VOL. XXXVIII. APRIL, 1916. No. 4.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 102.]

THE FREE ENERGY OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION.

BY JAMES H. ELLIS.

Received February 1, 1916.

1. Purpose and Outline of the Investigation.

The fact that the laws of perfect solutions, which are conformed to by un-ionized or slightly ionized substances in dilute aqueous solutions, are subject to large deviations in the case of largely ionized substances (salts, strong acids and bases), even at small concentrations, makes it necessary, in the absence of any theoretical explanation of the deviations, to treat dilute solutions of these substances like concentrated solutions of other substances, namely, to determine experimentally the behavior of the separate substances, with the hope that this empirical study may then lead to generalizations. Now the most important characteristic of ionizing substances is the chemical activity which results from their ionization, or more specifically the (mass action) effect which their ions exercise in determining chemical equilibria. This effect in the case of theoretically perfect solutes is proportional to the concentration of the ions, but in the case of deviating solutes there must be substituted for it a new quantity which may be regarded as the "effective ion concentration" and which has been appropriately called by Lewis[1] the activity of the ions. This quantity has been shown by Lewis to be thermodynamically related to various other properties of solutions, thereby on the one hand increasing its practical significance and on the other affording various means of evaluating it.

The most general of these thermodynamic relations, one, indeed, which may well be regarded as the best practical definition of activity is that afforded by the equation $F_1 - F_2 = R\,T\log(a_1/a_2)$, in which R is the perfect-gas constant and $F_1 - F_2$ represents the decrease in the free energy of the system attending the transfer at the absolute temperature T of one mol of any substance (for example, of an ion) from a solution of any concentration in which its activity is a_1 to another solution of any concentration in which its activity is a_2; the free-energy decrease, hereafter denoted by $-\Delta F$, being defined in general to be equal to the maximum work W producible by the change in the state of the system under consideration, diminished by the attendant increase in the product of its volume and pressure (that is, $-\Delta F = W - (p_2v_2 - p_1v_1)$).

The most direct way of determining the free-energy decrease attending the transfer of ions from one concentration to another, and thereby their relative activities, is the measurement of the electromotive force of cells in which such a transfer takes place; and it is with such a study of the ions of hydrochloric acid that this investigation deals. Namely, measurements have been made of the electromotive force at 18, 25, and 35° of cells of the type, H_2 (gas), HCl (at any concentration c), Hg_2Cl_2 (solid) + Hg. The change in state when one faraday passes through such a cell is

$$^1/_2H_2 \text{ (at } p) + {}^1/_2Hg_2Cl_2 \text{ (solid)} = Hg + H^+ Cl^- \text{ (at } c);$$

and the product of the electromotive force into the value (F) of one faraday in coulombs is equal to the free-energy decrease in joules which attends this change in state. The changes in state in two cells in which the concentrations are c_2 and c_1 differ only in the respect that the hydrochloric acid is produced at these different concentrations, and the difference $(E_2 - E_1)$ in their electromotive forces multiplied by F therefore equals the free-energy decrease $(-\Delta F)$ attending the transfer of 1 HCl

---

[1] In regard to the concept of activity see G. N. Lewis, *Proc. Am. Acad.*, **37**, 49 (1901); **43**, 259 (1907), and *Z. physik. Chem.*, **38**, 205 (1901); **61**, 129 (1907).

from a solution where its concentration is c_1 to a solution where its concentration is c_2.

From the free-energy decrease attending the transfer of 1 HCl is then calculated the ratio $a_1^{H}a_1^{Cl}/a_2^{H}a_2^{Cl}$ of the products of the activities of the two ions of the acid at the two concentrations by means of the equation $-\Delta F = R\,T \log \frac{a_1^{H}a_1^{Cl}}{a_2^{H}a_2^{Cl}}$, which is based on the general definition of activity. The simplifying assumption that the two ions have equal activities in the same solution (that is, that $a_1^{H} = a_1^{Cl}$ and $a_2^{H} = a_2^{Cl}$) is then made provisionally; and the activities so calculated are compared with the ion concentrations given by the conductance ratio with a view of throwing light on the deviation of the activity of these ions from the ion concentrations commonly assumed.

This research has been carried on with the coöperation of Professor A. A. Noyes and with the aid of the grant made to him by the Carnegie Institution of Washington. The preliminary experiments were made jointly with Dr. Louis Weisberg and the final measurements with Mr. Frank W. Hall. For all this assistance I wish to express my great indebtedness.

2. Review of Previous Investigations.

Tolman and Ferguson[1] have already made measurements with hydrogen-calomel cells of the kind here described at 18° and at HCl concentrations 0.1, 0.02, 0.01, and 0.002 *N*. It seemed, nevertheless, desirable to take up these measurements anew in the hope of securing more accurate results and for the sake of extending the measurements to higher concentrations and other temperatures. Jahn[2] has also measured at 18°, apparently with great accuracy, the electromotive force of concentration cells of the type $Ag + AgCl, HCl(c_1), HCl(c_2), AgCl + Ag$ with the concentrations varying from 0.033 to 0.00167. From these electromotive forces can also be calculated with the aid of the transference numbers of the ions the free energy attending the transfer of 1 HCl from one solution to another.

Dolezalek[3] has measured the electromotive force at 30° of hydrogen-chlorine cells with concentrated hydrochloric acid as electrolyte, thus determining directly the free energy of hydrochloric acid in solutions 5 *N* to 12 *N*. He has also determined the partial vapor pressure at 30° of hydrochloric acid in these concentrated solutions. Gahl[4] has also made similar vapor-pressure measurements at 25°.

Other accurate electromotive measurements from which the free energy

---

[1] THIS JOURNAL, **34**, 232–246 (1912).

[2] *Z. physik. Chem.*, **33**, 545–576 (1900).

[3] *Ibid.*, **26**, 334 (1898).

[4] *Ibid.*, **33**, 178 (1900).

of transfer of univalent electrolytes can be derived are those of Jahn made with potassium chloride and sodium chloride in the same way as with hydrochloric acid, and those of MacInnes and Parker.[1] The last-named investigators measured at 25° concentration cells with silver-silverchloride electrodes and potassium chloride as electrolyte at concentrations 0.5 to 0.001 N, and also cells of the type $Ag + AgCl$, $KCl(c_1)$, KHg_n, $KCl(c_2)$, $AgCl + Ag$, for concentrations between 0.5–0.005 N.

Recently S. J. Bates[2] has published a study of the most accurate freezing-point data available, from the results of which the free energy changes attending changes in concentration of largely ionized substances can be readily derived.

The results of these investigations will be considered later in connection with the new ones to be here presented.

3. Description of the Experiments.

(*a*) **Preparation of the Substances and Solutions.**—The mercury for use in the cells was purified by first electrolyzing it as the anode in a 2% solution of nitric acid, stirring both the mercury and the solution well, and using a current-density of 0.005 ampere per square decimeter, in the manner recommended by Wolff and Waters.[3] Electrolysis was continued for thirty hours, but six hours before its completion the mercury had ceased to tail. After this process the mercury was dried and twice distilled at a pressure of 30 mm. in a current of air. At the end of the second distillation no visible residue was left in the distilling flask. The mercury thus prepared preserved a mirror surface indefinitely.

The calomel first used in making the calomel electrodes was Kahlbaum's best product; but it did not give reproducible results. Calomel prepared by precipitation from a mercurous nitrate solution made by dissolving pure mercury in pure nitric acid was then tried. This also proved unsatisfactory, although great care was taken in its preparation. Finally, satisfactory calomel was secured by an electrolytic process analogous to that suggested by Wolff and Waters[4] for the preparation of mercurous sulfate for standard Weston cells. Pure mercury, placed in a large clean beaker, was covered with pure 1 N hydrochloric acid. Both the acid and mercury were kept well stirred by a glass stirrer. The mercury was made the anode; and the cathode consisted of a piece of clean platinum foil contained in another beaker filled with hydrochloric acid and connected with the first beaker by a siphon tube. On passage of the current the mercury surface became covered with a thin film of calomel; and, as this was swept away by the stirrer, it was re-formed continually.

[1] THIS JOURNAL, **37**, 1445–1461 (1915).

[2] *Ibid.*, **37**, 1423–1445 (1915).

[3] *Bull. Bur. Standards*, **3**, 625 (1907).

