# The Free Energy of Dilution and the Activities of the Ions of Hydrogen Iodide in Aqueous Solutions

J. N. Pearce
*State University of Iowa*

A. R. Fortsch
*State University of Iowa*

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## TIES OF THE IONS OF HYDROGEN IODIDE IN
### AQUEOUS SOLUTIONS

J. N. PEARCE AND A. R. FORTSCH

Because of their anomalous behavior solutions of strong electro-
lytes have long occupied the attention of numerous investigators.
Many attempts have been made to provide a theoretical expla-
nation of the abnormalities. Of the various solution properties
the free energies of dilution and the activities of the ions have
been especially studied. From calculations based on the assump-
tion that a common ion at any given concentration has the same
mobility regardless of the associated ion Lewis[1] has concluded that
the chlorides, bromides and iodides of hydrogen and of the alkali
halides are equally dissociated in 0.10 M solutions. In order to
explain changes in the transport numbers of the ions he advances
two hypotheses: (1) "that all the ions increase in mobility with
increasing ion-concentration, the increase being relatively greater,
the greater the original mobility; (2) that all the ions decrease in
mobility with increasing ion-concentration, the decrease being
greater the smaller the original mobility." He favors the first
of these and advances as probable causes: (1) a gradual dehydra-
tion which although undoubtedly present, does not play a domin-
ant part, and (2) an added increase in the ordinary conductivity
of the electrolyte due to a conduction of the Grotthus type.

MacInnes [2] using the same assumption has found that the alkali
chlorides are equally dissociated in 0.01 M solutions. His observa-
tions led him to assume that the activity of the chloride ion is in-
dependent of the cation associated with it. The similarity of the
potassium ion and the chloride ion with respect to atomic weight,
atomic volume, ionic mobility and other properties, led him to as-
sume that their activities are also equal in solutions of potassium
chloride.

Of the various investigations only those most closely connected
with this research will be mentioned here. Noyes and MacInnes [3]
have computed the mean activity coefficients of the ions of potas-

[1] Lewis, J. Amer. Chem. Soc., 34, 1631 (1912).
[2] MacInnes, Ibid., 41, 1086 (1919).
[3] Noyes and MacInnes, Ibid., 42, 239 (1920).

sium chloride, hydrogen chloride, lithium chloride and potassium
hydroxide for solutions ranging in concentration from 0.001 M
to 1.0 M. They have compared these activities with the correspond-
ing conductance-viscosity ratios. From the facts obtained they
conclude that the conductance ratio can no longer be regarded as
even an approximate measure of the activity of the ions of largely
ionized substances in their mass-action and thermodynamic rela-
tions. Harned[4], on the basis of theoretical considerations, has
developed a semi-empirical relation between the activity coefficient
of an electrolyte and the molal concentration and he has calculated
the activities of the various ions from the experimental data of
himself and others. He finds that the activity coefficient of an ion
is a function of the total ion concentration or activity, and not a
function of its own concentration. Furthermore, he concludes
that the assumptions of Noyes and MacInnes (loc. cit.) are true
within certain limits and that the theory of complete ionization of
strong electrolytes is a good working hypothesis. In connection
with the theory of complete ionization of strong electrolytes, we
may note that it was first suggested by Noyes[5] and was further
developed and substantiated by Milner[6], Ghosh[7], Bjerrum[8], Bron-
sted[9], Hill[10] and others. Finally we come to the very complete
work of Lewis and Randall.[11] They discuss the four methods of
experimentally determining activity coefficients, namely, activity
from the vapor pressure of the solvent; activity from vapor pres-
sure of the solute; activities from electromotive force; and activity
coefficients from freezing point data. They also give the numerical
values of the activities of the ions at different concentrations,
determined by one or more of the above methods.

