12. It is shown that assumption (*a*) has better theoretical and experimental support than have either of the other two assumptions.

13. The calculation of the degree of ionization from freezing-point data by the aid of the mol-number i assumes that assumptions (*b*) and (*c*) of paragraph 11 both hold and hence is theoretically incorrect.

14. It follows from the thermodynamic expression for equilibrium in solutions of electrolytes, that the necessary and sufficient condition that the law of mass action hold over a given concentration range is that $d\pi_i/dC_i = d\pi_u/dC_u$ for all solutions within this range.

15. There is nothing in the simple form of the electrolytic dissociation theory which necessitates the conclusion that the ions and the undissociated molecules of electrolytes obey van't Hoff's law. If they do not obey this law, the law of mass action cannot be followed. Hence the fact that solutions of strong electrolytes deviate from the requirements of the mass law is no argument against the theory of electrolytic dissociation.

16. The deviations from the law of mass action may be conveniently discussed in terms of the deviation of the ions and of the undissociated molecules from van't Hoff's law.

PASADENA, CAL.

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POTASSIUM CHLORIDE CONCENTRATION CELLS.

BY DUNCAN A. MACINNES AND KARR PARKER.

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1. Purpose and Outline of the Investigation.

As a method for studying salt solutions, the determination of the electromotive force of concentration cells has the advantage, when compared with the freezing-point measurements, that the temperature at which the determination is carried out is not fixed, and may be kept constant at any desired point. This advantage is shared by vapor-pressure lowering and osmotic-pressure measurements, but the experimental difficulties have been found to be great in these determinations, particularly so when dilute solutions are investigated. It is, therefore, rather surprising that this method of attack of problems connected with salt solutions has not received more attention, since the thermodynamic relations connecting the results of the measurements of the electromotive force of concentration cells with the colligative properties of the solutions may readily be derived. The presence of liquid junctions in most concentration cells, and the uncertainty as to the method of correcting for them, may have contributed to the comparative neglect of this field. The present investigation was undertaken with the double purpose of measuring the free energy of dilution of potassium chloride by the electromotive force method, and of investigating liquid junctions connecting salt solutions of different concentrations, by comparing the electromotive forces of cells in which these junctions are present with similar measurements on cells constructed so as not to involve this somewhat troublesome point of contact.

Among the few investigations yielding results suitable for interpretation in connection with the study of strong binary electrolytes is the accurate and much-discussed work of Jahn[1] on concentration cells of very dilute solutions of potassium and sodium chlorides and hydrochloric acid. Determinations of the electromotive force of concentration cells of hydrochloric acid have been made by Tolman and Ferguson.[2] Bell and Feild[3] and Cumming[4] have investigated cells containing silver nitrate solutions. There are, of course, many other measurements of the electromotive force of concentration cells in the chemical literature, but they deal with a single pair of solutions, are of doubtful accuracy, or else the solutions involved contain polyvalent ions. The latter introduce complexities which it is out of the province of the present paper to discuss.

Two forms of concentration cells have been investigated. The first, of which the following is typical:[5]

$$\begin{array}{l|ll|ll|ll}
\text{Hg} & \text{HgCl,} & \text{HCl} & \text{HCl,} & \text{HgCl} & \text{Hg} & \text{(A)} \\
 & \text{solid} & C_1 & C_2 & \text{solid} & &
\end{array}$$

consists of two nonpolorizable electrodes in equilibrium with solutions, of concentrations C_1 and C_2, which are connected by a liquid junction. Cells of this type were employed in Jahn's researches, and are usually called "concentration cells with transference."

The second variety, "concentration cells without transference," may be represented by the following example:

$$\begin{array}{l|c|c|c|ll}
\text{Hg} & \text{HgCl, HCl, } H_2 & \text{Pt — Pt} & H_2\text{, HCl, HgCl} & \text{Hg} & \text{(B)} \\
 & C_1 & & C_2 & &
\end{array}$$

These are composed of two independent cells, and involve no liquid junction. This latter type has been the subject of a research by Tolman and Ferguson.[6]

The cells without diffusion are capable of simpler theoretical interpretation, as will be shown in the next section. There is, however, the experimental difficulty of finding a reversible electrode for *both* the ions of

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

[2] THIS JOURNAL, **34**, 232 (1912).

[3] *Ibid.*, **35**, 715 (1913).

[4] *Trans. Faraday Soc.*, **2**, 213 (1907).

[5] In this paper the conventions adopted in the bibliography by Abegg, Auerbach and Luther, "Messungen electromotorischer Kräfte galvanischer Ketten" will be followed. A vertical line represents a junction; solid-liquid or liquid-liquid. A positive value for the E. M. F. means that current tends to flow from right to left through the cell.

[6] *Loc. cit.*

the electrolyte, and for uni-univalent electrolytes this condition has, so far, been met only in the case of cells involving the halogen acids.

The development of the alkali metal amalgam electrodes by Lewis and Kraus[1] has made it possible to investigate cells of the following form:

$$\mathrm{Ag}\ \left|\begin{array}{l}\mathrm{AgCl,\ KCl}\\ \text{solid}\quad C_1\end{array}\right|\ \mathrm{K(Hg)}_x - \mathrm{K(Hg)}_x\ \left|\begin{array}{l}\mathrm{KCl,\ AgCl}\\ C_2\quad \text{solid}\end{array}\right|\ \mathrm{Ag}\qquad (C)$$

a series of which, using various values of the concentrations C_1 and C_2, are dealt with in this paper. Electromotive force measurements on the corresponding cells with transference:

$$\mathrm{Ag}\ \left|\begin{array}{r}\mathrm{AgCl,\ \ KCl}\\ C_1\end{array}\right|\begin{array}{l}\mathrm{KCl,\ \ AgCl}\\ C_2\end{array}\left|\ \mathrm{Ag}\right.$$

have also been made. The results of these measurements will be considered in the light of the equations which will be derived in the next section.