[4] *Ibid.*, **3**, 631 (1907).

Various rates of stirring and various current densities ranging from 2 amp. to 0.2 amp. per sq. dm. were used, without affecting the electromotive properties of the product. The product was always of a moderately dark gray color, due to the presence of a large amount of finely divided mercury in the form of globules of diameter 0.3 mm. and less. Under the microscope, however, the calomel particles were visible as a perfectly white, amorphous, flocculent substance. Stirring was always continued for four hours after the electrolysis was terminated, in order to enable the precipitated calomel to come into equilibrium with the solution. The calomel prepared in this manner was transferred to a clean bottle and preserved under the mother liquor of the electrolysis. When tested for mercuric chloride it gave no reaction for it.

All water used in making up the solutions had a specific conductance less than 10^{-6} reciprocal ohms. It was preserved in resistance glass bottles.

Hydrochloric acid was prepared by redistilling the best commercial acid, retaining only the middle portion. The constant boiling acid thus secured was diluted with conductivity water in resistance-glass bottles to approximately 2 *N*, and analyzed by precipitating it with silver nitrate and weighing the silver chloride. Solutions of less strength were prepared by diluting a known weight of this acid with a known weight of water.

Hydrogen for the hydrogen electrode was prepared by the electrolysis of sulfuric acid solutions; it was washed before being admitted to the cell by passing it through a solution of potassium bichromate in strong sulfuric acid, alkaline pyrogallate solution, and a hydrochloric acid solution of the same temperature and concentration as that in the cell. In the preliminary work the hydrogen was also passed through a tube containing a platinum spiral at a dull red heat; but this precaution was found to be unnecessary.

(*b*) **Description of the Cell.**—The cell consisted, as shown in the figure, of two half cells containing the hydrogen and calomel electrodes, respectively. These half cells are shown in Figs. 1 and 2.

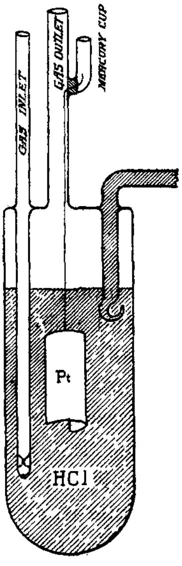

Fig. 1.

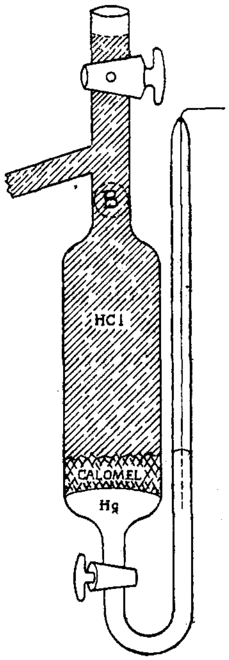

Fig. 2.

The hydrogen half cell contained sometimes two or four platinum electrodes and at other times only a single one. The electrodes were completely covered by the solution; and connection was made to them through platinum wires leading to mercury cups outside the cell. The portion of these wires within the cups was well amalgamated by electrolysis in a mercurous nitrate solution. The platinum electrodes were of thin foil and had a surface of 15 sq. cm. They were cleaned, before the cell was made up, by fusion with potassium acid sulfate, followed by careful washing in boiling water. After introduction into the cell they were heavily coated with platinum black.

Hydrogen was bubbled into the cell through a small capillary opening designed as shown in the figure, so as to give a large number of small bubbles. It escaped through an exit tube at the top of the cell. This exit tube was covered with a cap ending in a capillary bend into a hook. The tube by means of which liquid connection is established with the calomel cells also has a hook at its lower end, to prevent gas bubbles from entering it and interrupting the column of liquid.

The platinization of the platinum foil is of importance. Clean foil must be employed, and the platinizing solution should consist of pure chloroplatinic acid (containing 1% Pt). The addition of lead to secure a better coating of platinum black is objectionable. To deposit the coating a small auxiliary electrode of platinum foil is introduced into the cell through the hydrogen exit tube, and a current sufficient to liberate gas freely at both electrodes is passed. This current is commutated at intervals of five minutes for two hours or more, or until the coating is so thick that shaking causes some of it to fall off, after which the auxiliary electrode is removed, the platinizing solution poured off, and the coated electrode washed with many changes of conductivity water. The cell is then twice allowed to stand overnight full of conductivity water, to remove all the platinizing solution from the coating.

Platinum electrodes prepared in this manner are reproducible with the greatest certainty to less than 0.01 millivolt; and out of eight or ten electrodes made up successively, one is rarely found which differs from any of the rest by this amount, provided the precautions given above are observed. The essential points in securing reproducibility and constancy are that the electrode should be completely immersed in the hydrochloric acid solution, the coating of platinum black should be thick and black, the platinum foil should be initially clean, no lead should be used in the platinizing solution, the platinizing salts should be completely removed from the electrode after platinizing, and sufficient hydrogen should be fed to the electrode to insure saturation with the gas.

The hydrogen electrode assumes its equilibrium value within three or four hours after the passage of hydrogen is commenced; it functions as an oxygen electrode until the oxygen initially present upon it is displaced by the hydrogen. If the bubbling of hydrogen through the solution is reasonably continuous (a few bubbles every few seconds) and if the coating of platinum black is sufficiently thick, no variation whatsoever in the electromotive force of the electrode can be observed even with a very sensitive potentiometer. The electrode is quickly responsive to changes in barometric pressure; and it is possible to detect readily a change of one millimeter in the barometric height by observing the electromotive force of the hydrogen electrode. To test quantitatively the response of the hydrogen electrode to changes in hydrogen pressure, the hydrogen in one cell containing approximately 0.1 normal acid at 25° was subjected to a pressure of 38.5 cm. of mercury in excess of the atmospheric pressure, and the change of electromotive force observed. The figures given in Table I were obtained.

TABLE I.—RESPONSE OF THE HYDROGEN ELECTRODE TO CHANGES IN PRESSURE.

Elapsed time. Hr.	Elapsed time. Min	Barometer. Cm. Hg.	Excess pressure. Cm. Hg.	Electromotive force. Volt.
	0	...	0.0	0.40069
	16	...	0.0	0.40074
1	37	...	0.0	0.40081
2	5	76.90	0.0	0.40081
		Excess pressure then applied.		
2	20	76.90	38.5	0.405
2	28	76.90	38.5	0.4058
2	32	76.90	38.5	0.40602
2	41	76.90	38.5	0.40613
2	56	76.90	38.5	0.40625
3	18	...	38.5	0.40622
3	29	76.85	38.5	0.40618
3	56	76.85	38.5	0.40616
4	35	76.85	38.5	0.40623
4	55	76.77	38.5	0.40623
		Excess pressure then removed.		
5	7	76.77	0.0	0.40105
5	7	76.77	0.0	0.40097
5	21	76.77	0.0	0.40085
5	29	76.77	0.0	0.40085
5	39	76.77	0.0	0.40085
5	45	76.72	0.0	0.40087

It will be seen from this table that, before the pressure was applied, the electromotive force was constant at 0.40081 volt, that it rose to an approximately stationary value of 0.40623 volt in an hour or so after the excess pressure was applied, and that within an hour after the excess pressure was removed the electromotive force fell to a stationary value of 0.40085 volt. If this latter value is corrected for the change in barometric pressure from 76.90 to 76.72 cm. remembering that 1 cm. increase in the pressure corresponds for small pressure changes to an increase of 0.00017 volt in the electromotive force, it is found that, had the barometer not changed, the final value would have been 0.40090 volt. Although this value differs by 0.00009 volt from the initial value, the agreement is fairly satisfactory considering that these measurements were made in the early stages of the work, when neither the hydrogen nor the calomel electrode had been gotten well under control. The mean of the two values is 0.40086 volt, and the rise in electromotive force to 0.40623 thus means a rise of 0.00537 volt. If the rise to be expected is calculated by means of the formula $E_2 - E_1 = (R\ T/2\text{F}) \log (p_2/p_1)$, remembering to subtract from the recorded values of the pressures the pressure of aqueous vapor at 25°, the figure 0.00536 volt is obtained. There is thus good evidence that the hydrogen electrode acts in a reversible manner; and the data given above show that it responds quickly both to increase and to decrease of the hydrogen pressure.