A very important relation in regard to ionic activity was pointed
out by Lewis and Randall[11] and at about the same time independ-
ently by Pearce and Hart[12]. Lewis and Randall, using the data
of Bates and Kirschmann[13] on the partial vapor pressures of the
hydrogen halides, showed that the activities of the chloride, bro-
mide and iodide ions are equal at equal concentrations. Using
the electromotive force method, Pearce and Hart also proved the

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[4] Harned, J. Amer. Chem. Soc., 42, 1808 (1920); 44, 352 (1922).
[5] Noyes, Arts and Sciences, St. Louis Exposition, 4, 389 (1904).
[6] Milner, Phil. Mag., (6) 23, 551 (1918); 25, 753 (1913); 35, 352 (1918).
[7] Ghosh, J. Chem. Soc., 113, 449, 627, 707 (1918).
[8] Bjerrum, Z. Elektrochem., 24, 321 (1918); Z. anorg. Chem. 109, 275 (1920).
[9] Bronsted, J. Amer. Chem. Soc., 42, 761 (1920).
[10] Hill, Ibid., 43, 254 (1920).
[11] Lewis and Randall, Ibid., 43, 1152 (1921).
[12] Pearce and Hart, Ibid., 43, 2483 (1921).
[13] Bates and Kirschmann, Ibid., 41, 1991 (1919).

equality of the activities of the chloride and bromide ions at equal concentrations.   Since the electrometric method is the more direct and more accurate for work with dilute solutions we thought it worth while to test further the equivalence of the halide ions.  To this end we have extended the investigations to include the determination of the free energy of dilution and the activities of the ions in aqueous solutions of hydrogen iodide.

### APPARATUS AND MATERIALS

The general method employed in this research is similar to that described by Linhart, [14] the iodide electrode being substituted for the chloride.   The potassium iodide used in preparing the silver iodide was purified by recrystallizing twice from conductivity water.   The silver nitrate was the "Baker's Analyzed" product and was used without further purification.   The silver iodide was made by precipitation from a solution of potassium iodide.   The precipitate was first washed with distilled water until the washings gave no test for iodides, and then washed several times with conductivity water, the whole operation being carried out at night. It was finally stored under conductivity water, care being taken to exclude all light from the product.   By using these precautions the silver iodide could be preserved indefinitely without darkening. The metallic silver used in preparing the electrodes was obtained by electrolysis of a solution of silver nitrate, using a platinum wire as anode and a current of 4 to 5 amperes.   This gave a finely divided mass of metallic silver which was carefully washed and stored under conductivity water until needed.   Hydrogen iodide was made by passing washed hydrogen sulphide gas into an aqueous suspension of pure resublimed iodine.   The product was fractionally distilled and the fraction of constant boiling point separated.   This was kept in a flask over a trace of red phosphorus and was freshly distilled in a current of pure hydrogen gas when needed.

In making up the solutions approximately the required amount of hydrogen iodide was added to conductivity water which had been previously boiled, and about one liter of the solution was made up.   The cell, which held approximately 550 c. c., was thoroughly cleaned and then charged.   To this end the platinum wire at the bottom was closely packed with the finely divided silver crystals and covered by a layer of silver iodide, the cell was then rinsed several times with the solution, filled to the proper volume,

[14] Linhart, J. Amer. Chem. Soc., 41, 1175 (1919).

the hydrogen electrodes were inserted, and finally the cell was placed in a large oil-bath to come to equilibrium. The time required for equilibrium was from four to eight days, depending somewhat on the concentration of the acid used. The exact concentration of the hydrogen iodide used in each cell was determined at the end of each set-up, the iodine content being accurately determined in duplicate by precipitation with silver nitrate solution.

The hydrogen electrodes were prepared by the method of Lewis, Brighton and Sebastian [15]. Two platinum gauze electrodes were electrolyzed in a one per cent solution of platinum chloride with a current of about 0.05 ampere. The direction of the current was alternated every two hours. The preparation of the electrodes was completed by electrolyzing first in a dilute solution of potassium hydroxide and then in a dilute sulphuric acid solution. They were then thoroughly washed in conductivity water and allowed to stand in water for several hours, after which they were placed in the cell.

The hydrogen gas was obtained by the electrolysis of a strong sodium hydroxide solution. The gas was passed through a solution of potassium pyrogallate, then through concentrated sulphuric acid, and on through the saturator into the cell. The saturator was merely a system of bulbs containing a solution of the same strength as that in the cell and thus any change in concentration due to unsaturated hydrogen gas was avoided. The flow of hydrogen through the cell was regulated by means of a stop-cock to about 60 bubbles per minute.

The measurement of the potentials was made on a Wolff potentiometer, the standard of reference being a certified cadmium-Weston cell (No. 4554: 1.01871 volt at 23°).

