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THE ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS BY CENTRIFUGAL ACTION.[1]

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CONTENTS.—

1. Work of Previous Investigators and Purpose of this Research.

If the passage of an electric current is associated with the actual transfer of matter along the conductor, a number of phenomena, depending upon the inertia of this matter, are to be expected. The nature of these phenomena was completely discussed by Maxwell; but they have not yet been detected in metallic conductors.[2] In electrolytic conductors, however, the experiments of Hittorf have shown that there is an actual transfer of matter through the solution, accompanying the passage of a current. As an example of the electrical effects which may accompany such a motion of the carriers of electricity or ions, let us consider a solution of si ver nitrate placed in a vertical tube with silver electrodes at the top and bottom. The passage of a current of electricity through this solution from the lower to the upper electrode will be accompanied by a raising of the silver ions in the solution and an approximately equal lowering of the considerably lighter nitrate ions. The net effect produced by the current will be the lifting of a certain weight of material from the lower electrode to the upper; and the work thus done against gravity must correspond to a definite electromotive force which will oppose the passage of the current in this direction.

Effects of this kind were first predicted by Colley,[3] and have also been

[1] This investigation was financially assisted by the American Academy of Arts and Sciences, and a somewhat more extended article describing the research has been published in the *Proceedings of the American Academy of Arts and Sciences*, **46**, 110 (1910).

[2] Maxwell, "Treatise on Elec. and Mag.," 3rd edition, Vol. II, 211 *et seq.*; Lodge, "Modern Views of Elec. and Mag.," 3rd edition, 89; Nichols, *Physik. Z.*, **7**, 640 (1906).

[3] Colley, *Journal der St. Petersburg chem. und phys. Gesellschaften*, **7**, 333 (1875); *Pogg. Ann.*, **157**, 370 (1876); *Ibid.*, **157**, 624 (1876); *Wied. Beibl.*, **5**, 457 (1881); *Wied. Ann.*, **17**, 55 (1882).

considered by various other investigators.[1] Colley himself was able to detect the existence of potential differences between the upper and lower electrodes placed in solutions of silver nitrate and cadmium iodide. The small electromotive forces produced in these solutions by gravity are masked by the presence of much larger variable potential differences which are due to otherwise undetectable differences between the two electrodes used. The effect of gravity is only perceived when a series of measurements is made of the deflections of a very sensitive galvanometer, the positions of the upper and lower electrodes being interchanged between each two measurements by a reversal of the tube containing the electrolyte. The potential differences, which Colley thus found, were of the order of magnitude thoeretically predicted. Later he also showed the presence of a momentary electromotive force produced by the sudden stopping of a falling tube containing cadmium iodide solution.

The experimental problem was next attacked by Des Coudres, who substituted centrifugal force for the weaker action of gravity. He made use of a rotating apparatus in which were placed two tubes with electrodes connected in series, containing cadmium iodide solution. The electrodes were placed 31 cm. and 9 cm. from the center and at 5.8 revolutions per second he obtained an electromotive force of 155 microvolts. Individual measurements, however, varied at times more than 10 per cent. from the mean. Although the substitution of centrifugal force for the force of gravity greatly increases the size of the effect which can be

[1] Lodge, *Phil. Mag.*, 2, 367 (1876); Hertz, *Wied. Ann.*, 14, 590 (1881); Des Coudres, *Wied. Ann.*, 49, 284 (1893); *Ibid.*, 57, 232 (1896). The electromotive force which is produced in salt solutions by the action of gravity must be carefully distinguished from the actual changes in the concentration of the solute which gravity will produce. The difference in concentration between the solution in the upper and lower ends of a vertical tube, or the central and peripheral portions of a rotating tube can be calculated from simple thermodynamic considerations. It is to be expected, however, that this difference in *concentration* will be very *slowly* established (see Des Coudres, *l. c.*, below). The difference in *potential* between the two ends of the solution is an *immediate* phenomenon which occurs as soon as the tube is set up. It is evident that when the final change in the concentration of a salt solution has completed itself there will no longer be any potential difference between the upper and lower portion of the solution.

A complete bibliography of the theoretical and experimental work which has been done in this field follows: Gay-Lussac, *Ann. chim. phys.*, 11, 306 (1819); Gouy et Chaperon, *Ann. chim. phys.*, 12, 384 (1887); Nernst, *Z. physik. Chem.*, 2, 637 (1888); Duhem, *J. physique*, 7, 391 (1888); T. v. Turin, *J. russ. Geschichte*, 24, 90 (1892); *Wied. Beibl.*, 17, 16 (1893); Des Coudres, *Wied. Ann.*, 49, 284 (1893); 55, 213 (1895); Van der Waals, *Z. physik. Chem.*, 5, 157 (1890); Bredig, *Z. physik. Chem.*, 17, 459 (1895); Lobry de Bruyn et van Calcar, *Rec. trav. chim.*, 23, 218 (1904); Franklin and Freudenberger, *Trans. Am. Electrochem. Soc.*, 8, 29 (1905); Earl of Berkeley and C. V. Burton, *Phil. Mag.*, 17, 606 (1909); Gibbs, "Scientific Papers," Longmans, Green & Co. (1906), 1, 144.

obtained, it is accompanied by the introduction of new errors, produced, for example, by the unequal heating of the central and peripheral portions of the apparatus, as well as by other difficulties. The method was abandoned by Des Coudres in favor of measurements on specially constructed gravity cells. These measurements are of a considerable degree of accuracy, and the results will be given in detail.