After passage of hydrogen for thirty-six hours to thoroughly saturate the solution and electrode, several hydrogen half cells were sealed by drawing down the entrance and exit tubes for the hydrogen with a hand blast lamp. These cells maintained their electromotive force constant within one millivolt for about a week, but showed that, for an accuracy of 0.1 millivolt or better, it is essential to have a continual supply of hydrogen pass through the solution, thus making it impracticable to construct a standard cell with a hydrogen electrode.

It should also be mentioned that, if the entrance of mercury ions from the calomel electrode into the hydrogen half cell is prevented, the coating of platinum black apparently retains its effectiveness indefinitely. In the present work electrodes were used for a period of six months without showing any need of replatinization. On the other hand, if the hydrogen and calomel electrodes are not effectively separated, as they were not in the first stages of this work, nor in the work of Tolman and Ferguson previously referred to, the coating of platinum black becomes gray from deposited mercury within a few days, and cells containing such electrodes give results which may be low by 0.1 millivolt or more.

The type of calomel half cell employed is shown in Fig. 2 on page 741. It dispenses with the use of a platinum leading-in wire sealed through the glass, a mercury column taking its place. This is a distinct advantage; for such wires, even if well amalgamated originally, appear to become coated with a crust of solid matter if allowed to come into contact with the calomel, and they ultimately fail to make good contact with the mercury button in the bottom of the cell. Connection with the mercury column of my cells was made with an amalgamated platinum wire, it is true, but in such a way that no calomel could touch the wire.

Because of the lesser degree of reproducibility of the calomel electrodes four distinct calomel half cells were always made up. These were connected with one another by a horizontal tube indicated by the circle B in the figure.

Before charging the cell the calomel was shaken for two days or more with successive portions of hydrochloric acid of the concentration to be used, to bring it into equilibrium with the acid. The cell was then charged with the proper amount of this calomel and with the acid with which it had been shaken, the stopcocks were closed, the tube subsequently to be sealed to the tube coming from the hydrogen cell was closed with a glass plug and rubber connector, and the whole cell was rotated end-over-end for at least three hours to ensure perfect equilibration. This is essential, and it should be emphasized that, in order to secure reproducible electrodes, one must not allow any hydrochloric acid which has not been saturated with calomel in the manner just described to enter the cell.

Calomel electrodes prepared with these precautions assume (except when the acid is more dilute than 0.03 *N*) their true potential within thirty minutes after coming to the temperature of the thermostat in which they are placed, and then remain constant. But, unless the precautions are observed, the cells do not come to a steady value even after several days, and they show small capricious variations from second to second, which are greatly magnified by shaking the cell. Electrodes correctly prepared are reproducible to within 0.04 to 0.05 millivolt, and do not change their value on shaking, while electrodes prepared without thorough equilibration may be expected to vary from one another by a whole millivolt, and to change their value on shaking even after they appear to have come to a steady value. Indeed, the constancy of an undisturbed calomel electrode is no indication whatsoever of the satisfactory performance of the electrode; for, even when an electrode has not been rotated, it settles down to a steady value in the course of a few days, although this value may be as much as a millivolt (or even ten millivolts) removed from the correct value. It should be assumed that the electrode is acting satisfactorily only when a number of electrodes prepared simultaneously or at different times give substantially the same electromotive force, when these electrodes are steady in their values and not sensitive to shaking, when they show no tendency to polarize in ordinary use with a potentiometer, and when they exhibit no temperature hysteresis. All the electrodes used in the present investigation fulfilled these conditions.

It may be incidentally mentioned that the common practice of bringing electrodes into agreement by allowing them to stand connected together in the same solution does not afford evidence that the electrodes have become really identical; for by this treatment inherent differences in the electrodes may have been merely temporarily compensated by concentration changes automatically produced in the porous material upon their surfaces.

The complete hydrogen-calomel cell possessed nearly the steadiness of a cadmium standard cell. No variation in its electromotive force from instant to instant could be observed with a potentiometer reading to 0.01 millivolt, and the variations observed in the course of several days almost always agreed with those predictable from the changes in the barometric pressure and the slight temperature changes in the thermostat. The following set of values (corrected for barometric changes) indicates the constancy of the cell, and shows its entire freedom from temperature hysteresis. The acid used in these measurements contained 1.9278 mols HCl per 1000 g. water.

TABLE II.—RESPONSE OF THE CELLS TO CHANGES IN TEMPERATURE.

Elapsed time.			Corrected E. M. F.	Elapsed time.			Corrected E. M. F.
Hr.	Min.	Temperature.	Volt.	Hr.	Min.	Temperature.	Volt.
	0	35.00°	0.23302	3	50	18.00°	0.23767
	40	35.00°	0.23304	4	30	18.00°	0.23769
1	50	25.00°	0.23588	10	30	25.00°	0.23586
2	30	25.00°	0.23590	14	0	25.00°	0.23588

It will be noticed that this cell, which is a typical one, gave the same value at 25°, whether this temperature was approached from 35° or from 18°; and it may be stated in addition that the electromotive force of the cell appears to follow within a few minutes any temperature change.

The fact that the cells gave electromotive forces constant for days, indicates that the continued passage of hydrogen through the hydrogen half cell was accompanied by no progressive change in the concentration of the acid due to removal of water vapor.

It should be observed that the cells are satisfactory only with fairly concentrated acid. With acid of lower concentration than 0.03 *N* the calomel electrode is for some reason not at all reliable. This may be due to some change in the solid phase, such as the formation of a basic chloride or of a subchloride producing a solid solution with the original calomel At any rate, something happens at low concentrations which affects the measurements noticeably even at 0.03 *N*, and which produces so pronounced an error at 0.01 and at 0.003 *N* as to render the measurements at those concentrations valueless.

The measured electromotive forces of the cells containing the acid at the highest concentration (4.484 molal) might be slightly in error, owing to the solubility of calomel in acid of this strength. The data determined by Richards and Archibald[1] show, however, that a 4.484 molal HCl

---

[1] *Z. physik. Chem.*, 40, 391 (1902).

saturated with calomel is only 0.0016 molal in $HgCl_2$. The molal ratio $HgCl_2 : HCl$ is therefore only 0.035%, thus altogether too small to produce through complex formation or otherwise an appreciable change in the concentration or activity of the hydrochloric acid.

(*c*) **Method of Setting Up the Cell.**—The technique of preparing a hydrogen-calomel cell is somewhat complicated. The two separate half cells are first cleaned with an acid bichromate solution, and then thoroughly washed with conductivity water. The hydrogen half cell is then rinsed out several times with acid of the concentration to be used, allowing it to stand full of acid for some time between the rinsings. The calomel cells are then completely dried by passing through them a current of air filtered through cotton wool. Their stopcocks are freed from grease, and they are smeared anew with a small quantity of fresh grease. The small vertical side tubes of the four calomel half cells are then filled with pure mercury, as are also the bores of the four small stopcocks at the bottom of the cells. These stopcocks are then closed, and the tops of the side tubes are sealed off close to the top of the mercury columns with a hand blast-lamp. The tube leading to the hydrogen cell is closed by a glass plug held on by a short rubber connector. The air pressure in the cells is slightly reduced with a water pump, and acid of the proper concentration which has been equilibrated with calomel is allowed to flow in. The cell is shaken and then the acid is sucked out, this process being twice repeated. Finally, equilibrated calomel is introduced by the aid of the water pump, and enough equilibrated acid to fill the cell completely is allowed to flow in. The amount of calomel used is apparently immaterial provided it is sufficient to cover the mercury button later introduced.

The calomel half cells thus prepared are slowly rotated end-over-end for four hours or more, then shaken and tilted so as to distribute the calomel equally among the four separate cells. The sealed-off ends of the side tubes containing the mercury are then cracked off, and the stopcocks at the bottom of the cells are opened so as to allow the mercury to flow slowly into the bottom of each cell and form the mercury electrode.

