0.0186	0.0197	100 : 1000	....	0.0111
Hydriodic acid			Hydriodic acid		
1 : 10	....	0.0183	10 : 100	....	0.0178
1 : 100	....	0.0355	10 : 100	....	0.0350
1 : 1000	....	0.0573	100 : 1000	....	0.0184

In the experiments on the hydrogen concentration cells without diffusion, a U-tube, containing mercury, the mercurous salt of the acid as depolarizer and the two concentrations of the acid, was interposed between the two solutions surrounding the hydrogen electrodes. Other metals than mercury might have been taken without changing the electromotive force, as was predicted by Ostwald and verified experimentally by Goodwin.[1]

The mercurous salts were all made in the same general way as the mercurous[2] iodide. One hundred and twenty-five grams of air-dried mercurous nitrate were dissolved in two liters of water containing 20 cc nitric acid. Fifty grams of dissolved potassium iodide were added to the clear liquid, drop by drop, stirring vigorously the while. After running in the potassium iodide the liquid was shaken vigorously for fifteen minutes so as to maintain the closest contact between the precipitate and the mother-

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[1] Zeit. phys. Chem. **13**, 577 (1894).
[2] Jour. Pharm. Chem. (6) **6**, 612, (1897).

liquor, the precipitate changing from greenish-yellow to a much brighter color. The liquid was then left in the dark for twenty-four hours and well shaken at intervals. After that, the precipitate was washed ten times by decantation with two liters of water each time; washed on a filter-paper and dried in an air-bath at 50°. The product is a yellow salt of much the same color as lead chromate. No indications of decomposition were noticed with any of the mercurous salts in spite of the fact that no particular care was taken to preserve them from the light.

In Table III are given the data for hydrogen concentration cells without diffusion and the transference number of the anion as obtained by the method of Helmholtz from the ratio of the electromotive forces in Tables II and III. In Table IV are given Hittorf's data[1] and, under sulphuric acid, three measurements by Wiedemann,[2] these latter being marked W. There are no direct measurements for oxalic acid.

Table III

Hydrogen concentration cells without diffusion

Conc	E.M.F.	$\dfrac{v}{u+v}$	E.M.F.	$\dfrac{v}{u+v}$	E.M.F.	$\dfrac{v}{u+v}$
	Hydrochloric acid		Hydrobromic acid		Hydriodic acid	
1 : 10	0.1174	0.156	0.1218	0.161	0.1029	0.178
1 : 100	0.2253	0.155	0.2208	0.164	0.2246	0.158
1 : 1000	0.3394	0.160	0.3644	0.157	0.3500	0.164
10 : 100	0.1132	0.162	0.1281	0.159	0.1242	0.158
10 : 1000	0.2295	0.157	0.2750	0.151	0.2314	0.143
100 : 1000	0.1328	0.163	0.1266	0.156	0.1116	0.165
	Mean	0.159	Mean	0.158	Mean	0.161
	Sulphuric acid		Oxalic acid			
1 : 10	0.0575	0.160	0.0402	0.149	....	....
1 : 100	0.1120	0.167	0.0850	0.148	....	....
1 : 1000	0.1789	0.162	0.1303	0.176	....	....
10 : 100	0.0558	0.174	0.0510	0.165	....	....
10 : 1000	0.0984	0.196	0.0746	0.181	....	....
100 : 1000	0.0555	0.184	0.0706	0.157	....	....
	Mean	0.174	Mean	0.163		

[1] Pogg. Ann. **106**, 337 (1859).

[2] Ibid, **99**, 177 (1856).

Table IV

Conc	$\dfrac{v}{u+v}$	Conc	$\dfrac{v}{u+v}$	Conc	$\dfrac{v}{u+v}$
Hydrochloric acid		Hydrobromic acid		Sulphuric acid	
0.38	0.193	0.7	0.178	0.533	0.174
1.34	0.168	Hydriodic acid		2.3	0.177
3.00	0.161	0.61	0.201	9.62	0.212
5.21	0.171	15.2	0.258	15.9	0.206
11.77	0.218	Sulphuric acid		0.54	0.176W
78.1	0 210	0.055	0.400	0.89	0.189W
....	....	0.14	0.288	3.61	0.176W

These figures show that the transference numbers hold together very well but are considerably lower than Hittorf's values. It seems probable from the measurements with the gas cells that the transference number varies little, if at all, when the dilution changes from one to one thousand liters. The values obtained from the gas cells cannot be considered as right. Kohlrausch[1] has given 63 as the most probable value for the migration velocities of chlorine and iodine as ion at infinite dilution and 18°. From the conductivity measurements, the migration velocity of bromine as ion must also be 63, while sulphate is probably 67. Taking these figures and the mean values for the transference numbers from Table III, we find for the migration velocity of hydrogen, 333 in HCl, 336 in HBr, 328 in HI, 318 in H_2SO_4. The mean is 328, while Kohlrausch's value is 290. The most probable value for the transference number of hydrogen in the three halogen acids is 0.823 and for the transference number of the anion 0.177. It is clear that, for some reason, the Helmholtz equation is not applicable to these cells. The volatility of the solute can hardly be the cause of the error, so that the volatility of the hydrogen and its solubility in water would seem to be the chief points in which a hydrogen electrode differs from a zinc or a copper electrode. It is hoped that the development of this idea may form the subject-matter of a second paper.