### ACCURACY OF METHOD

Electromotive force readings were taken on the two electrodes independently and unless the variation between the two was less than 0.04 m. v. the process of preparation was repeated. Cases where repetition was necessary were very rare. All electromotive force readings were corrected by applying the formula:

$$E = \frac{0.00019837T}{2} \, log_{10} \, \frac{760}{x}$$

where $E$ is the correction, $T$ the absolute temperature, and $x$ is the partial pressure of the hydrogen. The value of $x$ was determined by means of a standard barometer, the readings being corrected

[15] Lewis, Brighton and Sebastian, J. Amer. Chem. Soc., 41. 1175 (1919).

for latitude, altitude and temperature. Preliminary experiments were made to determine the effect of the rate of bubbling. It was found that the rate could be varied from 30 to 250 bubbles per minute without affecting the constancy of the readings.

The temperatures of the experiments were 25°, 30° and 35°. They were taken in the order named and then to ascertain whether any changes had occurred during the experiment the temperature was again lowered to 25° and readings were again taken. The time required to complete this work was ten days. In the preliminary work it was found that there is a variation which becomes apparent when the electrodes are left in the solution over sixty hours. By removing the electrodes, allowing them to stand in concentrated nitric acid for an hour or more, and replatinizing this effect could be reduced to 0.10 m. v. or less in solutions whose concentrations were below 0.02 M. In the more concentrated solutions, however, it was apparently impossible to eliminate the variation in the electrodes, but at any one temperature the electromotive forces became constant showing that equilibrium had been reached. When four consecutive readings taken two hours apart and differing among themselves by less than 0.04 m. v. were secured, this was considered as evidence that equilibrium had been attained. The greatest variation of the electromotive force readings between the initial 25° set and the final 25° set was 0.85 m. v. for the highest concentration. Furthermore, a slight opalescence was obtained by adding a chloride to the solution secured by allowing the electrodes to stand in pure concentrated nitric acid. At a hydrogen iodide concentration of 0.24608 M the amount of silver deposited was larger but did not exceed a few milligrams. At still higher concentrations than this the amount of silver deposited on the platinum became considerable and no consistent readings could be obtained.

### MEASUREMENTS OF THE CELLS

Table I gives the final values of the electromotive forces of the cells at various concentrations and at 25°, 30° and 35°.

The values of E for the concentration 0.005 M were obtained by assuming E as an empirical quadratic function of (c), using the three concentrations, 0.01981, 0.01045 and 0.00505. The values for E for 0.100 M were obtained in a similar manner using the concentrations, 0.24608, 0.12972 and 0.07914. It will be noted that a change in the sign of E occurs between the concentrations 0.07914 and 0.05049 M. This is due doubtless to the fact that silver iodide is extremely insoluble, and by reason of the common

TABLE I

THE ELECTROMOTIVE FORCES OF THE CELLS

$H_2 \mid HI, AgI \mid Ag.$
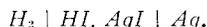
| c.<br>1000 g. | $E_{25}$<br>volts. | $E_{30}$<br>volts. | $E_{35}$<br>volts. |
|---|---|---|---|
| 0.24608 | —0.06905 | —0.06864 | —0.06829 |
| 0.12972 | —0.03615 | —0.03556 | —0.03531 |
| 0.10000 | —0.02273 | —0.02202 | —0.02162 |
| 0.07914 | —0.01210 | —0.01125 | —0.01073 |
| 0.05049 | +0.01006 | +0.01128 | +0.01235 |
| 0.01981 | +0.05735 | +0.05931 | +0.06083 |
| 0.01045 | +0.08825 | +0.09060 | +0.09262 |
| 0.00505 | +0.12417 | +0.12707 | +0.12964 |
| (0.00500) | +0.12453 | +0.12744 | +0.13991 |

ion effect a small concentration of hydrogen iodide is sufficient to reduce the concentration of the silver iodide to such an extent that the potential of the cell is reversed.

The free energy decrease accompanying the cell reaction at the various concentrations is given in Table II. The free energy decreases ($-\Delta F$) in joules is obtained by multiplying the corresponding value of the electromotive force in volts by 96494. The data are self explanatory.