The calomel half cells are now placed in the thermostat and tested for agreement with one another. If the process has been successful, as after practice it almost invariably is, the maximum variation between any two cells will not be greater than 0.05 millivolt, although occasionally with the less concentrated acids variations of 0.10 millivolt may be observed. If the calomel half cells prove satisfactory, they are sealed to the hydrogen half cell with a hand blast lamp, the two connection tubes having first been dried out with filter paper. Gentle suction is now applied at the top of the calomel half cells, enough liquid to fill the connection tube is drawn over from the hydrogen cell, and the stopcock at the top is closed. The liquid boundary is formed at the point where the connection tube joins the vertical tube leading from the top of the group of calomel cells, and when formed in the way described there is no introduction of acid from the hydrogen cell into the calomel cell nor the reverse. After the liquid junction has been formed, the cells are replaced in the thermostat, and hydrogen is started bubbling through the hydrogen half cell. In five or six hours measurements may be commenced.

(*d*) **Description of the Measurements.**—The temperature variations of the thermostat seldom exceeded 0.01°. The temperature was measured to 0.01° on two Baudin thermometers (Nos. 16344 and 16862), which had been calibrated at the Bureau of Standards. Their ice points were redetermined during the course of this investigation, and found to agree within 0.01° with those determined at the time of the calibration.

The apparatus for the measurement of the electromotive force consisted of a Leeds and Northrup potentiometer (instrument No. 9043) which has been recently overhauled and put into good condition by the makers. A Weston standard cell (No. 1103) was used, which was calibrated at the Bureau of Standards during the course of the work. It was kept in a box lined with heavy felt to prevent sudden changes of temperature. A correction for thermoelectric forces in the galvanometer circuit and in the potentiometer was always made, but it amounted at most to +0.00002 volt. The potentiometer settings were made with an accuracy of 0.00001 volt.

After setting up the cell in the manner previously described and allowing hydrogen to bubble through it for six hours, the potentiometer current was roughly adjusted by the aid of an auxiliary sub-standard cell; and then the electromotive force of each calomel half cell against the hydrogen half cell was measured. Immediately after this the electromotive force of the standard cell was measured, giving a calibration of the potentiometer scale more accurate than if the attempt were made to adjust the scale to read directly in the usual manner. The temperature of the thermostat was then measured on the Baudin thermometers, and the barometer reading was taken. The cell was then allowed to remain one hour or more at the same temperature, and the measurements were repeated. If the electromotive forces measured at these two times checked within 0.00002 volt after allowance had been made for the change in the barometric pressure, the cell was brought to the next temperature at which it was to be measured, and the same procedure was repeated. If a check within 0.00002 volt was not obtained (which happened only once during the course of the measurements), the cell was allowed to stand for another hour without changing its temperature, and the measurements were repeated. Preliminary work on the cells gave satisfactory evidence that, if cells kept the same value for one hour, they would in all likelihood retain it for days.

After the measurements at the three temperatures (18, 25, and 35°) were made, the cell was emptied, cleaned, and refilled for measurements with another concentration of acid.

4. The Experimental Data.

To reduce the observations to standard conditions, the following corrections were applied in the order given:

(1) The ice points of the Baudin thermometers having been redetermined and found to lie within 0.01° of the values obtained by the Bureau of Standards, the corrections determined by the Bureau were applied to the thermometer readings.

(2) The barometer readings were corrected for an instrumental error of +0.7 mm. and for the temperature of the mercury and scale with the aid of the table given in Landolt-Börnstein Tabellen; also for the variation of gravity due to the fact that the latitude of Boston is not 45°, but 42° 21′.

(3) The actual hydrogen pressure at the platinum electrode of the cell was obtained by subtracting from the corrected barometer reading the pressure of water vapor above the hydrochloric acid at the different temperatures of measurement; and then adding to this figure the mercury equivalent (0.33 mm.) of the column of liquid in the cell, measured from the middle of the platinum electrode to the upper surface of the liquid.

(4) The observed electromotive forces were treated as follows: (*a*) The mean of the values for the four cells was computed, and this mean was then corrected in the following manner for the error caused by the fact that the potentiometer was not accurately adjusted to be direct reading: From the value of its scale obtained each time by measuring the electromotive force of the standard cell, corrected electromotive forces of the hydrogen-calomel cell were computed by multiplying the observed electromotive force of that cell by the true electromotive force of the standard cell and dividing by the observed electromotive force of the latter. The standard cell (Weston No. 1103) was certified by the Bureau of Standards to have the value 1.01855 international volts. (*b*) This corrected electromotive force was further corrected by adding +0.00002 volt for the thermoelectric effects in the potentiometer. (*c*) The value thus obtained was corrected to what it would have been, had the hydrogen pressure in the cell been exactly one atmosphere (760 mm. mercury at zero degrees, sea-level, and 45° north latitude). This correction was made by the logarithmic formula correlating electrode potential and gas pressure: it amounted to —0.00000057 T per centimeter of mercury above 76 cm. (*d*) From the values so obtained the temperature coefficient of each cell was computed for different temperatures, and

corrections were made for the slight variations of the thermostat temperatures from 18, 25, and 35°.

The densities at 25° of the solutions were carefully determined, thus enabling the acid content to be expressed also in mols per liter of the solution at 25°. The values found (referred to water at 4°) are as follows:

TABLE III.—DENSITIES OF HYDROCHLORIC ACID SOLUTIONS AT 25°.

Mols HCl per 1000 g. water.	Density.	Mols HCl per 1000 cc. solution.	Mols HCl per 1000 g. water.	Density.	Mols HCl per 1000 cc. solution.
4.484	1.0654	4.1044	0.5095	1.0059	0.50345
1.9278	1.0291	1.8535	0.3376	1.0031	0.3346
1.0381	1.0149	1.0159	0.10040	0.9989	0.09999
0.7714	1.0105	0.7587	0.03332	0.9972	0.03324

The observed electromotive forces are presented in Table IV. The first column gives the temperature, and the second the pressure of the hydrogen obtained as described in Paragraph (3) above. The third column gives the time which elapsed after the first measurement was made. The remaining columns give the observed electromotive forces of the standard cell and of the four cells formed by combining the hydrogen half cell with each of the four calomel half cells. The acid concentrations are given in mols HCl per 1000 g. water, the weights being corrected for air buoyancy.

TABLE IV.—THE OBSERVED ELECTROMOTIVE FORCES OF THE SEPARATE CELLS.

			Observed electromotive forces.				
Temperature.	Hydrogen pressure.	Elapsed time.	Std. cell.	Cell I.	Cell II.	Cell III.	Cell IV.
Acid content: 4.484 mols HCl per 1000 g. water.							
24.96	74.95	0	1.01927	0.15494	0.15494	0.15494	0.15494
24.96	74.86	3:20	1.01927	0.15497	0.15497	0.15497	0.15497
35.02	73.14	5:08	1.01926	0.15085	0.15083	0.15080	0.15077
35.03	73.14	6:05	1.01926	0.15084	0.15083	0.15081	0.15078
17.81	75.62	7:35	1.01927	0.15763	0.15762	0.15763	0.15766
18.31	75.74	9:50	1.01927	0.15751	0.15752	0.15751	0.15756
Acid content: 1.9278 mols HCl per 1000 g. water.							
35.02	71.85	0	1.01931	0.23250	0.23242	0.23243	0.23244
35.00	71.85	0:40	1.01928	0.23251	0.23244	0.23243	0.23246
25.01	73.62	1:50	1.01929	0.23566	0.23559	0.23562	0.23564
25.00	73.62	2:30	1.01929	0.23567	0.23562	0.23563	0.23566
17.99	74.43	3:50	1.01926	0.23758	0.23753	0.23754	0.23757
18.00	74.43	4:30	1.01928	0.23761	0.23755	0.23756	0.23759
25.00	73.90	10:30	1.01933	0.23569	0.23564	0.23565	0.23568
25.01	73.81	13:55	1.01930	0.23569	0.23564	0.23565	0.23568
Acid content: 1.0381 mols HCl per 1000 g. water.							
17.93	74.87	0	1.02156	0.27984	0.27982	0.27978	0.27982
25.01	74.04	1:50	1.01930	0.27794	0.27789	0.27786	0.27788
25.01	74.05	2:40	1.01940	0.27793	0.27791	0.27789	0.27793
35.00	72.21	3:25	1.01921	0.27552	0.27546	0.27546	0.27551
35.00	72.21	4:00	1.01928	0.27549	0.27545	0.27544	0.27548

TABLE IV (*continued*).