2. Thermodynamics of Concentration Cells.

The thermodynamic differential equations connecting the osmotic work and the electrical energy for the two kinds of concentration cells may be derived most readily by the use of the thermodynamic engine devised by Washburn.[2]

Fig. 1 represents the engine used for deriving the equation for the concentration cells with transference. The chamber G contains the salt solution, KCl for instance, at the concentration C. The osmotic pressures of the ions at this concentration may be represented by Π_{K^+} and $\Pi_{Cl'}$. D represents a reversible electrode, such as silver covered with a layer of silver chloride. The cylinder A is fitted at one end with a membrane a permeable only to the potassium ion. The piston in the cylinder permits the passage of water only. The solution between the piston and the membrane consists, therefore, of a solution of potassium ion in osmotic equilibrium with the solution in chamber G. The membrane b is permeable only to chloride ions. The other half of the engine is similar to that just described, except that the vessel G' contains the salt at the concentration $C + dC$, and the ions have the osmotic pressures $\Pi_{K^+} + d\Pi_{K^+}$ and $\Pi_{Cl'} + d\Pi_{Cl'}$. A movement of the piston $A - A'$ from left to right is, obviously, against the osmotic pressure $d\Pi_{K^+}$. An electrolytic connection with the vessels G to G' is afforded by the liquid junction as shown.

If the key K is closed and one equivalent F of electricity is allowed to pass, one equivalent of chloride ion will be formed at the electrode D and a like amount will be removed from the solution by electrolysis at electrode D'. The passage of the electricity across the liquid junction will be accomplished by the movement of η_K equivalents of potassium

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[1] Lewis and Kraus, THIS JOURNAL, 32, 1459 (1910). See also Lewis and Keys, *Ibid.*, 34, 119 (1912); 35, 340 (1913).

[2] THIS JOURNAL, 32, 467 (1910).

ion in the direction of the current (from G' to G) and the migration of $(1 - \eta_K)$ equivalents of chloride ion in the reverse direction, where η_K is the Hittorf transference number of the cation. Thus the total effect of the operation of the cell will be the transfer of η_K equivalents of potassium chloride from the solution of the concentration $C + dC$ to one of the concentration C. To compensate for this change and to maintain a constant difference of concentration the pistons $A - A'$ and $B - B'$ are moved reversibly toward the right, withdrawing η_K mols of each ion from chamber G and forcing them into chamber G'. As the electrical energy must be equal to the osmotic work, the following relation holds:

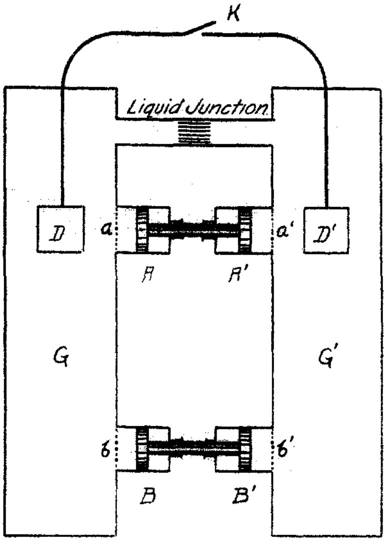

Fig. 1.

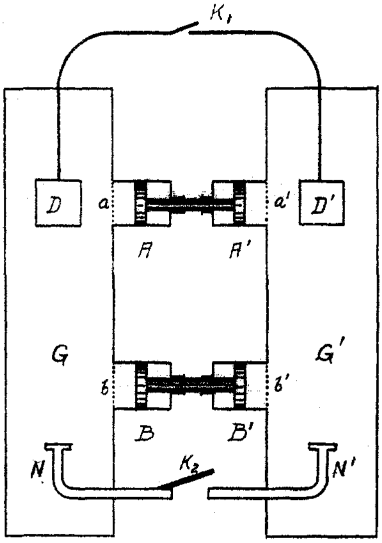

Fig. 2.

$$FdE = \eta_K (V_{K^+} d\Pi_{K^+} + V_{Cl'} d\Pi_{Cl'}) \qquad (1)$$

in which E is the electromotive force and V_{K^+} and $V_{Cl'}$ are the volumes of solution containing one gram equivalent of ion.

Fig. 2 is a thermodynamic engine for the cells without transference. It is similar to that shown in Fig. 1 except that the liquid junction has been replaced by the electrodes $N - N'$, which, in the case under discussion, are potassium amalgam electrodes. The concentrations of the salt are C and $C + dC$ in the chambers G and G' as before. On closing keys K_1 and K_2 and allowing F coulombs to pass, one gram equivalent each of potassium ion and of chloride ion will be formed in chamber G and a like amount will be removed by the electrodes from chamber G'. To maintain equilibrium the pistons $A - A'$ and $B - B'$ must be moved reversibly toward the right, each through a volume containing one gram equivalent of ion. Equating the osmotic work and electrical energy we have:

$$FdE = V_{K^+}\, d\Pi_{K^+} + V_{Cl'}\, d\Pi_{Cl'} \qquad (2)$$

an expression which differs from (1) only in the fact that it does not contain the transference number η_K. Equations 1 and 2 are as far as we can go using purely thermodynamic reasoning.

If we assume that the ions are normal solutes and the solutions are dilute, *i. e.*, that $\Pi = RT/V = CRT$ (C = concentration) hold for each ion, Equation 2 becomes $FdE = 2RTd\ln C$, which on integration gives:

$$E = 2RT/F \ln C'_i/C_i \qquad (3)$$

for the electromotive force of concentration cell without transference, in which C_i and C_i' are the concentrations of either ion in the two solutions.