Although it was not within the scope of this paper to con-

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[1] Wied. Ann. **50**, 385 (1893).

sider the application of Nernst's theory of electromotive forces[1]
to the gas cells, it seemed a pity not to utilize the data obtained
to their fullest extent and the values for the gas cells with and
without diffusion have therefore been calculated, taking 290 for
the migration velocity of hydrogen and 63 for the migration
velocity of the halogen. The values for the dissociation have
been taken from Kohlrausch.[2] The results for the cells with
diffusion are given in Table V. In the second column are the
values calculated by Smale,[3] who does not state what numbers
he took for the migration velocities. In the third column are
the values calculated from Kohlrausch's figures. In the remain-
ing columns are the experimental data for the three halogen
acids. In Table VI are the calculated and experimental values
for the cells without diffusion.

Table V

Conc	Smale	Calc	HCl	HBr	HI
1 : 10	0.0172	0.0190	0.0183	0.0196	0.0183
1 : 100	0.0367	0.0372	0.0350	0.0364	0.0355
1 : 1000	0.0568	0.0555	0.0544	0.0571	0.0573
10 : 100	0.0188	0.0199	0.0183	0.0204	0.0178
10 : 1000	0.0379	0.0397	0.0360	0.0417	0.0350
100 : 1000	0.0190	0.0188	0.0216	0.0197	0.0184

Table VI

Conc	Calc	HCl	HBr	HI
1 : 10	0.1073	0.1174	0.1218	0.1029
1 : 100	0.2101	0.2253	0.2208	0.2246
1 : 1000	0.3136	0.3394	0.3644	0.3500
10 : 100	0.1124	0.1132	0.1281	0.1242
10 : 1000	0.2243	0.2295	0.2750	0.2314
100 : 1000	0.1062	0.1328	0.1266	0.1116

If we compare the mean of the values for the three halogen
acids with the calculated values, it will be seen that the cells
without diffusion give uniformly higher values than the theo-

[1] Zeit. phys. Chem. 4, 129 (1889).
[2] Wied. Ann. 26, 196 (1885).
[3] Zeit. phys. Chem. 14, 577 (1894).

retical, while the cells with diffusion give, as a rule, slightly lower values than those calculated. The percentage as well as the absolute variation is much smaller for the cells with than for the cells without diffusion.

Having the hydrogen electrode made up, it seemed worth while to measure the electromotive force of the cell formed by combining it with a normal calomel electrode. The calomel electrodes were made from carefully purified material and were compared by checking one against the other. Those used agreed to within two millivolts. The data are given in Table VII.

Table VII

Hydrogen and calomel electrodes

Conc	HCl	HBr	HI	H_2SO_4	$H_2C_2O_4$
1	0.313	0.312	0.325	0.340	0.355
10	0.358	0.356	0.361	0.365	0.381
100	0.396	0.401	0.410	0.401	0.408
1000	0.436	0.455	0.461	0.439	0.433

It was thought that it might be possible to gain some informa-tion as to the reason for the low values for the transference num-ber of the anions, as given in Table III, by studying the behavior of cells with chlorine electrodes. If we have the two combina-tions $Pt_{Cl} | c_1HCl | c_2HCl | Pt_{Cl}$ and $Pt_{Cl} | c_1HCl | Pt_H | c_2HCl | Pt_{Cl}$, the ratio of the two electromotive forces should give the trans-ference number of hydrogen. For this reason some measure-ments were made with chlorine electrodes. Owing to the limited time at my disposal, I was not able to study the matter as thor-oughly as I should have wished and the results can only be con-sidered as preliminary.

Chlorine electrodes. — The apparatus was similar to that used for hydrogen. The hydrochloric acid was saturated with washed chlorine, made from manganese peroxide. Platinum electrodes were used and the cell was measured after standing twenty-four hours carefully protected from the light. The current flows in the opposite direction to that of the hydrogen cell, through the cell from the concentrated to the dilute solution.

In Table VIII are the data for the chlorine concentration cells with and without diffusion, together with the transference number for hydrogen. The cells without diffusion were not measured directly as reversed cells. The single cells were measured and the values for the double cells obtained by subtraction. The electromotive forces of the cells $Pt_H | HCl | Pt_{Cl}$ are 1.368 V for normal hydrochloric acid, 1.486 V for tenth-normal hydrochloric acid and 1.555 V for hundredth-normal acid.