Temperature.	Hydrogen pressure.	Elapsed time.	Observed electromotive forces.				
			Std. cell.	Cell I.	Cell II.	Cell III.	Cell IV.
Acid content: 0.77137 mol HCl per 1000 g. water.							
24.98	74.68	0	1.01919	0.29573	0.29561	0.29564	0.29570
24.99	74.63	2:10	1.01926	0.29572	0.29561	0.29564	0.29568
35.00	72.71	4:55	1.01929	0.29373	0.29369	0.29367	0.29369
35.00	72.44	7:30	1.01924	0.29373	0.29366	0.29359	0.29366
18.00	75.11	9:30	1.01922	0.29663	0.29657	0.29654	0.29662
18.01	75.09	10:35	1.01950	0.29672	0.29666	0.29663	0.29669
Acid content: 0.50948 mol HCl per 1000 g. water.							
18.00	75.08	0	1.01928	0.31921	0.31914	0.31907	0.31917
18.00	74.94	1:30	1.01926	0.31921	0.31913	0.31907	0.31918
24.96	74.06	4:55	1.01928	0.31857	0.31850	0.31846	0.31853
24.96	74.02	6:15	1.01929	0.31858	0.31851	0.31847	0.31855
35.00	72.16	7:30	1.01929	0.31726	0.31722	0.31713	0.31718
34.99	72.20	8:30	1.01929	0.31727	0.31721	0.31712	0.31719
Acid content: 0.33757 mol HCl per 1000 g. water.							
25.02	73.87	0	1.01930	0.33827	0.33831	0.33832	0.33831
25.02	74.23	1:00	1.01932	0.33830	0.33833	0.33834	0.33832
35.02	72.16	1:35	1.01931	0.33753	0.33756	0.33753	0.33752
35.01	72.19	2:55	1.01929	0.33752	0.33754	0.33752	0.33751
17.87	74.85	4:00	1.01930	0.33837	0.33840	0.33844	0.33842
17.89	74.82	4:35	1.01927	0.33848	0.33849	0.33853	0.33851
17.89	74.82	5:05	1.01929	0.33850	0.33851	0.33853	0.33852
Acid content: 0.10040 mol HCl per 1000 g. water.							
25.00	74.56	0	1.01995	0.39917	0.39919	0.39912	0.39911
17.86	75:42	8:00	1.01925	0.39781	0.39782	0.39774	0.39775
17.95	75.42	8:26	1.01928	0.39783	0.39787	0.39777	0.39778
18.05	75.42	8:52	1.01928	0.39787	0.39789	0.39777	0.39780
35.00	72.48	19:45	1.01961	0.39982	0.39990	0.39984	0.39986
35.15	72.48	20:25	1.01934	0.39981	0.39984	0.39979	0.39980
Acid content: 0.033315 mol HCl per 1000 g. water.							
25.04	74.25	0	1.01972	0.45265	0.45287	0.45283	0.45283
25.10	74.17	1:00	1.01930	0.45248	0.45270	0.45266	0.45267
35.00	72.36	2:50	1.01927	0.45507	0.45527	0.45520	0.45522
35.02	72.44	4:10	1.01929	0.45516	0.45535	0.45528	0.45530
17.81	75.19	7:10	1.01930	0.45018	0.45036	0.45036	0.45038
17.91	75.23	8:10	1.01926	0.45021	0.45038	0.45038	0.45040
Acid content: 0.01001 mol HCl per 1000 g. water							
18.03	75.10	0	1.01930	0.52732	0.52731	0.52709	0.52742
18.06	75.21	1:05	1.01928	0.52743	0.52742	0.52717	0.52756
24.99	74.48	3:45	1.02038	0.53173	0.53182	0.53145	0.53242
24.99	74.47	9:15	1.01933	0.53034	0.53034	0.52985	0.53080
35.02	72.60	12:25	1.01933	0.53671	0.53681	0.53621	0.53746
35.02	72.58	13:30	1.01927	0.53664	0.53672	0.53613	0.53741
Acid content: 0.00333 mol HCl per 1000 g. water.							
25.00	74.24	0	1.01932	0.80798	0.81148	0.79777	0.79982
35.00	72.40	1:30	1.01935	0.81592	0.81594	0.80585	0.80439
35.00	72.40	2:25	1.01931	0.81596	0.81617	0.80577	0.80398

In Table V are summarized the final values of the electromotive force of the hydrogen-calomel cell for a hydrogen pressure of exactly one atmosphere, for temperatures of exactly 18, 25, or 35°, and at the indicated concentrations of hydrochloric acid. The values here given are the means for the four cells, the last made measurements being used in each case, and these being corrected as described at the beginning of this section. In this table and in the following ones values at small concentrations which are seriously affected by the unreliability of the calomel electrode referred to above (at the end of Section 3(*b*)) are enclosed within parentheses.

Table V.—Summary of the Electromotive Forces of the Cells and their Temperature Coefficients.

Mols HCl in 1000 g. water.	Electromotive force.			$10^6\alpha_{25}$.	$10^6\beta_{25}$.
	At 18°.	At 25°.	At 35°.		
4.484	0.15759	0.15506	0.15124	—2384	— 7.82
1.9278	0.23769	0.23589	0.23304	—1137	— 7.06
1.0381	0.27919	0.27802	0.27595	—663	— 8.23
0.77137	0.29654	0.29571	0.29411	—460	— 8.20
0.50948	0.31912	0.31865	0.31765	—253	— 6.00
0.33757	0.33845	0.33836	0.33794	—75	— 4.96
0.10040	0.39764	0.39884	0.40013	+386	— 6.47
0.03332	0.45020	0.45258	0.45557	+715	— 5.47
0.01001	(0.5271)	(0.5302)	(0.5369)	(+1010)	(+26.10)
0.003333	...	(0.8040)	(0.8105)	...	...

From these values of the electromotive force there have been derived equations expressing it as a temperature function for each concentration of acid. These equations are of the form

$$E_t = E_{25}\,[1 + \alpha_{25}\,(t - 25) + \beta_{25}\,(t - 25)^2].$$

The values of $10^6\,\alpha_{25}$ and $10^6\,\beta_{25}$ are given in the last two columns of Table V. These values of α give a good curve when plotted against the logarithm of the concentration; and are probably reliable; but the values of β exhibit only faint traces of regularity, owing to the fact that they are too small to be accurately determined.

5. Decrease in Free Energy and in Heat Content Attending the Cell Reaction.

Since on the passage of two faradays through the cell the change in state H_2 (1 atm.) + Hg_2Cl_2 (solid) = 2Hg (liquid) + 2 HCl (at *c*) takes place, the free-energy decrease accompanying this reaction at any temperature and concentration is obtained by multiplying the corresponding electromotive force by 2 × 96500.

If the free-energy decrease at any of these concentrations is expressed by a temperature function of the same form as that used for electromotive force, the temperature coefficients α_{25} and β_{25} will have the same values as they had in the electromotive force function.

Moreover, the decrease of heat content attending the change in state at 25° may be calculated from α_{25}, the temperature coefficient of the electromotive force, by the aid of the fundamental thermodynamic equation $d/dT\ (-\Delta F/T) = \Delta H/T^2$. On substituting in this equation the expression for $-\Delta F$ as a temperature function for any given concentration, performing the indicated differentiation, and rearranging the terms, there is obtained

$$-\Delta H_{25} = -\Delta F_{25}\ (1 - 298\ \alpha_{25}).$$

Table VI contains the so calculated values of the free-energy decrease and also of the heat-content decrease in joules.

TABLE VI.—DECREASE IN FREE ENERGY AND IN HEAT CONTENT ATTENDING THE CELL REACTION.

Mols HCl per 1000 g. H_2O.	Free energy decrease. At 18°.	At 25°.	At 35°.	Heat decrease. at 25°.
4.484	30415	29927	29190	51187
1.9278	45874	45527	44977	60952
1.0381	53884	53657	53257	64260
0.7714	57232	57072	56762	64896
0.5095	61590	61500	61307	66137
0.3376	65322	65303	65222	66766
0.10040	76745	76977	77224	68124
0.03332	86888	87348	87925	68734
0.01001	(101740)	(102330)	(103630)	(71530)
0.00333	..	(155170)	(156430)	...