With the further assumption that η_K is independent of the concentration, the integration of Equation 1 gives the familiar Nernst equation:

$$E = 2\eta_K RT/F \ln C'_i/C_i \qquad (4)$$

3. The Concentration Cells without Transference.

As already mentioned, the concentration cells without transference that have been investigated may be represented by:

$$\text{Ag} \left| \begin{matrix} \text{AgCl, KCl} \\ \text{solid} \quad C_1 \end{matrix} \right| \text{K(Hg)}_x - \text{K(Hg)}_x \left| \begin{matrix} \text{KCl, AgCl} \\ C_2 \quad \text{solid} \end{matrix} \right| \text{Ag}$$

These cells involve (*a*) reversible silver-silver chloride electrodes and (*b*) reversible potassium amalgam electrodes.

(*a*) **Silver halide electrodes** have been thoroughly investigated by Jahn[1] and by Halla.[2] In most particulars the directions for their construction given by the latter have been followed. A disadvantage of the forms used by both these investigators was the limited extent of surface exposed to the solution, since they were made from a single piece of silver or platinum wire. As the tendency to polarize when small currents are applied and the electrical resistance of the solid liquid boundary both decrease with an increase of surface, the electrodes represented by R — E and *R'* — *E'* in Fig. 3 were used. They consist of a piece of platinum gauze of about three square centimeters area, welded to a platinum wire which made contact with mercury through a seal in a glass tube. The gauze was plated with a thick coating of silver from a $KAg(CN)_2$ solution, using a current density of about 0.5 ampere per square decimeter of surface. The electrodes were then thoroughly washed and allowed to stand twenty-four hours in pure water. They were next made anodes in a dilute potassium chloride solution, to which a few drops of hydrochloric acid had been added. After electrolyzing five or ten minutes with a current of 5 to 7 milliamperes per electrode, the electrodes were covered with a coating

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

[2] *Z. Electrochem.*, 17, 179 (1911).

of silver chloride, of a reddish brown color, the shade of which was the same whether the electrolysis was carried out in the light or in complete darkness.

Forty electrodes were made in this manner in sets of eight. Electrodes chosen at random from different sets were checked against each other

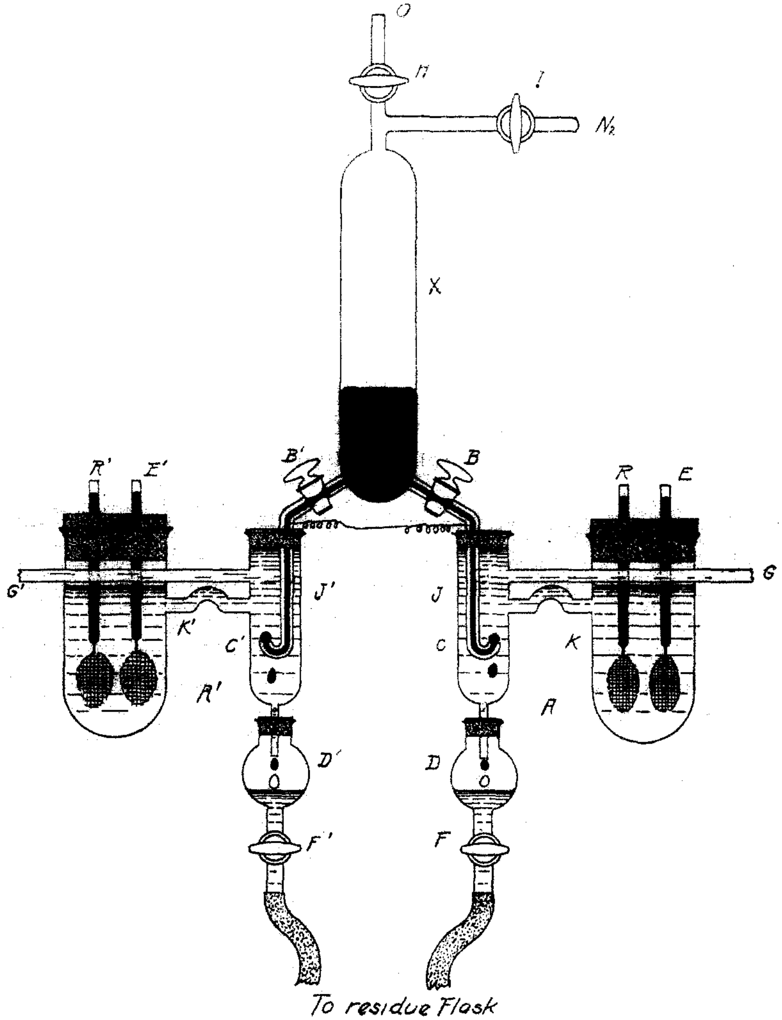

Fig. 3.

frequently, with the result that "normal"[1] electrodes were always found to be within a few tenths of a millivolt of each other. When polarized

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[1] Two kinds of abnormal electrodes were encountered (*a*) those which became abnormal because of the attack of a parasitic mold, and (*b*) those in which a white

by the application of one millivolt they returned to their original potential in a few minutes. New electrodes from one set generally showed potential differences of only a few hundredths of a millivolt. There was a slight ageing effect noticed, the older electrodes being electropositive to the newer ones. As this effect was always in the same direction and of the same magnitude within 0.05 mv. no error arose from this source, since similar electrodes were always opposed to each other.