As we shall see in the next section, it is possible to derive a relation connecting the electromotive force produced by the action of gravity and the transference number of the electrolyte. The measurements of Des Coudres were made for the purpose of comparing the transference numbers calculated from electromotive force with those determined by the Hittorf method. In his first gravitational experiment he again made use of cadmium iodide solution which, owing to complex ion formation, apparently has a transference number greater than unity, and hence gives a large electromotive force. In the experiment the solution was placed in a glass tube with the electrodes at the two ends about 91 cm. apart. The gravitational electromotive force was deduced from a series of readings of galvanometer deflection, the positions of the upper and lower electrodes being interchanged between each two measurements. The transference number of the solution was found by calculation to be 1.236, differing by at least five per cent. from that determined in the analytical way.

In order to test the theory on more simple solutions, such as the chlorides of the alkali metals, which do not have abnormal values of the transference number, it was necessary to compensate for the decreased size of the effect by the construction of an apparatus with greater difference in height between the electrodes. The electrodes were placed in glass vessels and connected together by a rubber tube full of the solution. The electrode containers could be raised and lowered at will, permitting a difference in level of 377 cm.

The following table gives a summary of his results, including a comparison between the value T_a for the transference number of the anion as calculated from his results and as determined by the Hittorf method. The measurements were made with calomel electrodes (in the case of $CdCl_2$ with Cd amalgam electrodes as well). The e. m. f. is expressed in microvolts per centimeter difference in height:

Salt.	% Conc.	E. m. f.	T_a.	T_a Hittorf.
KCl	16.8	+0.0510	0.50	0.52
NaCl	19.9	—0.0315	0.66	0.65
LiCl	17.3	—0.109	0.77	0.75
HCl	3.56	—0.0218	0.150	0.175
$BaCl_2$	17.0	+0.170	0.64	0.65
$CdCl_2$ (Cal. elect.)	30.1	—0.183	1.10	0.82
$CdCl_2$ (Amalg. elect.)	30.1	—0.221	1.02	

Des Coudres estimates that the uncertainty in the values of the electromotive forces given is not greater than ± 0.009 microvolt.

In the present investigation a new attempt was made to increase the accuracy of this method of determining transference numbers, by substituting for the effect of gravity the force produced by a centrifugal machine of considerable power. As will be seen in the sequel, the average deviation between successive measurements has in this way been reduced to a very small amount. An estimation of the actual error in the results is, however, somewhat difficult to make.

2. Derivation of an Expression for the Electromotive Force.

In order to derive an expression for the electromotive force produced in an electrolytic solution by the action of gravity, let us consider a vertical tube of height h, filled with the solution and provided with electrodes at the top and bottom. If E is the potential difference in volts between the upper and lower electrodes produced by the action of gravity, then by allowing one faraday of electricity to flow under this electromotive force we could obtain the external work $10^7\ EF$ ergs. The passage of this electricity through the solution is accompanied, however, by the transfer of a certain net weight of material from the upper electrode to the lower one. From the principles of energetics, it is evident that this external energy $10^7\ EF$ which we could obtain will just be sufficient to restore the solution to its original condition, that is, will do the work of raising the transferred material back from the lower electrode to the upper one. For the sake of definiteness, let us suppose that the electrolyte is a solution of an iodide (C^+I^-) and that we are using iodine electrodes, consisting in practice of platinum electrodes with a small amount of iodine dissolved in the solution. If now, we let one faraday of electricity flow through the solution, we know from the experiments of Faraday and of Hittorf that one atomic weight of iodine or M_I grams will be liberated at the anode or upper electrode and will disappear from the lower electrode, and at the same time that there will be a change in the ratio of salt to water at the two electrodes, such that T_cM_s grams of salt will have apparently been transferred from the anode to the cathode, where T_c is the ordinary or Hittorf transference number of the cation and M_s is the molecular weight of the salt. In order, therefore, to restore the solution to its original condition of uniform concentration, it is necessary to raise T_cM_s grams of salt from the lower electrode to the upper one, at the same time lowering one atomic weight of iodine. If we raise and lower these substances *through* the solution it is evident that they will be buoyed up by force equal to the weight of the volume of solution which they displace. Hence if g is the acceleration due to gravity, and d the density of the solution, the downward forces acting respectively on the salt and the iodine will be $g\,T_cM_s\,(1 - v_sd)$ and

$gM_I(1 - v_{I_2}d)$ where v_s and v_{I_2} are the "partial" specific volumes[1] of the substances. Equating the external electrical work to the work done against these forces in transferring the substance from one electrode to the other, we have the desired relation[2]

$$10^7 EF = hg\,[T_c M_s(1 - v_s d) - M_I(1 - v_{I_2}d)]. \qquad (1)$$

If instead of using a gravity cell we should rotate our solution n times per second, with electrodes at r_1 and r_2, since the centrifugal force acting on one gram at any radius r is $4\pi^2n^2r$, the work done in carrying one gram from r_2 to r_1 would evidently be[3]

$$\int_{r_1}^{r_2} 4\pi^2n^2r\,dr = 2\pi^2n^2(r_2^2 - r_1^2),$$

and our equation for electromotive force becomes

$$10^7 EF = 2\pi^2n^2(r_2^2 - r_1^2)\,[T_c M_s(1 - v_s d) - M_I(1 - v_{I_2}d)]. \qquad (2)$$

We see that the value of the electromotive force which is to be measured is proportional to the factor hg or $2\pi^2n^2\ (r^2_2 - r_1^2)$. In the experiments of Des Coudres on gravitational cells, the factor hg was 360,000, while with his rotating apparatus the value of the corresponding factor was 583,000. In the centrifugal experiments which are to be described in this paper the value of the factor was raised to 114,000,000.

The Effect of Hydration.

It has been shown by the careful researches of Buchböck[4] and especially of Washburn[5] that it is possible to distinguish between the ordinary Hittorf transference number and the so-called "true" transference number in which the motion of the ions is referred to a non-electrolytic indicator dissolved in the solution instead of to the water. If water is carried by the current, owing to hydration of the ions, then the two transference numbers will be different

The Hittorf transference number gives, however, the actual number of equivalents of salt which apparently disappear in the neighborhood of one electrode and appear at the other when one faraday of electricity is sent through the solution, and hence the Hittorf transference number gives us the amount of salt which must be moved in order to restore the solution to its original condition of uniform concentration. From a consideration of the method by which the equation for the electromo-

[1] For a definition of "partial" volumes, see Section 8.