The value of ΔH at 25° and 0.1 molal HCl calculated from the electromotive forces may be compared with that derived directly from thermochemical measurements. The heat of formation of 1 Hg_2Cl_2 is 62,600 cal. (Nernst[1]), 62,640 cal. (Varet[1]), 65,210 cal. (Thomsen[1]), 62,900 (Koref[2]), 63,675 cal. (Wolff[3]), and 62,650 (Pollitzer[4]), the mean of these values, omitting Thomsen's, being 62,890 cal. The heat of formation of 1 HCl (gaseous) is 22,000 cal. according to Thomsen and Berthelot. The heat of solution of 1 HCl in 20 H_2O is according to Thomsen[5] 16,760 cal. By plotting the values of the heat of dilution determined by Thomsen,[5] Steinwehr,[6] and Richards,[7] it has been found that the heat of dilution of $1HCl.20H_2O$ to 1 $HCl.555H_2O$ (where the HCl is 0.1 molal) is 590 cal.,[8] making the heat of solution of 1 HCl in 555 H_2O 17,350 cal. From

---

[1] *Landolt-Börnstein Tabellen*, 4th Ed., p. 869.

[2] *Z. Electrochem.*, **18**, 818 (1912).

[3] *Ibid.*, **20**, 19 (1914).

[4] *Ibid.*, **19**, 513 (1913).

[5] *Landolt-Börnstein Tabellen*, 4th Ed., p. 885.

[6] *Z. physik. Chem.*, **38**, 185 (1903).

[7] THIS JOURNAL, **32**, 1776 (1910).

[8] In order to enable this plot to be readily reconstructed, it may be stated that the heats of dilution of $1HCl.20H_2O$ corresponding to the curve best representing the re-

the plot, by drawing a tangent to the curve at the proper point, the heat of solution of 1 H_2O in an infinite amount of $HCl.555H_2O$ was determined to be 0.104 cal., the corresponding value of the heat of solution of 555 H_2O being 58 cal. This gives for the heat of solution of 1 HCl in an infinite amount of $HCl.555H_2O$ the value 17,290 cal.[1] From these values we get for the decrease in heat content attending the reaction $H_2 + Hg_2Cl_2 = 2Hg + 2HCl$ (at 0.1 molal) the value 15,690 cal. The value of the decrease in heat content derived from the electromotive force data and given in Table VI is 68,124 joules, corresponding to 16,290 cal. The agreement is probably as close as the accuracy of the thermochemical data permits.

6. Decrease in Free Energy and in Heat Content Attending the Transfer of Hydrochloric Acid from Any Concentration to 0.1000 Molal.

From the energy effects attending the reduction of calomel by hydrogen with formation of hydrochloric acid at various concentrations we can, by simple subtraction, obtain the energy effects attending the transfer of hydrochloric acid from a solution of one concentration into one of another concentration. It seems best to adopt 0.1000 molal as the concentration of reference, as this is the smallest concentration at which the electromotive forces are apparently still entirely free from error. The decreases in free energy and in heat content attending the cell reaction have therefore been first calculated for this round concentration from empirical equations expressing the electromotive forces at the three neighboring concentrations, 0.3376, 0.10040, and 0.03332 molal, at each of the three temperatures. In this way the following values (in volts and joules) for the cell reaction at the concentration 0.1000 were obtained.

Temperature.	18°.	25°.	35°.
Electromotive force	0.39783	0.39904	0.40033
Free-energy decrease	76782	77015	77263
Heat-content decrease	...	68134	...

By subtracting from these values of the free-energy decrease and heat-content decrease those given in Table VI and dividing by 2, values for the free energy of transfer and heat of transfer of 1 HCl from any concentra-

---

sults of the three investigators were as follows: to $1HCl.30H_2O$, 192 cal.; to $1HCl.50H_2O$, 336 cal.; to $1HCl.100H_2O$, 445 cal.; to $1HCl.200H_2O$, 515 cal.; to $1HCl.400H_2O$, 564 cal.; to $1HCl.800H_2O$, 605 cal.; to $1HCl.2000H_2O$, 646 cal.

[1] This follows from the relation $\frac{\partial Q}{\partial N_A} + 555 \frac{\partial Q}{\partial N_W} = Q_0^{555}$ in which the partial derivatives represent the "partial" heats of solution of one mol of the acid (A) and water (W), respectively, and Q_0^{555} represents the heat of solution of 1 HCl in 555 H_2O. This relation follows from the fact that the solution $1HCl.555H_2O$ may be produced either by mixing directly the two constituents 1 HCl and 555 H_2O or by introducing them in succession into an infinite quantity of solution of this composition.

tion to the concentration 0.1000 molal were obtained. These values expressed in joules are given in Table VII.

Table VII.—Decrease in Free Energy and in Heat Content Attending the Transfer of 1 HCl from any Concentration to 0.1000 Molal.

Conc. HCl.	$-\Delta F_{15}$.	$-\Delta F_{25}$.	$-\Delta F_{35}$.	$-\Delta H_{25}$.	$10^6 a$.	$10^6 b$.
4.484	23184	23544	24037	8474	2149	5.5
1.9278	15454	15744	16143	3591	2591	5.5
1.0381	11449	11679	12003	1937	2790	2.2
0.77137	9775	9971	10250	1619	2811	1.3
0.50948	7596	7757	7978	999	2924	8.0
0.33757	5730	5856	6021	684	2963	15.0
0.10000	0	0	0	0	..	..
0.033315	—5053[1]	—5167[1]	—5331[1]	—300	3161	7.3
0.01001	(—12477)	(—12657)	(—13183)	(—1700)	(2904)	..

The variation of the free energy of transfer with the temperature may be expressed for each concentration of acid by equations of the form

$$(-\Delta F_t)_c = (-\Delta F_{25})_c\,[1 + a(t - 25) + b(t - 25)^2];$$

where $(-\Delta F_{25})_c$ means the free-energy decrease attending the transfer of 1 HCl at 25° from concentration c to concentration 0.1000 molal. The values of these coefficients a and b (multiplied by 10^6) are given in the last two columns of Table VII.

The values of a just given would be equal to $1/T$ or 0.00335, if the change in heat content accompanying the transfer of 1 HCl from one concentration to another were zero, as would be the case if the hydrochloric acid were a perfect solute. The values of a approach this theoretical value as the acid concentration decreases, but they are still far from it even for the two lower concentration intervals 0.3376 to 0.1000 and 0.1000 to 0.03332. Correspondingly the values of the change in heat content are still large for these two concentration intervals.

These heats of transfer may be compared with values of the same quantity computed from the calorimetric measurements made by Thomsen, Steinwehr, and Richards mentioned near the end of Section 5. From the curve there referred to were read off values of the heat change on adding a definite amount of water to a definite amount of HCl solution of a given concentration. From tangents drawn to the curve the heat changes on adding 1 mol H_2O to an infinite amount of various HCl solutions (the so-called partial heat of solution of water) were obtained. From these two quantities the heats of transfer of 1 HCl into a solution containing 1 HCl in 10 liters of water from solutions containing 1 HCl in 0.494 liter, 1.30 liters, and 2.965 liters of water were calculated to be 990, 279, and 117 calories, respectively. The electromotive forces of this article lead

---

[1] It seems not improbable that these values are about 130 joules too large (arithmetically), judging from the magnitude of the error at the two lowest concentrations.

to the values 859, 387, and 164 calories for the same heats of transfer. The agreement is probably as good as can be expected from the data.

7. Relative Activities of the Ions of the Acid at Various Concentrations.

From the values for the free energy of transfer of hydrochloric acid the relative activities of the hydrogen ion and chloride ion in different solutions may be calculated by the equation $-\Delta F = 2RT \log (c_1\alpha_1/c_2\alpha_2)$. In this equation $-\Delta F$ is the free energy of transfer of 1 HCl from concentration c_1 to concentration c_2, and the symbols α_1 and α_2 represent the coefficients by which it is necessary to multiply the concentration of the acid in any solution in order to obtain the activity of the hydrogen ion or chloride ion in the solution. This quantity α will be called the activity coefficient. This equation involves the assumption that the activity of the hydrogen ion is equal to that of the chloride ion in each of the hydrochloric acid solutions. If this assumption is not valid, the calculated values of α represent the square root of the product of the activities of the two ions.

The values calculated by this equation for the ratio $(\alpha/\alpha_{0.1})$ of the activity coefficient of the acid at any concentration c to that at the concentration 0.1000 molal at 18, 25, and 35° are given in Table VIII.

TABLE VIII.—RELATIVE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID.