(*b*) **The alkali metal amalgam electrode** employed is represented by *X* in Fig. 3. It differs from that used by Lewis and his associates only in having two capillary outlets *J* and *J′* for the amalgam, in order that it could be used in the two half cells at one time. To fill the electrode cell with the amalgam, the amalgam reservoir shown in Fig. 4 was inverted and connected by a **T**-tube to *O* in Fig. 3. The other branch of the **T**-tube was then connected to the Gaede pump. After exhausting and thoroughly drying the cell, the stopcock to the amalgam reservoir was opened and the amalgam was run from the reservoir. Dry, pure nitrogen was then introduced through the tube marked N_2. The surface of the amalgam either remained bright after the introduction of the nitrogen or else an exceedingly thin film slowly formed over the surface.

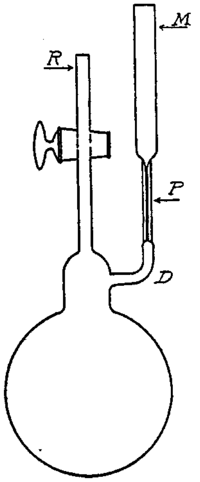

Fig. 4.

The potassium amalgam was prepared by a method which is a simplification of that used by Lewis and Kraus.[1] A diagram of the vessel used for this purpose is shown in Fig. 4. It consists of a distilling flask with

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allotropic silver chloride appeared to be formed in place of the "normal" plum colored AgCl.

(*a*) Some of the electrodes were attacked by an organism after some weeks, although the solutions in which they were placed were made up from conductivity water and pure KCl. The electrodes so attacked invariably became electrically different from the "normal" ones, developing in some cases a potential difference as high as 10 mv. This potential difference was always in the same direction, negative to the "normal" electrode. The mold was investigated by Dr. F. L. Stevens of the Botanical Department of the University of Illinois and, although conditions were very unfavorable for its development and culture, was identified as a parasitic mold (Aspergilna).

(*b*) The second class of "abnormal" electrodes appeared to have an allotropic form of AgCl on their surface. This form of AgCl, white in color and unaffected by diffused daylight even after weeks of exposure, sometimes appeared in spots on a "normal" electrode and sometimes covered the entire surface. These electrodes were always electronegative to the "normal" electrodes by varying amounts. The electrodes were all prepared under like conditions and the reason for the development of this modification of AgCl on some electrodes and on certain spots on a "normal" electrode is not clear.

[1] THIS JOURNAL, 32, 1459 (1910).

a stopcock fitted to its neck and a capillary tube, *P*, of about 0.4 mm. bore, sealed at one end to the delivery tube of the flask and at the other end to the tube *M* with an internal diameter of 6 mm. Pure mercury was first poured into the carefully dried apparatus. Pellets of potassium were placed in the tube *M*, which was then fused together at upper end. These pellets can be conveniently made by forcing a cork borer into a piece of the metal and then pushing the resulting small cylinder of the metal directly into the tube *M* by means of a closely fitting glass tube. The surface of the metal thus obtained was covered with a very thin film of oxide. The whole apparatus was next evacuated through the tube *R* by means of a Gaede pump. The pumping was continued for half an hour or more, during which time the apparatus was gently warmed to aid in removing the last traces of air and moisture from the mercury, after which the side tube from *M* to *D* was slowly and uniformly heated with a small, free flame. The potassium soon melted and passed through the capillary, collecting as a brilliant spot of metal in the bend of the tube at *D*. The capillary was then sealed off at *P* and the whole apparatus inverted, thus bringing the potassium and mercury into contact. The amalgamation took place quietly, little heat being evolved. When solution was completed, the apparatus was shaken for some time in order to be sure that the resulting amalgam was uniform. In appearance the surface to the amalgam was as bright as the mercury from which it was prepared. Amalgams of various concentrations were prepared from the stock amalgam by diluting, *in vacuo*, with pure mercury.

4. Design and Operation of the Cell.

The apparatus for the concentration cell without transference is shown in Fig. 3. The design finally adopted is the result of considerable preliminary experimenting, as it was found that there were a number of obstacles in the way of realization of complete reversibility at the amalgam electrode. One of the greatest difficulties was the side reaction:

$$2K + 2H_2O = 2KOH + H_2$$

It this takes place a rapid drop of the potential between the electrode and solution must follow, since the concentration of the amalgam is thereby lowered and the ion concentration in the immediate vicinity of the electrode is increased. This difficulty was, it is believed, entirely overcome by having a constantly moving amalgam. The arrangement of the cell also permits the immediate removal of the drops of amalgam as they get detached, since they fall directly into bulb *D* and thence into the residue flask. Streams of fresh solution, run in through the tubes *G* and *G'*, were made to pass by the amalgam electrodes. This made sure that measurements were carried out with solutions uncontaminated by the passage of the amalgam. The air spaces in the bulbs *D* and *D'* permitted the worker to observe the rapidity of the flow of the solution and prevented short circuiting through the rejected material or through the thermostat water. It was found that readings of the voltage of this cell became constant within about 0.05 millivolt when the flow of amalgam was about thirty drops per minute. After this an increase in the rate of flow had no influence on the results. The rate of flow of the solution was also found to have no influence, above a certain minimum. It is apparent that the effect of the side reaction given above was eliminated by this arrangement and also that the amalgam had time to come to electrical equilibrium in the short time that it was in contact with the solution. The formation of hydrogen was never observed in the cell, even when very few drops of amalgam per minute were passing.

The separation of each half cell into two portions, C, K and C', K', made it possible to leave the Ag, AgCl electrodes in contact with solution with which they were in equilibrium and which was also not disturbed by the solution flowing past the amalgam electrodes. The bent connecting tube aided in preventing mixing.