[2] In order to derive this equation, any reversible method might be used for restoring the solution to its original condition of uniform concentration. For example the apparent difficulty of moving the substances *through* the solution can be obviated by removing them from the solution with the help of semipermeable membranes. It is easy to show, however, that the relation derived is the same.

[3] It may also be pointed out that the expression $2\pi^2n^2(r_2^2 - r_1^2)$ is the increase in kinetic energy when one gram of material is transformed from r_1 to r_2.

[4] Buchböck, *Z. physik. Chem.*, **55**, 563 (1906).

[5] Washburn, *Tech. Quart.*, **21**, 164 (1908); THIS JOURNAL, **31**, 322 (1909).

tive force is derived, it is obvious that the *Hittorf* transference number is the one which has been determined in this research.

3. Kinetic Derivation of the Electromotive Force Expression.

In order to derive the equations used in this article, we have considered the production of the electromotive force in a rotating solution from a thermodynamic standpoint. The fact that more work was needed to send a current through a salt solution from the outer to the inner electrodes than in the reverse direction, could be predicted from thermodynamic principles, and the electromotive force, corresponding to this work, could be calculated merely from a knowledge of certain properties of the solution such as transference number and density, which can be experimentally determined. It is also instructive, however, to look at the question from a "kinetic" or molecular point of view. The fact that an electromotive force *is spontaneously* produced by centrifugal force gives us a real knowledge of the internal structure of an electrolytic conductor. It is, indeed, the most striking proof of the existence of free ions in an electrolyte.

Considered from a "kinetic" point of view, a solution of potassium iodide contains free potassium ions and free iodide ions. The iodide ions, however, corresponding to their greater atomic weight, are much denser than the potassium ions, and hence when the solution is rotated they move more readily towards the outer portion of the solution and charge it negatively. In fact from a consideration of the forces acting on the ions in the solution, it is possible to derive the same equation for the electromotive force of a gravity cell as that already obtained from thermodynamic reasoning. The method of proof is similar to that used by Nernst in his consideration of the diffusion cell.

Consider an iodide (C^+I^-) of molecular weight M_s dissociating into the ions C^+ and I^- of atomic weights M_c and M_I. Let v_s be the partial specific volume of the salt in solution and v_c and v_I be the same quantities for the positive and negative ions respectively. Now let us subject a solution of this salt to the action of gravity. If the positive ion C^+ is denser than the iodide ion, it will tend to move downward through the solution more rapidly and will produce a potential gradient in the solution $-dE_1/dh$. As this potential gradient is produced, however, it tends to decrease the downward velocity of the positive ion and increase the velocity of the negative ion so that under the final potential gradient produced they will move downward through the solution with equal velocities We may now proceed to derive expressions for these equal velocities.

The total downward force acting on one mol. of positive ions is the weight (gM_c), minus the buoyant force exerted by the solution (gM_cv_cd), minus the electrical repulsion $(10^7FdE_1/dh)$ corresponding to the potential gradient. If u and v are the velocities with which the positive and negative ions move under unit force, the velocity with which they will move under the actual forces can now be calculated by simple multiplication, since the validity of Ohm's law in solutions shows us that the velocity with which the ions move is proportional to the force acting on them.

Equating the velocities of the negative and positive ions, we have[1]

$$u\left(gM_c(1-v_cd) - 10^7 F\frac{dE_1}{dh}\right) = v\left(gM_I(1-v_Id) + 10^7 F\frac{dE_1}{dh}\right).$$

Solving for dE_1/dh and integrating between the limits o and h, where h is the difference in height between the electrodes, we have

$$10^7 E_1F = hg\left[\frac{u}{u+v}M_c(1-v_cd) - \left(1-\frac{u}{u+v}\right)M_I(1-v_Id)\right]. \quad (3)$$

In order to obtain the actual electromotive force between the electrodes, we must consider not only the potential gradient in the solution, but also the potential drops which occur directly at the electrodes due to the electrode reaction $^1/_2I_2 + (\overset{-}{}) = I^-$. Since this reaction is accompanied by the changes in volume $M_I(v_I - v_{I_2})$ and takes place under the difference in pressure between the upper and lower electrodes which is equal to hgd, we must add to the electromotive force E_1, as given in equation (3), the electromotive force E_2 given by the equation below, which is derived by equating the external electrical work to the work produced by the change in volume:

$$10^7 E_2F = M_I(v_I - v_{I_2})hgd.$$

Noticing that

$$\frac{u}{u+v} = T_c,$$

we obtain

$$10^7(E_1+E_2)F = hg[T_cM_c(1-v_cd) + T_cM_I(1-v_Id) - M_I(1-v_{I_2}d)]$$

or

$$10^7 EF = hg[T_cM_s(1-v_sd) - M_I(1-v_{I_2}d)],$$

which is the same equation we originally obtained by thermodynamic reasoning.

The real interest attached to this kinetic consideration is the almost absolute proof it offers that some degree of dissociation or at least polarization of the salt molecules exists in aqueous solution, since unless the positive and negative components of the salt can move relative to one another we cannot see how a potential gradient is set up by centrif-

[1] It should be noted that when the concentration of the salt in the lower portion of the tube has appreciably increased, the concentration gradient adds new forces tending to slacken the downward motion of the ions. When the final equilibrium is reached the concentration gradient will be such that no potential gradient exists. We are interested, however, in the original condition before appreciable concentration changes have taken place.

ugal separation. The method gives, of course, no idea of the magnitude of the ionization.