Table VIII

Chlorine concentration cells

Conc HCl	With diffusion	Conc HCl	With diffusion	No diffusion	$\dfrac{u}{u+v}$
0.2 : 1	0.1180	1 : 10	0.1032	0.118	0.874
0.2 : 10	0.2177	1 : 100	0.1315	0.187	0.703
0.2 : 100	0.2543	10 : 100	0.0411	0.069	0.596

It will be noticed that the transference number varies enormously. This is not surprising because the measurements are very difficult to make and exceedingly unsatisfactory when made. Even if the variations in the transference number were due entirely to experimental error, the mean of the three measurements is 0.724, which differs widely from the most probable value, 0.823. The discrepancy may be due to the action of chlorine on the electrode, the electrolyte, or the water. On the other hand, it is a curious coincidence, though possibly nothing more, that 0.724 is about eighty-eight percent of 0.823, while the mean of the values for hydrochloric acid in Table III, 0.159, is about eighty-eight percent of 0.177. In other words, the found value seems to be the same percentage of the calculated values in the two cases. This point will be examined more carefully in the future.

Incidentally the chlorine electrodes were measured against the normal calomel electrode. The values are 0.957 V for five-normal hydrochloric acid, 1.064 V for normal, 1.138 V for tenth-normal and 1.160 V for hundredth-normal acid.

Bromine electrodes. — A few measurements were made with bromine and iodine electrodes for concentration cells with dif-

fusion. The bromine and iodine cells were made up in test-
tubes, the various solutions being left with an excess of bromine
or iodine for several days. They were shaken from time to time.
Except when the electromotive force of a cell was being deter-
mined, the solutions were carefully protected from the light.
The platinum electrodes were saturated with bromine or iodine
by electrolyzing normal solutions of the acids with the platinum
electrodes as anodes.

The bromine concentrations were determined at 21° by add-
ing a measured portion of the solution to an excess of potassium
iodide and titrating with sodium thiosulphate, using starch as an
indicator. The iodine concentrations were determined by titra-
tion with sodium thiosulphate.

The values for the bromine concentration cells with diffusion
and for the bromine electrode against the normal calomel elec-
trode are given in Table IX, the concentration of the bromine in
the solutions being given in grams per liter.

Table IX

Bromine concentration cells

Conc HBr	With dif- fusion	Conc HBr	Conc Bromine	Calomel electrode
1 : 10	0.112	1	207.20	0.817
1 : 100	0.249	10	45.93	0.918
1 : 1000	0.266	100	39.24	1.023
10 : 100	0.127	1000	34.81	1.062
10 : 1000	0.162			
100 : 1000	0.031			

Since the concentration of the bromine varies greatly, no
measurements were made of the hydrogen electrode against the
bromine electrode. A few experiments were made with iodine
cells having different iodine concentrations,[1] the results of which
are given in Table X, the iodine concentrations being grams per
liter.

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[1] Theoretically, this is analogous to a hydrogen electrode under varying
pressures.

Table X

Concentration cells with iodine

Conc HI	Conc Iodine	Cell	E.M.F.
1	153.40	1 : 1(a)	0.049
1(a)	17.21	1 : 1(b)	0.075
1(b)	3.20	1(a) : 1(b)	0.028
10	13.02	10 : 10(a)	0.037
10(a)	1.73	10 : 10(b)	0.050
10(b)	0.32	10(a) : 10(b)	0.015

Iodine electrodes. — Saturated solutions of iodine in various concentrations of hydriodic acid were arranged as concentration cells with diffusion and as an iodine electrode against the normal calomel electrode. The results are given in Table XI, the iodine concentrations being grams per liter.

Table XI

Iodine concentration cells

Conc HI	With diffusion	Conc HI	Conc Iodine	Calomel electrode
1 : 10	0.0679	1	153.40	0.239
1 : 100	0.1224	10	13.02	0.302
1 : 1000	0.1928	100	0.83	0.363
10 : 100	0.0604	1000	0.26	0.451
10 : 1000	0.1197			
100 : 1000	0.0829			

Berthelot[1] has shown that a compound $KInI_2$ exists in solution. This was confirmed by Le Blanc and Noyes[2] who showed from the conductivity and freezing-point phenomena, that this compound changed, with increasing dilution, into potassium iodide and iodine — the conductivity at infinite dilution having about the same value as potassium iodide in water. It is therefore not improbable that compounds such as $HBrnBr_2$ and $HInI_2$ are formed. It would, of course, be impossible to apply the Helmholtz formula to measurements with the bromine and iodine

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[1] Ann. Chim. Phys. (5) **21**, 375 (1880).
[2] Zeit. phys. Chem. **6**, 397 (1890).

electrode until more is known about the conditions prevailing in the solutions.

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The general results of this investigation are :

1. The Helmholtz method of determining transference numbers is not applicable to gas cells.

2. It is probable that the source of error is to be found in the solubility of the electrode in the electrolytic solution.

3. It is probable that the transference number for hydrogen in hydrochloric acid does not change with the dilution between normal and thousandth-normal solutions.

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