TABLE II

THE FREE ENERGY CHANGES ATTENDING THE CELL REACTION

| c.<br>1000 g. | $(-\Delta F)_{25}$<br>joules | $(-\Delta F)_{30}$<br>joules | $(-\Delta F)_{35}$<br>joules |
|---|---|---|---|
| 0.24608 | — 6663. | — 6623. | — 6589. |
| 0.12972 | — 3488. | — 3431. | — 3407. |
| 0.10000 | — 2193. | — 2125. | — 2086. |
| 0.07914 | — 1167. | — 1088. | — 1035. |
| 0.05049 | + 970. | + 1088. | + 1191. |
| 0.01981 | + 5533. | + 5723. | + 5869. |
| 0.01045 | + 8516. | + 8742. | + 8937. |
| 0.00505 | +11982. | +12262 | +12509. |
| 0.00500 | +12016. | +12297. | +12545. |

The values of the temperature coefficients, $a$ and $\beta$, were calculated from the free energy data of Table II by means of the relation:

$$(-\Delta F)_t = (-\Delta F)_{25} [1 + a (t - 25) + \beta (t - 25)^2].$$

The free energy decrease and the heat content decrease accompanying the cell reaction are related by the fundamental thermodynamic equation:

$$\frac{d\left(\frac{-\Delta F}{T}\right)}{dT} = \frac{-\Delta H}{T^2}$$

Upon substituting the expression for ($-\Delta F$) as a temperature func-

tion, performing the differentiation indicated and rearranging the terms we obtain the relation:

$$(-\Delta H)_{25} = (-\Delta F)_{25} [1 - 298.09\alpha].$$

By means of the relation we have calculated the heat content decrease accompanying the cell reaction at the given concentrations. These are incorporated in Table III.

TABLE III

THE HEAT CONTENT DECREASE ACCOMPANYING THE CELL
REACTION

| c. 1000 g. | $\alpha \cdot 10^6$ | $\beta \cdot 10^6$ | $(-\Delta H)_{25}$ joules |
|---|---|---|---|
| 0.24608 | — 1277. | + 17.7 | —9199. |
| 0.12972 | — 4211. | +188.6 | —7867. |
| 0.10000 | — 7909. | +272.6 | —7168. |
| 0.07914 | —16151. | +445.4 | —6789. |
| 0.05049 | +25909. | —309.2 | —6524. |
| 0.01981 | + 7608. | —153.9 | —7016 ? |
| 0.01045 | + 5699. | — 74.8 | —5953. |
| 0.00505 | + 4950. | — 53.1 | —5699. |
| 0.00500 | + 4950. | — 54.9 | —5715. |

It will be noted that the values of $\alpha$ and $\beta$ change sign between the concentrations 0.05049 M and 0.07914 M. Ellis[16] likewise notes a change in the sign of $\alpha$ for similar cells containing hydrochloric acid between the concentrations 0.33757 M and 0.10040 M. In his case, however, the change is due to a distinct change in the temperature effect, whereas, in the case of hydriodic acid in every instance the free energy of the cell reaction is greater the higher the temperature, the change being caused by a change in the sign of the electromotive force of the cell. At some concentration intermediate to 0.05049 M and 0.07914 M the electromotive force and hence the free energy decrease is zero. Thus the values of $\alpha$ change with dilution from a small negative number to an infinitely large negative number, and then from an infinitely large positive number to a small positive number. We are here dealing apparently with a case where the sign changes from positive to negative by passing through infinity, rather than by passing through zero. This is mathematically possible. Except for the one value at 0.01981 M the values of $-\Delta H_{25}$ show an increase (positively) with decrease in the concentration similar to those found by Ellis for hydrochloric acid. The values of $(-\Delta H)$ for hydriodic acid, however, are much smaller and are negative instead of positive.

From the free energy decrease attending the cell reaction at

[16] Ellis, J. Amer. Chem. Soc., 38, 737 (1916).

the various concentrations (Table II) we can obtain, by adding algebraically, the free energy decrease attending the transfer of one mole of hydrogen iodide from a solution of any given concentration (c) to one exactly 0.100 M. These values are given in Table IV.

### TABLE IV
### THE FREE ENERGY DECREASE ATTENDING THE TRANSFER OF ONE MOLE OF HYDROGEN IODIDE FROM CONCENTRATION (c) to 0.100 M

| c. 1000 g. | $(-\Delta F)_{25}$ joules | $(-\Delta F)_{30}$ joules | $(-\Delta F)_{35}$ joules |
|---|---|---|---|
| 0.24608 | + 4469. | + 4498. | + 4503. |
| 0.12972 | + 1295. | + 1306. | + 1321. |
| 0.07914 | — 1028. | — 1036. | — 1086. |
| 0.05049 | — 3163. | — 3213. | — 3278. |
| 0.01981 | — 7727. | — 7848. | — 7956. |
| 0.01045 | —10709. | —10867. | —11023. |
| 0.00505 | —14175. | —14386. | —14596. |
| (0.00500) | (—14210.) | (—14422.) | (—14631.) |