4. Description of Apparatus.

The general arrangement of the rotating apparatus is shown in Fig. 1. It consists of a steam turbin, *A*, with vertical shaft, driving the rotator *B*, which contains the tubes of solution. Electrical connection with the electrodes in the solution was made through the mercury contacts *C*.

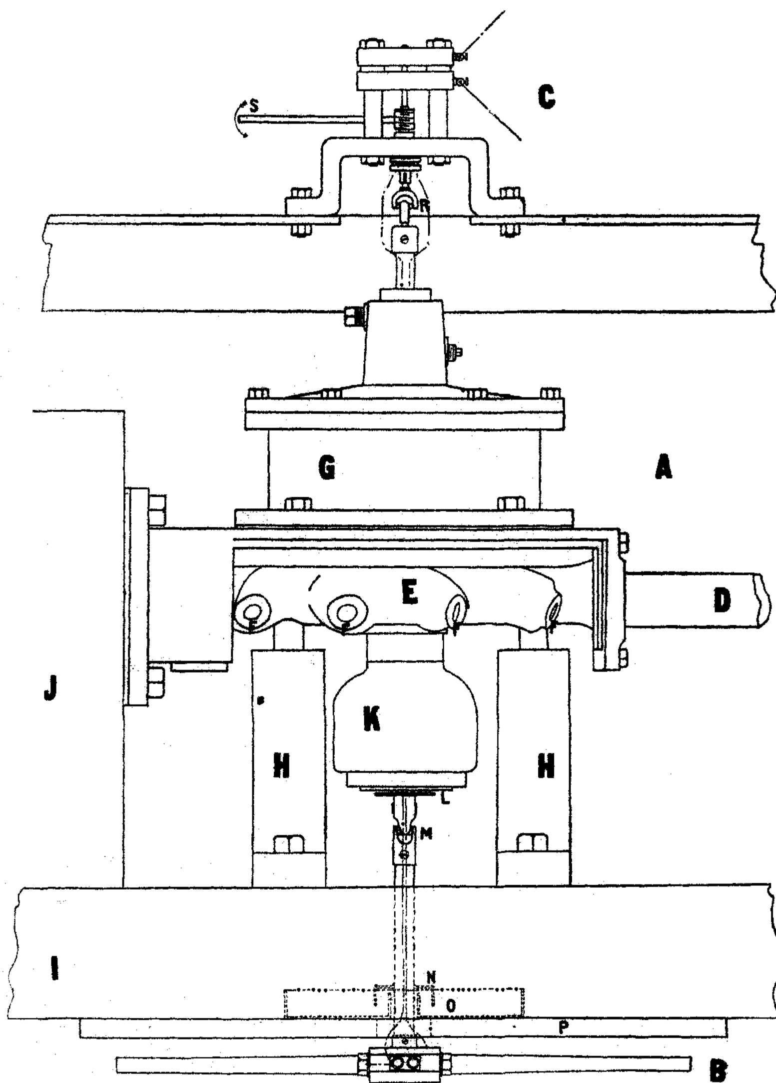

Fig. 1.—General arrangement of the rotating apparatus. 1/8 size.

a. The Steam Turbin.—The turbin used was a thirty horse-power de Laval loaned for this investigation by the General Electric Co. The turbin wheel was ten inches in diameter. A 2-inch steam pipe, *D*, leads into the annular space *E*, from which the nozzles lead up to the turbin wheel. The holes *F* are opposit the openings to the nozzles and are threaded to receive the bonnets of the nozzle valves (not shown in the drawing). A 3-inch exhaust pipe leads from the exhaust chamber *G*, on the side away from that shown in the drawing. The turbin is supported on the legs *H*, bolted to the cross beams *I*. It is also bolted to the block *J*. Largely for the sake of safety, the apparatus was redesigned with a vertical shaft and was placed in a specially constructed pit. The vertical shaft necessitated the design of some form of thrust bearing to support the rotating system.

b. The Thrust Bearing.—The thrust bearing used was contained in the case *K*, Fig. 1. The details are shown in Fig. 2. It consists of a series of five ball bearings, placed one above the other, so as to distribute the total relative motion which must be cared for. Each ball bearing consists of a series of balls, *F*, in a brass cage, between two hardened steel washers. A shoulder on the shaft *D* rests on the topmost washer *E*, and the lowest bearing rests on the levelling washer *G*, which has a spherical seat. The nut *K* locks the adjustment of the bearing at the proper height. The lateral bearings *A* and *H*, as well as the top bearing of the turbin itself, consist of eminently satisfactory graphite-lined bushings supplied by the Graphite Lubricating Co., Bound Brook, N. J. The lubrication of the ball bearings was also with graphite, which was applied with oil in the form of a paste.