Mols HCl per 1000 g. H_2O.	Activity coefficient ratios $(\alpha/\alpha_{0.1})$. At 18°.	At 25°.	At 35°.
4.484	2.647	2.571	2.424
1.928	1.260	1.241	1.209
1.038	1.024	1.017	1.001
0.7714	0.975	0.970	0.957
0.5095	0.942	0.939	0.931
0.3376	0.967	0.966	0.959
0.10000	1.000	1.000	1.000
0.03332	1.057	1.058	1.061
0.01001	...	(0.779)	...
0.003333	...	(0.0113)	...

8. Combination of the Free Energy Values with those Derivable from Other Electromotive-Force Measurements.

The results here presented can not be compared with those of Jahn or of Tolman and Ferguson because their measurements relate to a range of concentrations below 0.1 molal. By combining, however, my results with the apparently very accurate ones of Jahn a series of free energy values for hydrochloric acid in solution can be obtained extending from 0.00167 to 4.48 molal. The free-energy decrease in joules attending the transfer of 1 HCl at 18° from 0.03336 molal (the highest concentration used by Jahn) to various lower concentrations c have been calculated by me from the electromotive forces and the cation transference number (0.826) given by Jahn. By adding to these values 5039 joules (which is equal to the quantity (5053 joules) given in Table VII for the transfer from 0.1000 to 0.03332 molal plus the quantity, —14 joules, calculated for the transfer from 0.03332 to 0.03342 molal), the free energy of transfer of 1 HCl at 18° from 0.1000 molal to various lower concentrations is obtained.

The values so found are given, expressed in joules, in Table IX. The concentrations have been calculated over from the volume concentrations used by Jahn to mols HCl per 1000 g. water.

TABLE IX.—THE FREE ENERGY ATTENDING THE TRANSFER AT 18° OF 1 HCl FROM 0.1000 MOLAL TO VARIOUS SMALL CONCENTRATIONS.

Mols HCl per 1000 g. H_2O.	Free-energy decrease.
0.03342	5039
0.01668	8224
0.01115	10084
0.00832	11447
0.006683	12472
0.005569	13325
0.003334	15717
0.001667	19031

By combining the values of the free-energy decrease attending the cell reaction given in Table VI with the free-energy decrease attending the reaction $2Hg + Cl_2$ (1 atm.) = Hg_2Cl_2 (solid) one may obtain the free energy of 1 HCl (referred to its elements) in solution at the various concentrations and temperatures. Now Lewis and Rupert[1] found the electromotive force of the cell $Hg + Hg_2Cl_2$, HCl (0.1 *M.*), Cl_2 (1 atm.) to be 1.0896 volts at 25°. The free energy of formation of 1 Hg_2Cl_2 at 25° is therefore —50,250 cal. With the aid of its heat of formation (—62,890 cal.) its free energy of formation is found to be —50,510 cal. at 18° and —49,860 cal. at 35°.

Table X contains the values calculated in this manner for the free energy in calories of 1 HCl in solution, the free energies of its elements being regarded as zero at each temperature.

TABLE X.—FREE ENERGY OF 1 HCl IN SOLUTION AT VARIOUS CONCENTRATIONS AND TEMPERATURES.

Mols HCl per 1000 g. H_2O.	Free energy in calories.		
	At 18°.	At 25°.	At 35°.
4.484	—28890	—28700	—28410
1.9278	—30750	—30570	—30300
1.0381	—31700	—31540	—31290
0.7714	—32100	—31950	—31710
0.5095	—32620	—32480	—32250
0.3376	—33070	—32930	—32720
0.1000	—34440	—34330	—34160
0.03332	—35650	—35570	—35440
Mols HCl per 1000 g. H_2O.	Free energy at 18°.		
0.01668	—36410		
0.01115	—36850		
0.008324	—37180		
0.006683	—37420		
0.005569	—37630		
0.003334	—38200		
0.001667	—38990		

This table might be extended so as to include more concentrated solutions with the aid of Dolezalek's[2] measurements of the electromotive

---

[1] THIS JOURNAL, **33**, 305 (1911).

[2] *Z. physik. Chem.*, **26**, 334 (1898).

force of cells H_2, HCl (4.98 to 12.25 normal), Cl_2. However, as his measurements were at 30° and as his electromotive forces were not reproducible closer than 6 millivolts, this reference to them will be sufficient.

By combining these free energies with vapor-pressure data it would be possible to obtain also the free-energy content of hydrogen chloride gas at any pressure. Such data have been obtained by Gahl[1] at the acid concentrations involved in this investigation; but calculation shows that Gahl's results do not agree well with the electromotive-force data above presented. He gives 0.0094 and 0.00117 mm. mercury as the partial pressures at 25° of HCl in the solutions containing 4.007 and 2.011 mols HCl per 1000 g. water. From these vapor pressures the free energy of transfer of HCl from 4.007 molal to 2.011 molal is found by the equation $-\Delta F = RT \log (940/117)$ to be 5170 joules. Interpolation from the electromotive-force measurements gives 6280 joules for the same free-energy decrease. Since Gahl's results at higher concentrations are also discordant with those of Dolezalek,[2] it is doubtful whether they are accurate enough to warrant the calculation of the free energy of gaseous hydrogen chloride from them.

9. Discussion of the Activity Coefficients of Hydrochloric Acid and Potassium Chloride.

From the free-energy values derived from Jahn's measurements we can calculate in the same way as was done above the relative activity coefficients of the acid at various concentrations; and, by combining these with the activity coefficients presented in Table VIII, a series of relative activity coefficients extending from 0.00167 to 4.484 molal is obtained. Assuming provisionally that at this lowest concentration the activity coefficient is substantially equal to the so-called ionization-coefficient derived from the conductance ratio, a series of absolute activity coefficients may be calculated. This assumption, to be sure, probably introduces a considerable error; for Jahn's data indicate that the activity coefficient continues to increase more rapidly than the conductance ratio even below the concentration 0.00167, which would make all the activity coefficients considerably smaller than those calculated. Any attempt to extrapolate would, however, be so arbitrary that it has not been attempted at this time, and the stated assumption has been employed provisionally.

The values of the activity coefficients at 18° so calculated and interpolated for round concentrations are given in Table XI. In this table in a neighboring column are given also, for the sake of comparison, values of the conductance-viscosity ratio $\Lambda\eta/\Lambda_0\eta_0$ at the same concentrations.

---

[1] *Z. physik. Chem.*, **33**, 178 (1900).

[2] *Ibid.*, **26**, 334 (1898).

The values employed up to 0.2 molal are those of Bray and Hunt[1] as corrected for viscosity by Noyes and Falk,[2] and those at the concentrations 0.5 and 1.0 molal are based on the data of Kohlrausch[3] and the viscosity determinations of Reyher.[4]

TABLE XI.—ACTIVITY COEFFICIENTS AND CONDUCTANCE VISCOSITY RATIOS FOR HYDROCHLORIC ACID AT 18°.

Mols HCl per 1000 g. H_2O.	Activity coefficient.	$\Lambda\eta/\Lambda_0\eta_0$.	Mols HCl per 1000 g. H_2O.	Activity coefficient.	$\Lambda\eta/\Lambda_0\eta_0$.
0.001677	0.988	0.988	0.20	0.818	0.909
0.002	0.987	0.988	0.30	0.804	0.903
0.005	0.971	0.981	0.50	0.793	0.890
0.010	0.947	0.972	0.75	0.820	0.870
0.020	0.918	0.962	1.00	0.857	0.845
0.050	0.874	0.944	2.00	1.086	...
0.100	0.843	0.925	4.484	2.228	...

It will be seen that with increasing concentration the activity coefficient first falls much more rapidly than the conductance-viscosity ratio, the two values at 0.1 molal being 0.843 and 0.925. The activity coefficient, however, unlike the conductance-viscosity ratio, passes through a minimum at about 0.50 molal, and then increases rapidly with the concentration, becoming about equal to that ratio at 1 molal, and attaining at 4.48 molal a value 2.23 times as great as that at zero concentration.