Early in the investigation it was recognized that oxygen dissolved in the solutions can influence the results on account of the side reaction:

$$K_2 + O + H_2O = 2KOH,$$

and for this reason the solutions were prepared so that they came in contact with the air for only a very short time. The effect of this side reaction is the same as the previous one, *i. e.*, to lower the electromotive force, since the addition of potassium ions to both solutions will lower the ratio of the ion concentrations.

The solutions were made at first by collecting the water very hot in "Resistenz-glas" bottles from the still used for preparing conductivity water, pumping out the air remaining above the water and replacing it by pure nitrogen. The correct amount of salt necessary to make a solution of the required strength (in mols per liter) with all weights calculated to vacuum standard, was then added in a small glass capsule and allowed to dissolve. A small amount of air was carried into the solution in this last operation. Table I gives measurements of the E. M. F. of the cell:

$$\mathrm{Ag}\ \left|\ \begin{matrix}\mathrm{AgCl,\ KCl}\\ 0.5\ N\end{matrix}\ \right|\ \mathrm{KHg}_x - \mathrm{KHg}_x\ \left|\ \begin{matrix}\mathrm{KCl,\ \ AgCl}\\ 0.005\ N\end{matrix}\ \right|\ \mathrm{Ag}$$

the solutions in which were made as has just been described, using amalgams of widely varying concentration in the amalgam electrode.

TABLE I.

Conc. of amalgam	0.02% approx.	0.002% approx.	0.0002% approx.
E. M. F.........	+0.10603 ± 0.00001	+0.10600 ± 0.00001	+0.1060 ± 0.0005

These figures indicate that the electromotive force is independent of the concentration of the amalgam within wide limits. The amalgam in the last determination was too dilute to allow the most accurate measurements to be made. When, however, the results of several series of determinations similar to the above, and involving solutions of different concentrations, were plotted, irregularities appeared which could only be explained by assuming that the small amount of dissolved oxygen remaining in the solution reacted instantaneously with the amalgam, lowering the potential at both amalgam-solution boundaries. As can be seen from Table I this effect is, however, surprisingly constant. Accordingly, the final measurements were made using solutions from which every trace of oxygen was excluded.

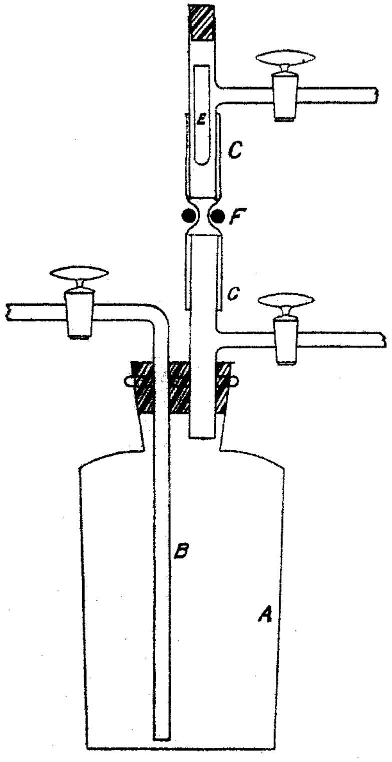

Fig. 5.

The apparatus used for preparing the air-free solutions is shown in Fig. 5. The stopper of the "Resistenz-glas" bottle *A* is fitted with two tubes. Tube *B*, which reaches to the bottom of the flask, is used for the delivery of the solution to tube *G* of Fig. 3. Tube *C—C'* is in two parts, which may be shut off from each other by a piece of carefully cleaned rubber tubing and a pinchcock, represented by *F*. Both parts are fitted with stopcocks, as shown. In making the solution, the water was collected by placing the outlet from the still well within the mouth of the bottle and regulating the flow through the condenser of the still so that the water was collected as hot as possible and the air originally in the bottle was displaced by the large volume of steam which was evolved. When the bottle was nearly full, the stopper was inserted, the tube *B* filled with water, and the water boiled for fifteen or twenty minutes by evacuating through the outlet from tube *C*. After this pure nitrogen was run in through this tube and the water allowed to cool with a pressure of this gas upon it. The required amount of salt was then weighed out into the capsule *E* and placed above the pinchcock in the tube *C'*, which was then closed at its upper end. After the air had been removed from this space by evacuating and filling with nitrogen several times, the capsule was made to drop into the water by opening the pinchcock *F*. The water in tube *B* was then displaced by nitrogen and the bottle was shaken until the solution was uniform.

Table II gives a summary of the results obtained from cells in which the solutions used were prepared in the manner just described.

TABLE II.—THE ELECTROMOTIVE FORCE OF POTASSIUM CHLORIDE CONCENTRATION CELLS WITHOUT TRANSFERENCE AT 25°.

Ag	AgCl, KCl soln.	K_xHg — K_xHg	KCl soln. AgCl	Ag,	E. M. F.
"	Solid 0.5 N	0.02%	0.05 N solid	"	—0.10735
"	" 0.5 "	0.002%	0.05 " "	"	—0.10745
"	" 0.1 "	0.004%	0.01 " "	"	—0.10885
"	" 0.1 "	0.002%	0.01 " "	"	—0.10900
"	" 0.05 "	0.004%	0.005 " "	"	—0.11085
"	" 0.05 "	0.002%	0.005 " "	"	—0.11085

The amalgam concentrations are approximate.

The electromotive force measurements were carried out with a Leeds & Northrup potentiometer which had been calibrated by the Bureau of Standards. The Weston Standard cell used was compared several times during the investigation with a similar cell which had recently been calibrated by the same Bureau. The measurements were carried out in a thermostat kept constant within 0.01°. The thermometer used was also calibrated by the Bureau of Standards.