For the sake of comparison let us consider the transfer of one mole of hydrogen iodide from 0.01045 M to 0.100 M, and from 0.00500 M to 0.05049 M. In the first case the value of $-\Delta F_{25}$ is -10709 joules; in the second case the corresponding value is -11046 joules. For hydrochloric acid Noyes and Ellis [17] found for the transfer from 0.00948 M to 0.100 M $-\Delta F$ to be 11044 joules, and from 0.003378 M to 0.3324 M, 10924 joules. As these concentration changes are approximately tenfold they may be compared with the theoretical value 11418 joules, (2.303 N R T). It will be seen that during the range of concentration 0.00500 M to 0.05049 M hydrogen iodide functions more nearly as a perfect solute than hydrogen chloride. As we shall see later, this is shown also by the values of the activity coefficients.

### THE CALCULATION OF THE ACTIVITY COEFFICIENTS

The values of the electromotive force at concentration 0.00500 M were found by assuming that E is a quadratic function of the concentration, using the values 0.00505, 0.01045 and 0.01981 for the concentrations and the corresponding values of the electromotive forces at 25°. The cell combination was of the type:

$$H_2 \mid HI\ (0.005\ M),\ AgI\ Ag - Ag\ AgI,\ Hi\ (c) \mid H_2.$$
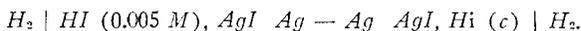
The product of the activity coefficients of the ions has been calculated according to the usual formula:

$$-\Delta F = E \cdot F = RTlog\frac{a\frac{+}{2} \cdot a\frac{-}{2}}{a\frac{+}{1} \cdot a\frac{-}{1}} = RTlog\frac{(c_2)^2 a\frac{+}{2} \cdot a\frac{-}{2}}{(c_1)^2 a\frac{+}{1} \cdot a\frac{-}{1}}$$

[17] Noyes and Ellis, J. Amer. Chem. Soc., 39, 2532 (1917).

where $a_1^+$, $a_1^-$ and $a_2^+$, $a_2^-$ represent the activities of the two ions
and the activity coefficients at the concentrations $c_1$ and $c_2$, re-
spectively. The other symbols have their usual significance.
These computations have been made on the assumption
that the product of the activities of the two ions, $a^+ \cdot a^-$, and the
product of the activity coefficients, $a^+ \cdot a^-$, for 0.005 M hydrogen
iodide have the same value as for 0.005 M hydrogen chloride. Ac-
cording to Noyes and MacInnes[3] this value is $(0.965)^2$ or 0.9312,
while according to Lewis and Randall [11] it is $(0.948)^2$ or 0.8968.
The results of these calculations are collected in Table V. Column
3 gives the values of the product of the activity coefficients,
$a_H^+ \cdot a_I^-$, referred to 0.9312 as a basis, while column 4 gives the
corresponding values referred to 0.8968. These values were plot-
ted against the concentrations on a large scale and the values of
$a_H^+ \cdot a_I^-$ corresponding to round concentrations were read off. The
square roots of these values give us the geometric mean activity
coefficients of the ions. These and the corresponding values for
hydrochloride acid, added for the sake of comparison, are given in
Table VI.

TABLE V

ACTIVITY COEFFICIENT PRODUCTS AT MEASURED
CONCENTRATIONS

| c.<br>1000 g. | ΔF<br>volts | $a_H^+ \cdot a_I^-$ | $a_H^+ \cdot a_I^-$ |
|---|---|---|---|
| 0.00500 | 0.00000 | 0.9312 | 0.8968 |
| 0.01045 | 0.03628 | 0.8748 | 0.8331 |
| 0.01981 | 0.06718 | 0.8111 | 0.7724 |
| 0.05049 | 0.11447 | 0.7866 | 0.7491 |
| 0.07914 | 0.13663 | 0.7585 | 0.7223 |
| 0.12972 | 0.16068 | 0.7200 | 0.6856 |
| 0.24608 | 0.19358 | 0.7201 | 0.6857 |