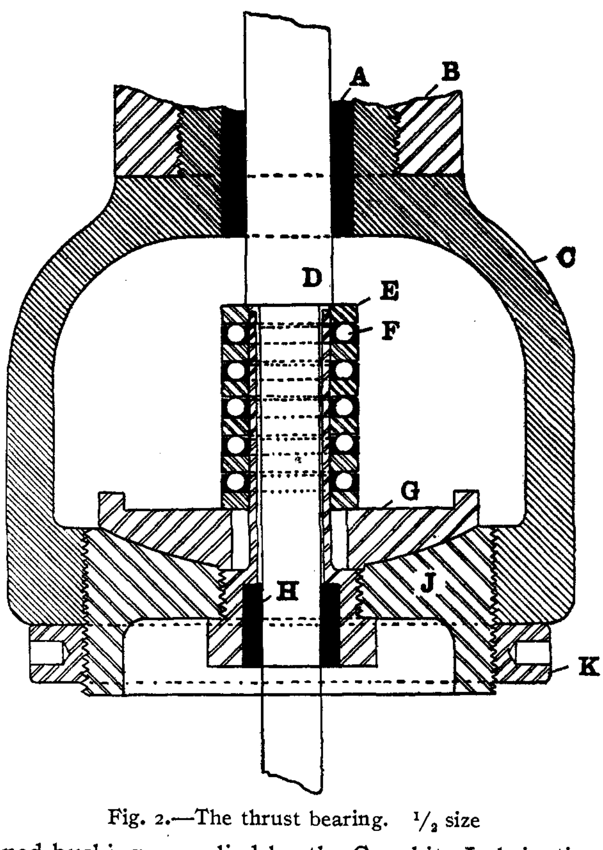

Fig. 2.—The thrust bearing. $^1/_2$ size

This form of ball bearing was tried only after a number of bearings, including one specially designed for the purpose by The Standard Roller Bearing Co., had failed. The individual ball bearings of which this bearing was constructed were stock $^{13}/_{16}$ inch "ball thrust collar" bearings made by the above firm. The ingenious idea of replacing the series of disks sometimes used in step bearings by a series of ball bearings came in a conversation with Dr. C. A. Kraus, of this laboratory, to whom, in general, I am under the deepest obligation for an intelligent and sympathetic understanding of the many difficulties involved in the construction of an apparatus of this kind.

c. The "Spinning Top."—The rotator *B*, Fig. 1, is two feet in diameter and consists of two hollow steel arms, screwed into a central hub, *Q*. The rotator is hung on a shaft $^{13}/_{16}$ inch in diameter and $8^1/_2$ inches long. This shaft is flexibly connected to the turbin shaft with a Hooke joint, *M*, which permits the rotator to revolve about its own center of gravity. The arrangement is in the nature of a "spinning top." In order to prevent a precessional motion of the top which would quickly raise the rotator shaft to a horizontal position, the shaft was steadied at the point *N* by a system of cords not shown in Fig. 1, but indicated in plan in Fig. 3. The two cords *MN* and *OP* prevent motion of the shaft in the direction *AA*, and two others not shown in the figure are arranged to prevent motion in the direction *BB*. The cords were drawn tight against the shaft through the stationary supports at *W*, *X*, *Y*, and *Z*. The cords were braided cotton $^5/_{32}$ inch in diameter and the wear on them, strange as it may seem, was very inconsiderable. This arrangement of cords was adopted after experimenting with many forms of steadying bearing, in which it was attempted to prevent the precessional motion with rubber washers, springs, or pneumatic dash pots.

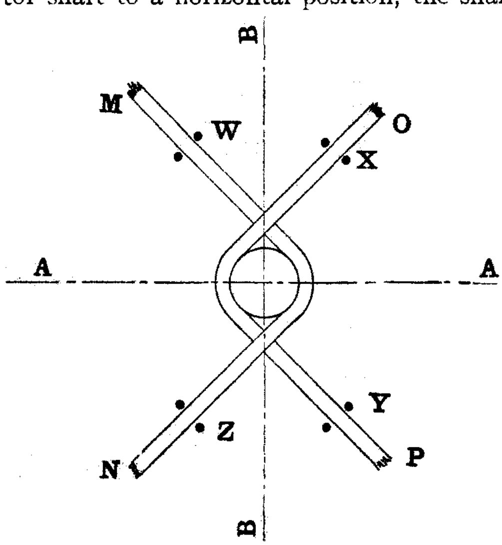

Fig. 3.—The steadying cords.

This plan of driving the rotator as a spinning top must be considered as one of the distinctive features of the apparatus. By this means the rotator was driven up to a speed of 7850 revolutions per minute, giving a rim speed of nearly 50,000 feet per minute. At this speed there was a certain amount of vibration of the steadying cords. In general, however, it was found possible to raise the speed at which this vibration took place by moving the supports W, X, Y, and Z nearer to the shaft, and there is no doubt that the apparatus could be arranged to go to still higher speeds. As will be seen later, for other reasons, the actual measurements had to be made at speeds of 5000 revolutions or less.

The fact to be specially noticed with regard to this "spinning-top method" is that it permits the driving at a very high speed of a rotator which has not been specially adjusted for either "stationary" or "running" balance. The method was adopted after considerable experimenting with a rotator driven on a shaft with fixed bearings. Although this rotator had been put into "stationary" balance, it caused so great a vibration that one of the bearings gave way at a speed under 2000 revolutions per minute, wrecking a machine upon which a considerable amount of labor had been expended.

The mathematical theory of a symmetrical top rotating with one fixed point and acted upon by gravity alone has been completely developed. It has further been shown by H. Lamb[1] that, in the case of a rotating top hanging below its fixed point, as in this apparatus, the effect of *viscous forces* in the Hooke joint is to produce a gradually increasing precessional motion which would finally raise the axis of the top horizontal. This is the precessional motion which was prevented by the steadying device described above. It must be noticed in general, in designing rotating apparatus of this kind, that the actual motion may differ considerably from that predicted by the dynamical equations since, among other things for example, the latter take no account of restraining forces such as were introduced in this case by the steadying cords.

Some experiments, on a small scale, were made with rotating tops, driven through a Hooke joint from below. There were indications that this would be a most satisfactory method of driving an unbalanced rotor. The whole field is a very profitable one for research.

As a practical detail, it should be pointed out that the rotator shaft must be made short enough not to reach its own period of vibration at the speed employed. It was found impracticable to run this rotator with a shaft 22 inches long.

d. The Rotator.—Fig. 4 gives a detail of one of the two arms which screw into the central hub of the rotator. These arms were made from seamless steel tubing bored out to one-half inch inside diameter. The peripheral end of the tube was closed by screwing in a plug of steel, the threads of which were figured to withstand the shear at 8000 revolutions per minute, produced by the combined outward action of the centrifugal force of the plug and that of the contents of the tube, assuming them to

[1] H. Lamb, *Proc. Roy. Soc., London*, 80, *A*, 168 (1908).

be a liquid of specific gravity 1.3. In order to prevent leakage of liquid through the screw threads, the plug was silver-soldered in position.