5. The Concentration Cells with Transference.

Cumming and Gilchrist[1] have described the best conditions for the formation of liquid junctions giving reproducible results. These are (*a*) the use of wide tubes in making the connections, (*b*) the formation of a new boundary shortly before the measurements are taken, (*c*) the mechanical mixing of the solutions at the boundary. The cell used for the purpose in this investigation is shown in Fig. 6. The vessels *M* and *M'* contain the identical silver-silver chloride electrodes used with solutions of the corresponding concentrations in the cells without transference. The tubes *L* and *L'*, of about 5 mm. internal diameter, are brought together in the small vessel *K* which contains a solution formed by mixing together equal parts of the solutions contained in *M* and *M'*. The tubes can be readily filled by pressing the rubber stoppers deeper into the vessels *M* and *M'* or by placing a slight air pressure on the surface of the solutions by means of tubes (not shown) which pass through the stoppers. The "time change" which is apparently always present where a liquid

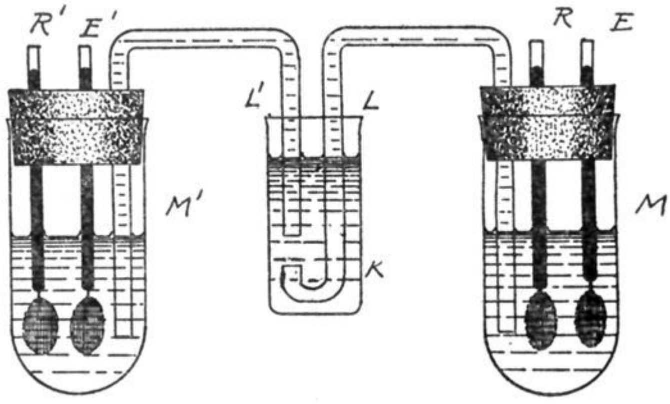

Fig. 6.

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[1] *Trans. Farad. Soc.*, **9**, 174 (1913).

junction is involved, was less than one millivolt per hour, and as new boundaries which gave the original reading could readily be obtained, it is believed that maximum values of the electromotive force were measured in each case.

The results of these measurements are given under Table III.

TABLE III.—ELECTROMOTIVE FORCE OF POTASSIUM CHLORIDE CONCENTRATION CELLS WITH TRANSFERENCE AT 25°.

Ag	AgCl,	KCl		KCl		AgCl	Ag	E. M. F.
"	Solid	0.5	*N*	0.05	*N*	Solid	"	—0.05357
"	"	0.5	"	0.05	"	"	"	—0.05357
"	"	0.1	"	0.01	"	"	"	—0.05400
"	"	0.05	"	0.005	"	"	"	—0.05470
"	"	0.05	"	0.005	"	"	"	—0.05475
"	"	0.01	"	0.001	"	"	"	—0.0560

6. Purification of Materials.

Mercury.—The mercury used in this investigation was purified by passing it in a thin stream through a tube, a meter long, filled with dilute nitric acid, and then distilling with diminished pressure in a current of air.

Potassium Chloride.—A well known manufacturer's best grade of potassium chloride was recrystallized one or more times from conductivity water, and the mother liquor drained off with the help of a centrifuge. It was always fused immediately before using.

Nitrogen.—Since most of the operations carried out in this work were found to be disturbed by the presence of oxygen, even if present in very small amounts, a rather large volume of an inactive gas was found to be a necessity. Nitrogen was found to fill all the requirements. It was prepared from sodium nitrite and ammonium chloride as described by Tucker and Yang[1] and kept over water in a gasometer. To remove the small amount of oxygen remaining, as well as the moisture present, it was passed through a train consisting of sulfuric acid, soda lime, copper heated to redness, and when necessary, through U-tubes filled with P_2O_5. The copper, which had been reduced by hydrogen from copper oxide, was contained in a quartz tube. The latter was a convenience as it could be heated and cooled rapidly without danger of breaking.

7. Discussion of Results.

On page 1448 we obtained the differential equation

$$\mathrm{F}d\mathrm{E} = \eta(\mathrm{V}_1\, d\Pi_1 + \mathrm{V}_2 d\Pi_2)$$

connecting the osmotic work and the electromotive force of a "concentration cell with transference," and the expression

$$\mathrm{F}d\mathrm{E} = \mathrm{V}_1 d\Pi_1 + \mathrm{V}_2 d\Pi_2$$

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[1] *Orig. Comm. 8th Int. Congr. Appl. Chem.*, 21, 121 (1912).

for a "concentration cell without transference." From these equations it is apparent that whatever the relations between II and V may be the ratio:

$$\frac{\text{E. M. F. of cell with transference}}{\text{E. M. F. of cell without transference}}$$

for cells containing the same pair of salt solutions, should be equal to the transference number of one of the ions. By referring to the derivation of the equations it can be seen that in the present case the ratio gives the transference number of the cation. The derivation, however, involves the assumption that thermodynamics can be applied to the cell containing the liquid junction. This, in the authors' minds, needed proof, since this point of contact of two solutions of different concentrations is certainly not in the ordinary sense of the word a system in equilibrium. Table IV gives values of the above ratio, and also, from Noyes and Falk's[1] most useful compilation, the values of the transference number obtained by the Hittorf and by the moving boundary methods.

TABLE IV.—COMPARISON OF THE TRANSFERENCE NUMBERS OF THE CATION IN KCl, AT 25°, OBTAINED BY THE E. M. F., HITTORF, AND MOVING BOUNDARY METHODS.