On the assumption of the independent activity of the ions and
also that the activities of the chloride, bromide and iodide ions
are equal we should expect the same activity coefficients for hy-
drogen iodide as were found for hydrogen chloride. Whether we
use the value 0.965 or 0.947 for the geometric mean activity coef-
ficient of 0.005 M hydrogen iodide a glance at Table VI shows that
the corresponding activity coefficients for the two acids are not equal
throughout the whole range of concentrations investigated. The
agreement with similar magnitudes for hydrochloric acid as
found by Noyes and MacInnes is good where the concentrations
are less than 0.030 M, but the agreement with the data of Lewis
and Randall is better for a slightly greater range, namely, for con-

TABLE VI
A COMPARISON OF THE ACTIVITY COEFFICIENTS OF
HYDROGEN CHLORIDE AND HYDROGEN IODIDE
AT ROUND CONCENTRATIONS

| c. 1000 g. | HI. (exp) | HCl. (N-M) | HI. (exp) | HCl. (L-R) |
|---|---|---|---|---|
| 0.005 | 0.965 | 0.965 | 0.947 | 0.947 |
| 0.010 | 0.937 | 0.932 | 0.920 | 0.924 |
| 0.020 | 0.901 | 0.899 | 0.886 | 0.894 |
| 0.030 | 0.893 | 0.880 | 0.877 | |
| 0.050 | 0.884 | 0.855 | 0.868 | 0.860 |
| 0.100 | 0.862 | 0.823 | 0.846 | 0.814 |
| 0.200 | 0.849 | 0.796 | 0.834 | 0.783 |

centrations from 0.005 M to 0.050 M. From the original data
of Noyes and MacInnes on the activity coefficients of hydrochloric
acid it may be noted that these coefficients pass through a mini-
mum value between 0.50 M and 1.0 M. From this investigation
we are led to the conclusion that the same type of variation is
exhibited by the activity coefficients of the ions of hydriodic acid,
but that the minimum occurs at a lower concentration, about 0.20
M. For concentrations from 0.005 M to 0.050 M the assumption
that the activities of the halide ions are equal at equal concentra-
tions of their acids appears to be valid. At concentrations greater
than these the evidence seems to contradict the validity of the as-
sumption. This may be due in part to instability of the silver
iodide and hydriodic acid. It would be desirable to obtain addit-
ional information from a similar study of hydrogen bromide so-
lutions before passing a final opinion.

In regard to the slightly different values for the activity coef-
ficients from different sources it is apparent that the difference lies
mainly in the standard of reference chosen. Noyes and MacInnes
have arbitrarily set the activity coefficient at the lowest concentra-
tion at which the electromotive forces are dependable equal to the
conductance-viscosity ratio. In the case of hydrochloric acid the
activity coefficient of a 0.003324 M solution has been taken as
0.985. In determining their values for the activity coefficients of
hydrochloric acid Lewis and Randall have used a method of ex-
trapolation described by Linhart.[14] Pearce and Hart[12], working
with solutions of potassium bromide and using a method similar
to that of Noyes and MacInnes, have obtained activity coefficient
products which agree excellently with the results of those investi-
gators in their work on potassium chloride solutions. In this
research, using the method of Linhart[14], data have been obtained
for hydrogen iodide which agree with his values of the activity

coefficients for hydrochloric acid for a considerable range of concentration in the dilute solutions. Thus, with the meager information at hand we are not justified in definitely stating which standard is correct.

## SUMMARY

1.    Measurements of the electromotive force of cells:

$$H_2 \mid HI\ (c),\ AgI \mid Ag,$$
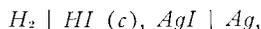
have been made for various concentrations of hydriodic acid.

2.    The free energy decrease and the heat content decrease accompanying the cell reaction have been computed.

3.    The free energy decrease accompanying the transfer of one mol of hydrogen iodide from various concentrations (c) to 0.10 M have been calculated.

4.    From the values of the electromotive force of the combination,

$$H_2 \mid HI\ (0.005\ M),\ AgI\ Ag - Ag\ AgI,\ HI\ (c) \mid H_2,$$
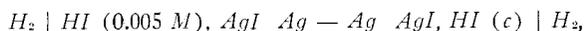
the activity coefficients of the ions of hydriodic acid have been calculated by the usual formula. From these values the activity coefficients at round concentrations have been determined. From the data obtained it has been concluded that the activities of the chloride and iodide ions in equal concentrations of their salts are equal up to 0.050 M, but beyond that concentration the assumption of equal ionic activities does not appear to hold.

PHYSICAL CHEMISTRY LABORATORY,
    STATE UNIVERSITY OF IOWA.