The thickness of wall at the peripheral end of the tube was enough to prevent bursting as calculated by Clavarino's formula for thick hollow cylinders. This thickness of wall was also great enough to sustain the

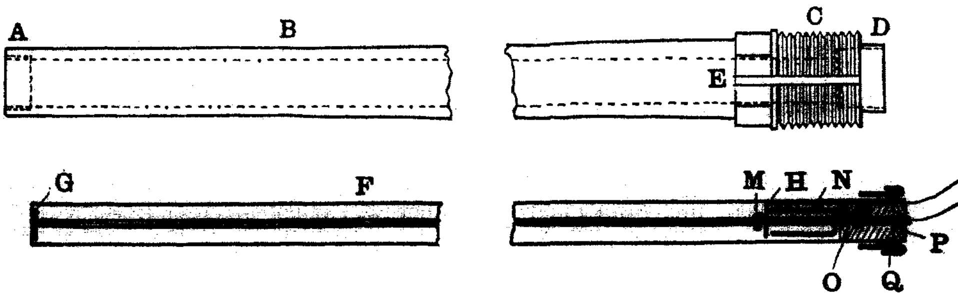

Fig. 4.—Rotator arm and solution tube. $^1/_2$ size.

outward tension as far as the point B, 3 inches from the end of the tube. From this point on towards the center the tube had to gradually increase in diameter in order to sustain the constantly increasing load. If r is the radius at any point where the section is s, D the density, f the tensil strength of the material, and n the number of revolutions, evidently $fds = 4\pi^2n^2rDsdr$. Integrating this equation and solving, the proper dimensions for the inner end of the arm were found. The screw thread on the inner end of the arm was sufficient to prevent the arm from shearing out from the hub.

e. The Solution Tube.—The solutions experimented on were iodides with iodine electrodes. The actual tubes which contained the solutions were made of glass. This was the only material found which was an insulator and at the same time was not attacked by the iodine. The latter condition was of great importance since the slightest loss of iodine in the neighborhood of either of the electrodes created a large potential difference between them. The tubes were carefully annealed and were floated in oil inside the rotator arms; nevertheless, the end thrust produced by the centrifugal force was great enough to break many tubes even at speeds as low as five thousand revolutions per minute.

With the hope of obtaining some material which would stand higher speeds, a great many other materials for tubes were investigated, including porcelain, paraffined paper and wood, celluloid, vulcanite, and steel tubes lined with paraffin, sulfur, and enamel, but none was found satisfactory. Tubes of vulcanite, which has a specific gravity only slightly greater than water, practically floated in the steel arm without danger of breakage, and many experiments were made with them. There seemed, however, to be a distribution of iodine between the hard rubber and the solution which made it very difficult to keep the iodine concentration the same at the two electrodes, and they were finally discarded in favor of glass.

Fig. 4 gives a detail of one of the tubes with its electrodes. The tubes were annealed by carefully wrapping them in asbestos and heating in a large electric furnace to about 500° and then allowing the furnace to cool, which took a day and a half. The electrodes were platinum. The outside electrode *G* rested on the bottom of the tube. The connecting wire had to be platinum-iridium in order to stand the centrifugal force. This wire was insulated from the solution by a glass tube which is slightly enlarged at *M*. On the enlargement *M* rests the inner electrode *H*. *N* shows the cross section of a glass thimble which is slipped down on to the electrode. A bubble of air was entrained in this thimble to allow for temperature expansion, and to provide a means of stirring the solution. Melted ceresin which had been specially purified was poured on top of the thimble at *O* and this was covered with a thin layer of a molten cement, *P*, which consisted of a mixture of wood tar and shellac.[1]

The tube is made to slip into the rotator arm and rests at the outside end on a disk of rubber packing. It is surrounded by oil to equalize the hydrostatic pressure. A short piece of rubber tubing is slipped onto the glass tube and turned back on itself as shown in the figure at *Q*. The tube projects from the end of the arm far enough so that the turned-back rubber just meets the end of the arm at *D*, and a piece of "bill-tie" tubing is slipped over the rubber tubing and the arm to prevent leakage of oil.

The leads from the electrodes come out from the rotator in the grooves *E* and are covered with small rubber tubing. Ordinary optical tubing was not a good enough insulator, but insulation was used which was stripped from 22-gage rubber-covered wire supplied by the Simplex Electrical Co., of Cambridgeport. The wires were attached to binding posts on the rotator hub, from which electrical connection was carried up to the mercury contacts.

f. The Electrical Connections.—The path taken by the electrical connections is indicated by dot and dash lines in Fig. 1. Leads from the binding posts on the rotator hub pass up through the center of the hollow rotator and turbin shafts and make connection with the mercury contacts. The wire used was 22-gage rubber-covered, as ordinary insulation would not stand the severe conditions of temperature and the effect of moisture.