		Transference numbers.		
Concentrations.	E. M. F. ratio.	E. M. F.	Hittorf.	Mov. boundary.
0.5 — 0.05	53.57/107.4	0.498	496	...
0.1 — 0.01	54.00/108.9	0.496	496	0.493
0.05 — 0.005	54.70/110.85	0.494	496	0.493

From these figures it is evident that the thermodynamic theory as outlined is confirmed within the experimental error. This method for the determination of the transference number was first suggested by Helmholtz.[2]

The general applicability of this method for obtaining transference numbers may be tested by comparing the value it gives of the transference number of the hydrogen ion in hydrochloric acid with that determined in the usual way. Jahn[3] has found the E. M. F. of the following cells with transference at 18°:

Ag |	AgCl,	HCl |	HCl	AgCl |	Ag	E. M. F.
"	"	0.03330 *N*	0.003329 *N*	"	"	—0.09162 ± 0.00005
"	"	0.01665 *N*	0.001665 *N*	"	"	—0.09235 ± 0.00005

and Tolman and Ferguson's[4] paper contains measurements of the voltage of the cell without transference:

Hg |	HgCl, HCl |	H_2 —	H_2 |	HCl,	HgCl |	Hg	E. M. F.
"	" 0.02 *N*	1 atm.	1 atm.	0.002 *N*	"	"	—0.1109 ± 0.001

at the same temperature. Making a linear interpolation from the elec-

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[1] THIS JOURNAL, 33, 1454 (1911).

[2] *Ges. Abhl.*, 1, 840; 2, 979.

[3] *Loc. cit.*, page 1446.

[4] *Ibid.*, page 1446.

tromotive forces of the first mentioned cells for a value of the voltage of the cell:

$$\begin{array}{cccccc} \mathrm{Ag} & \vdots\ \mathrm{AgCl}, & \mathrm{HCl} & \vdots\ \mathrm{HCl}, & \mathrm{AgCl} & \mid \mathrm{Ag} \\ '' & '' & 0.02\ N & 0.002\ N & '' & '' \end{array}$$

we obtain —0.09210. The ratio 0.09210/0.1109 is 0.830, which agrees, well within the experimental error, with the directly determined transference number 0.833, as given by Jahn[1] and by Drucker and Krsnjavi.[2]

On applying the integrated equations:

$$E = 2\eta RT/F \ln C'_i/C_i \tag{4}$$

$$E = 2RT/F \ln C'_i/C_i \tag{3}$$

for the electromotive force of a concentration cell with and without transference, respectively, to our data, and calculating ion concentrations in the usual way from conductance measurements, we do not find the same agreement of the theory with the results of experiment. It is found that in every case the calculated values of the electromotive force are too high. This is shown in a slightly different ways in Table V, in which the ratio of the ion concentrations C'_i/C_i obtained from the electromotive force measurements by means of Equation 3 are compared with the same ratios calculated from conductance data. Column I of the table gives the salt concentrations involved. Column II contains values of the ratio C'_i/C_i computed from the conductance measurements of Kohlrausch and Maltby[3] at 18°. The measurements by Melcher[4] on KCl solns. at 25° show that little error is involved in assuming that the ratio does change appreciably in the temperature range, 18° to 25°. The ratio as calculated from electromotive force measurements is placed in the last column. The values of R, T_0, and F used in obtaining these last figures are 8,316, 273.1, and 96,500, respectively, the last being the value of the Faraday recommended by Bates and Vinal[5] for general use. It will be observed that the salt concentrations have the same ratio: 1 to 10, in each pair of solutions. The figures in italics refer to Jahn's work at 18°.

TABLE V.—RATIOS OF ION CONCENTRATIONS OF POTASSIUM CHLORIDE SOLUTIONS CORRESPONDING TO VARIOUS TEN TO ONE SALT CONCENTRATIONS.

Salt concentrations.	C'_i/C_i from conductance measurements.	C'_i/C_i from E. M. F. measurements.
0.5 —0.05	8.85	8.09
0.1 —0.01	9.16	8.33
0.05 —0.005	9.30	8.64
0.03349–0.003347	9.36	*8.76*
0.01669–0.001670	9.47	*8.86*
0.01 —0.001	9.62	9.04

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[1] *Z. physik. Chem.*, **37**, 673 (1901).

[2] *Ibid.*, **62**, 731 (1908).

[3] *Wiss. Abhandl. der Reichanstalt*, **3**, 154 (1900).

[4] THIS JOURNAL, **33**, 1669 (1901).

[5] *Ibid.*, **36**, 916 (1914).

From these figures and from Fig. 7, where the ratios are plotted as ordinates, and the higher concentration of each pair of solutions as abscissae, it can be seen that, although the ratios differ widely when calculated by the two methods, both sets of figures are apparently approaching the same value: 10, which would be the ratio of the ion concentrations of two solutions both near infinite dilution, but whose total salt concentrations were in the proportion 10 to 1. In other words, the Nernst equation can be used to calculate the electromotive force of concentration cells of potassium chloride only when the solutions involved are near infinite dilution.

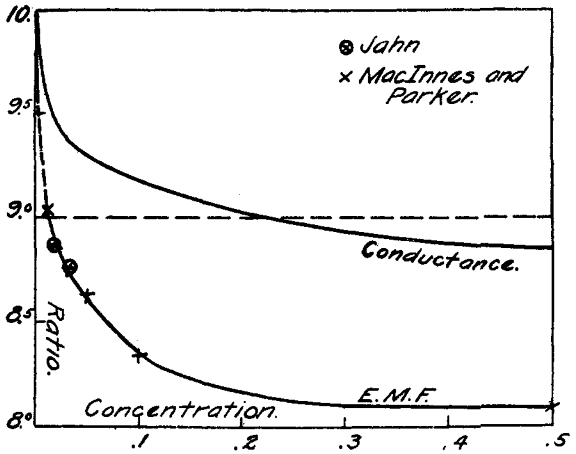

Fig. 7.