It is of interest to compare the activity coefficients of hydrochloric acid with those of potassium chloride at 25° derived from the accurate electromotive-force measurements of MacInnes and Parker.[5] The reliability of their results is evidenced by the fact that their two series of measurements made with cells of the two types Ag + AgCl, KCl(c_1), KCl(c_2), AgCl + Ag, and Ag + AgCl, KCl(c_1), K_nHg, KCl(c_2), Ag + AgCl gave closely concordant results, and that their results agree well with those obtained by Jahn at 18°. The electromotive force values obtained by MacInnes and Parker have, for the sake of comparison, been treated in the same way as have those obtained in this investigation. Namely, the free-energy decrease attending the transfer of 1 HCl from concentration c_1 to concentration c_2 was calculated from them, using as the cation-transference number[6] 0.497 for concentrations up to 0.1 normal and 0.495 for the concentration-interval 0.05–0.5. Then the corresponding activity-coefficient was calculated from them by the usual logarithmic formula, making the same provisional assumption as MacInnes and Parker made in their own calculations of the activity coefficients, namely,

---

[1] THIS JOURNAL, 33, 787 (1911).

[2] *Ibid.*, 34, 475 (1912).

[3] *Landolt-Börnstein Tabellen*, 4th Ed., p. 1104.

[4] *Z. physik. Chem.*, 2, 744 (1888).

[5] THIS JOURNAL, 37, 1445–1461 (1915).

[6] Noyes and Falk, *Ibid.*, 34, 474 (1912).

that the activity coefficient and conductance ratio are identical at 0.001 molal, the smallest concentration employed.

The results are presented in Table XII. The type of cell by means of which they were derived is indicated by the letters A and B, A referring to the simple concentration cell with silver-silverchloride electrodes, and B to the double cell with amalgam electrodes.

TABLE XII.—FREE ENERGY OF TRANSFER OF POTASSIUM CHLORIDE AND ITS ACTIVITY COEFFICIENTS.

Concentration.		Type of cell.	Free-energy decrease.	Activity coefficient at c_1.	Conductance ratio at c_1.
c_1.	c_2.				
0.50	0.05	A	10360	0.636	0.779
		B	10440		
0.10	0.01	A	10510	0.727	0.860
		B	10485		
0.05	0.005	A	10700	0.781	0.889
		B	10630		
0.01	0.001	B	10870	0.876	0.941
0.005				0.911	0.956
0.001				(0.979)	0.979

MacInnes and Parker have already drawn from their data the more essential conclusions; but this table, especially when considered in connection with Tables IX and XI for hydrochloric acid, brings out clearly certain relations. In the first place it shows the close agreement of the results obtained by MacInnes and Parker with the two types of cells. Then it shows that even for the lowest ten-fold concentration interval the free-energy decrease (10,870 for KCl, 10,810 for HCl) is still far from the value (11,420 joules) for a completely ionized perfect solute, and that correspondingly the activity coefficient still changes considerably during that interval, namely, by over 10% for both substances. It shows further that with potassium chloride, as with hydrochloric acid, the activity coefficient up to 0.1 normal decreases much more rapidly than the conductance ratio, being at this concentration 15% lower for potassium chloride and 9% lower for hydrochloric acid. It shows finally that the activity coefficient at corresponding concentrations is many per cent. smaller for potassium chloride than for hydrochloric acid, thus disproving the assumption sometimes made that the activity coefficients of these two substances can be regarded as equal.

Finally, a comparison may be made between the values of the activity coefficients of potassium chloride derived from the electromotive-force measurements and those derived from freezing-point determinations by the method recently described by Bates.[1] With the aid of the laws of thermodynamics and of the two assumptions that the two ions in the same solutions have equal osmotic pressures and that the true value

---

[1] THIS JOURNAL, 37, 1421–1445 (1915).

of the ionization is given by the conductance-viscosity ratio, he found that the change at 0° of the osmotic pressure π of either ion with its concentration $c\gamma$ is expressed in the case of potassium chloride by the equation $d\pi/d(c\gamma) = RT(1-0.0552(c\gamma)^{0.207})$. From this equation and the two thermodynamic relations

$$-\Delta F = \int_{\pi_2}^{\pi_1} \frac{d\pi}{c\gamma} \text{ and } -\Delta F = \mathrm{RT} \log \frac{c_1\alpha_1}{c_2\alpha_2},$$

supplemented by the assumption that the activity coefficient α approaches unity as the salt concentration c approaches zero, the activity coefficients corresponding to Bates' osmotic pressure calculations are found to have the values given in the second line of Table XIII while those derived from the electromotive-force measurements of MacInnes and Parker were shown in Table XII to have the values recorded in the third line of Table XIII.

TABLE XIII.—COMPARISON OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE DERIVED FROM FREEZING-POINT AND FROM ELECTROMOTIVE-FORCE MEASUREMENTS.

Salt concentration	0.01	0.05	0.10	0.50
Activity coefficient (Bates)	0.884	0.772	0.732	0.640
Activity coefficient (M. & P.)	0.876	0.781	0.727	0.636

The close agreement throughout the whole range of concentration of the two sets of activity values based upon entirely independent experimental data is highly remarkable. If confirmed by results with other substances it will afford proof of the hypothesis that the conductance viscosity ratio is a substantially correct measure of ion concentration (though not of ion activity); for, as stated above, Bates' calculations involve this assumption, while the calculations from the electromotive forces are independent of it. Unfortunately, sufficiently accurate freezing-point data are not available for hydrochloric acid to enable corresponding computations to be made in the case of this substance.

10. Summary.

In this article the preparation of calomel electrodes reproducible to 0.05 millivolt when in contact with hydrochloric acid 0.1 molal or higher has been described; and measurements of the electromotive force of cells of the type H_2 (1 atm.), HCl solution, $Hg_2Cl_2 +$ Hg at 18°, 25°, and 35°, and with HCl concentrations from 0.033 to 4.5 molal have been presented (Table V).

From these electromotive-force values have been computed:

1. The change in free-energy content and in heat content attending the reaction H_2 (1 atm.) + Hg_2Cl_2 (solid) = 2Hg (liquid) + 2HCl at various concentrations (Table VI).

2. The change in free-energy content and in heat content attending the change HCl (at c_1) = HCl (at c_2) (Table VII).

3. The ratio of the activities of the hydrogen ion or chloride ion in solutions of various concentrations (Table VIII).

By combining these results with those derived from Jahn's measurements of the electromotive force at 18° of cells Ag + AgCl, HCl(c_1), HCl(c_2), AgCl + Ag the series of free-energy values has been extended from 0.033 to 0.00167 molal (Table IX). And with the aid of calorimetric data and an electromotive force determination of the cell H_2, HCl, Hg_2Cl_2 + Hg by Lewis and Rupert, the absolute free energy of HCl (referred to the free energies of the elements as zero) at 18, 25, and 35° in solutions from 0.00167 molal to 4.5 molal has been calculated and tabulated (Table X).

From these free-energy data, with the aid of the assumption that at the lowest concentration (0.00167 molal) the ion activity is equal to the ion concentration, a series of absolute activity coefficients for hydrochloric acid covering the concentration range 0.00167–4.5 molal has been computed (Table XI). These have then been compared with the activity coefficients of potassium chloride derived from the electromotive-force measurements of MacInnes and Parker (Table XII) and the osmotic pressure calculations of Bates (Table XIII).

The results lead to the conclusions that the activity coefficients both of hydrochloric acid and potassium chloride decrease up to 0.1 molal far more rapidly than do the conductance ratios. The difference at this concentration amounts to 9% for hydrochloric acid and 15% for potassium chloride, so that in using the conductance ratio as a measure of ion activity in mass-action expressions, as is commonly done, a corresponding error is involved. At a concentration of about 0.5 molal the activity coefficient of hydrochloric acid reaches a minimum, and then increases very rapidly with increasing concentration, becoming at the highest concentration (4.48 molal) 2.23 times as great as at zero concentration. The results show further that the activity coefficients of potassium chloride derived independently from electromotive force and from freezing-point measurements are in remarkable agreement, affording evidence that in the case of this salt the conductance ratio is a true measure of ion concentration (though not of ion activity), since this assumption is made in the calculation from the freezing points, but not in that from the electromotive forces.

BOSTON, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE ATOM AND THE MOLECULE.

BY GILBERT N. LEWIS.

Received January 26, 1916.

In a paper entitled "Valence and Tautomerism"[1] I took occasion

---

[1] THIS JOURNAL, 35, 1448 (1913); see also the important article of Bray and Branch, *Ibid.*, 35, 1440 (1913).