At *L*, in Fig. 1, is a brass disk about 2.5 inches in diameter fastened to the rotating shaft. This disk prevents any leakage of water from the turbin trickling down the Hooke joint and getting into the hollow rota-

[1] This useful cement was discovered by Dr. C. A. Kraus and Mr. R. D. Mailey, of this laboratory.

tor shaft and thus interfering with the insulation. O is a stationary pan about 10 inches in diameter with a central hole for the shaft to pass through. This pan catches accidental dripping from the turbin and protects the hub of the rotator and its binding posts. Further protection is provided by a copper disk, N, with turned-down edges. This disk rotates with the shaft and covers the central hole in the pan O. The disk also radiated the heat from the turbin and from the friction of the steadying cords, which otherwise traveled down the shaft and produced bad temperature differences between the central and peripheral electrodes.

g. The Mercury Contacts.—Connection between the leads, which came up through the hollow shafts, and the external measuring circuit was made through the mercury contacts C indicated in Fig. 1 and shown in detail in Fig. 5. The leads from the electrodes were made fast to the binding posts M and N, and e ectric connection was made through the

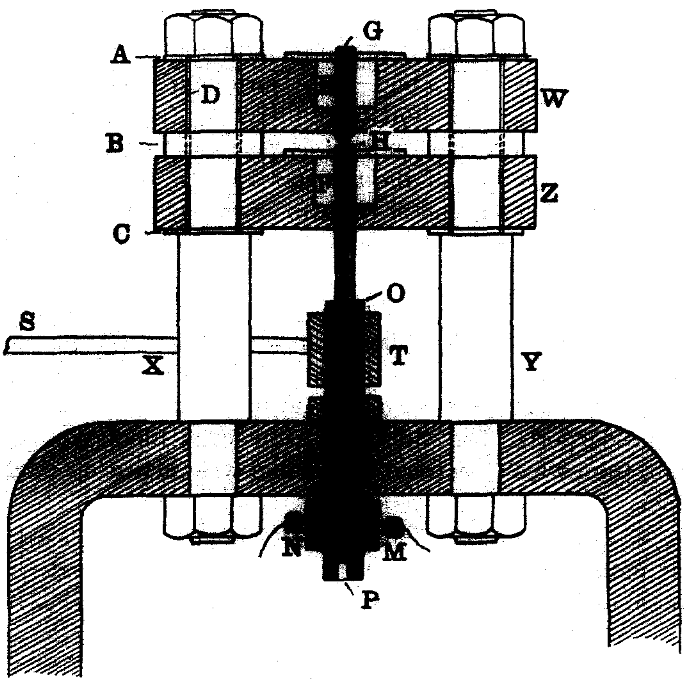

Fig. 5.—The mercury contacts. $^1/_2$ size.

small rotating shafts G and H with mercury, which was placed in the circular troughs E and F in the steel blocks W and Z. The two small shafts are insulated from one another and from the outside driving shaft O by fine rubber tubing, and at the bottom by vulcanite disks. The steel blocks are insulated from each other and their supports X and Y

by vulcanite washers and sleeves. Connection is made from the steel blocks to the measuring instruments.

The apparatus was specially designed with the purpose of eliminating the production of electromotive forces at the point of contact between the moving and stationary parts. For this reason the shafts were made as small as possible, $^3/_{16}$ inch in diameter, thus reducing the relative velocity at the point of contact; mercury was chosen as the contact substance, and the whole apparatus was made of the same material, steel, throughout. Measurements of the electromotive forces occurring in these mercury contacts were made by driving the apparatus with the contacts short-circuited. The potential differences found were in the neighborhood of $^1/_{20}$ millivolt.

h. The Magneto.—Returning again to Fig. 5, T is a worm driving the shaft S through a worm wheel not seen in the drawing. Measurements of the speed of rotation of the apparatus were made by reading the voltage produced by a magneto driven from this shaft S. This was a small three-bar magneto manufactured a number of years ago by the Holtzer Carbot Co., of Brookline. This was the least satisfactory part of the apparatus, since the voltage readings at a constant speed were liable to small, sudden fluctuations largely due to poor contact at the commutator. Both graphite and woven wire commutator brushes were tried. The accuracy of the speed determinations, however, seemed to be of the same order of magnitude as that of the other measurements, and it did not seem advisable to procure one of the newer magnetos or any of the more costly forms of apparatus for speed measurement. A small motor was arranged for driving the magneto independently, and the magneto was standardized after each series of measurements with the help of a stop-watch and suitable counter.

i. The Electrical Measuring Instruments.—The potential differences obtained were of the order of a few millivolts. For their measurements a Leeds and Northrup potentiometer and a suitable galvanometer were used. A cadmium element supplied by the Weston Electric Co. was used as a standard cell, and this was further compared with another Weston cell both at the beginning and end of the measurements. In the actual experiments a reading of the voltmeter, which gave the speed of the apparatus, and the potentiometer reading were taken as nearly simultaneously as possible.

5. The Method of Procedure.

With the apparatus described, measurements were made on solutions of potassium, sodium, lithium, and hydrogen iodides. The solutions contained exactly 1 mol of the salt and $^1/_{100}$ mol of I_2 in a kilogram of water. In the case of hydrogen iodide, owing to the oxidation of the acid, there was a gradual increase in the amount of I_2 present in the solution.

A rough colorimetric analysis of the solution as finally used showed the presence of about $^2/_{100}$ mol I_2 per kilogram of water.

The glass tubes whi h contained the rotating solutions have already been described. In the experiments as finally performed only one tube was used, an approximate counterbalance being placed in the other arm of the rotator. By connecting two tubes in series, it would have been possible to double the electromotive force to be measured. This would not have greatly increased the certainty of the measurements, however, since, on stopping the rotator, the residual potential differences between the two electrodes were always found to be in the same direction, and by connecting two tubes in series the size of the error as well as that of the potential difference to be measured would have been increased.

Before filling the tubes, they were carefully rinsed with some of the solution to be used. The electrodes were heated to incandescence in a blast lamp and placed in the solution without being touched by the fingers.[1] By using care, it is possible in this way to reduce the original electromotive force between the two electrodes to the neighborhood of 0.2 millivolt or less. The small variable electromotive forces which do persist are probably partly due to differences in temperature between the two ends of the solution. As already described, the tubes were sealed with purified ceresin. This was almost the only material found whose presence near one of the electrodes did not produce a large electromotive force.