Equations 3 and 4 may also be written

$$E \doteq 2RT/F \ln a'/a$$

and

$$E = 2\eta RT/F \ln a'/a$$

where a and a' are the "activities"[1] of the ions. In this form the equations are, by definition, thermodynamically valid, provided the positive and negative ions in any solution have the same activity. The figures in the last column of Table V are therefore activity ratios. It is evident that the "activity" ratios approaches the "concentration" ratios as the solutions become more and more dilute.

In order to obtain an idea of the magnitude of the "activities" of the ions at various concentrations let us assume provisionally that at 0.001 N the activity of the ions is equal to their concentration as calculated by multiplying the total salt concentration by the conductivity ratio: Λ/Λ_0. From this value, and the activity ratios given in Table V, we can calculate the activities corresponding to the salt concentrations 0.01 N and 0.1 N. The following table gives, for the concentrations mentioned, the values of the "activity" calculated as has been described, the usually accepted degrees of dissociation, and the "thermodynamically effective" degrees of dissociation which are obtained by dividing the activity by the corresponding total concentration.

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[1] Lewis, *Proc. Am. Acad.*, 43, 259 (1907).

Salt conc.	"Activity."	Degrees of dissociation.	**"Thermodynamically effective" degrees of dissociation.**
0.001 *N*	0.000979	97.9	(97.9)
0.01 *N*	0.00885	94.1	88.5
0.1 *N*	0.0738	86.1	73.8

Readers of Lewis' recent paper on "The Activity of Ions and the Degree of Dissociation of Strong Electrolytes,"[1] will recall that he decides from thermodynamic considerations on the basis of solubility and freezing-point measurements, that 74% is the effective or "corrected" degree of ionization of a 0.1 *N* solution of potassium chloride. The close agreement (0.2%) of this value with the one for the same concentration given in the table is not, as might appear at first sight, an independent piece of evidence in favor of this low degree of ionization, but simply means that measurements on all the colligative properties must lead to the same values of the activity of the ions if thermodynamic reasoning is employed.

That the conductivity method does not give the same degree of dissociation as the electromotive force or related methods has been known for some time, and has been explained in a number of ways. Jahn believed that the E. M. F. method gives the correct measure of ionization and accounted for the higher results from conductance data by assuming that the ions "speed up" as the concentration increases. Another explanation, which also starts from the lower values of the degree of ionization as the correct ones, makes use of the hypothesis that in addition to the usual conduction by ions the undissociated molecule also takes part in the conduction by a series of rapid dissociations and recombinations, usually known as the Grotthus chain effect. This would, obviously, increase as the salt concentration increases. Most of the investigators in this field, however, regard the conductivity ratio Λ/Λ_0 (or this ratio multiplied by some function of the viscosity) as the degree of dissociation, and consider the decreasing activity of the ions as the concentration increases as being due to a change of the nature of the solution as a solvent medium, due, in part at least, to the charges on the ions. Walden and others have shown that it is probable that the dielectric constant of water increases when electrolytes are added. It seems quite possible that neither degree of dissociation is the correct one and that all the influences mentioned may have their effect.

8. Summary.

The electromotive forces of the cells without transference:

$$\begin{array}{c|c|c|c|c} \mathrm{Ag} & \mathrm{AgCl,\ KCl} & \mathrm{K(Hg)}_x - \mathrm{K(Hg)}_x & \mathrm{KCl,\ AgCl} & \mathrm{Ag} \\ & \mathrm{C}_1 & & \mathrm{C}_2 & \end{array}$$

have been measured and compared with measurements of the voltage of the cells with transference.

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[1] THIS JOURNAL, 34, 1631 (1912).

$$\mathrm{Ag} \left| \begin{matrix}\mathrm{AgCl,\ KCl}\\ C_1\end{matrix} \right| \begin{matrix}\mathrm{KCl,\ AgCl}\\ C_2\end{matrix} \left| \ \mathrm{Ag} \right.$$

With the same solutions in cells of both types, the ratio of the potentials is shown to give accurate values of the transference number of the cation.

The measurements indicate that the "activities" of the ions from potassium chloride are much lower than the concentrations as calculated from conductance measurements. The values of the "activity" and of the concentration, however, apparently approach the same limit for very dilute solutions.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 250.]

THE DROP WEIGHT METHOD FOR THE DETERMINATION OF THE SURFACE TENSION OF A LIQUID.

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This method for the determination of the surface tension is one of the results of the extended, *purely experimental and statistical*, investigation of the relationship between the falling drop weight and the surface tension of a liquid, reports of which have appeared from time to time from this laboratory.[1] As no description of this method, in its present form, has appeared in any one place, however, for it has developed only gradually; and since some misunderstanding appears to exist concerning it; it is thought desirable that a brief résumé of the conditions necessary for its holding, in the light of the searching and conclusive, experimental tests to which it has been subjected in this laboratory, be presented here. This résumé will perhaps be of advantage also, in that it will render the future work published from this laboratory more intelligible; and, further, will make the method available to those other workers who may wish to determine accurate surface-tension values.

The drop weights considered throughout this work are those found by aid of the apparatus already described in some detail in THIS JOURNAL,[2] which enables one to determine with a high degree of precision the weight of any desired number of drops of liquid falling from any sharp-edged capillary dropping tip, at any fixed temperature below 90°; and that, *free from any effect of evaporation*, even when within but a few degrees of the boiling point of the liquid. The drops here are always formed very slowly, at any rate immediately before their fall, so that they drop unaided and of their own weight alone.

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[1] See Morgan and co-workers, "The Weight of a Falling Drop and the Laws of Tate," in a series of eighteen papers, THIS JOURNAL, **30**, **33** and **35** (1908–1913).

[2] Morgan, THIS JOURNAL, **33**, 349–62 (1911).