After the apparatus had been set up ready for rotation it was tested for insulation. This is very important, since any leakage between the leads coming from the solution would apparently have decreased the size of the electromotive force produced. This test was carried out by disconnecting one of the leads from its binding post on the hub of the rotator and applying a drop of 1.5 volts at the other end of the leads where they joined the measuring system. A galvanometer was in series with the potential drop to measure the current leaking from one lead to the other.[2]

In general, for the final experiments the galvanometer was absolutely stationary, and if there was more than a trace of a deflection, the trouble was eliminated before making a run. A deflection of one millimeter on the galvanometer scale would have corresponded to a resistance of about 1.5×10^9 ohms between the leads.

In the experiments a number of readings of the residual electromotive force were taken with the rotator stationary. It was then brought up to speed and a new series of readings commenced as soon as possible.

[1] Laurie, *Z. physik. Chem.*, 64, 617 (1908).

[2] In order to make the test more thorough, the lead which had been disconnected from the binding post was connected to the steel rotator. Until considerable experience had been gained, it was very difficult to eliminate leaks between the wires coming from the electrodes and the rotator.

After running for several minutes, the steam was shut off and more readings of the residual electromotive force commenced as soon as the rotator had stopped. The voltmeter attached to the magneto was placed near the potentiometer so that a determination of the speed of the apparatus was made immediately after each measurement. The approximate time when each measurement was taken was also recorded.

At the end of a day's measurements, the magneto was standardized with a stop-watch and counter. Usually about half a dozen standardizing runs were made at speeds in the neighborhood of those used in the actual measurements. Each run lasted about a minute. The stop-watch was started when some even figure appeared on the counter, and stopped similarly about a minute later. In general, five readings of the voltmeter were made, one before the stop-watch was started, the next three at intervals of fifteen seconds, and the last one after the watch had been stopped. It was not easy to hold the speeds constant enough to make standardizing runs of over a minute desirable.

6. The Experimental Results.

In the following tables are given the data on which the calculations for each of the salts investigated are based. The first column gives the time when the observation was taken, the second column the reading of the voltmeter, V (in decivolts), which indicated the speed of the apparatus, and the third column the potential difference in millivolts, $E \times 10^3$, this being called negative when in the opposit direction from that produced by the centrifugal force. The radii of the two electrodes, r_2 and r_1, are also given, and the data for the standardization of the magneto. In the case of all salts investigated, the inside electrode was positive with respect to the outside one during rotation.

It is a striking fact that upon stopping the rotator the residual electromotive force is always found to be in the opposit direction from that produced by the centrifugal force. It will also be seen from an examination of the data that there is a general tendency for this residual electromotive force to increase somewhat in magnitude and then in the course of a few minutes gradually to disappear. The average magnitude reached by this residual electromotive force is 0.2 to 0.3 millivolt.

At first sight, it might seem possible to explain this residual potential difference by assuming that the outer electrode was heated more by the friction of the air, during rotation, than the inner one, since, as a matter of fact, a difference in temperature of 1° would have produced a residual electromotive force of about 0.25 millivolt in the direction actually found.[1]

[1] In order to determin the value of the electromotive forces produced by temperature differences between the electrodes, the thermoelectric power was carefully measured for a number of different circuits of the type—platinum ⟶ salt solution: salt solution ⟶ platinum. The writer hopes to present the results of measurements of this kind in a later paper.

This explanation, however, would not account for the fact that the residual electromotive force tends to increase after the machine had been stopped, and the very conditions removed which were supposed to create the temperature difference.[1] This increase in the magnitude of the residual electromotive force after stopping the machine was much easier to follow and the final value reached was much larger, in some earlier experiments where *vulcanite* tubes were used instead of glass for containing the solution.[2] This might indicate that the gradual increase of electromotive force after stopping the rotation is due to the gradual emergence into the solution of some constituent which had been forced into the pores of the tube by the centrifugal force or the pressure. Whatever the true explanation, the phenomenon is so complicated that it seemed best not to hazard a guess as to the probable size of the residual electromotive force *during* rotation and no correction was made for it in the calculations.

Further development of the centrifugal method should be in the direction of eliminating these residual potential differences between the electrodes. This could best be done by having the liquid circulate through the apparatus so as to pass from one electrode to the other and thus assure the same conditions at both.

7. Ratio of the Electromotive Force to the Square of the Number of Revolutions Per Second.

From equation (2) it is evident that the electromotive force produced by the rotation should increase as the square of the number of revolutions per second, that is, E/n^2 for a given solution should be a constant. The degree of the constancy of this quantity is illustrated by the fifth column in Tables I–IV, which gives the values of E/n^2 as calculated from the data. Considering the separate runs in a series of measure-

[1] Attempts were made to actually measure the temperature difference between the two electrodes, by placing in the tube an ordinary thermoelectric circuit with iron-nickel junctions at the outer and inner ends. Connection between this thermoelectric circuit and the measuring instruments was made through the mercury contacts already described. It was found, however, that the small electromotive forces arising in these mercury contacts were large enough to obscure those produced by the iron-nickel junctions, and the method was abandoned. There seems to be no practical metallic junction of higher thermoelectric power than the iron-nickel combination.

In some earlier experiments very definit temperature effects were produced by heat which traveled down the rotator shaft. These effects were eliminated; however, by the copper radiating disk N, Fig. 1, already described, see p. 134.

[2] In these experiments made with vulcanite tubes, there was also the difference that the rotator was driven in a closed case instead of in the open air. Since the air in the case was considerably heated by the rotation, larger temperature differences might have been expected between the two electrodes. Nevertheless, this would not account at all for the increase in residual electromotive force after the rotator had been brought to rest.

TABLE I.

(Dec. 2, 1909.)

Solution: Molal KI, $^1/_{100}$ Molal I_2. $r_2 = 29.40$ cm., $r_1 = 4.3$ cm.

Standardization of magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 1.050$ (7 exp. av. dev. ± 0.0145).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 1.050$ = rev. per sec.	$E/n^5 \times 10^6$.	Dev. from mean.
10.54	0	—0.30	....	...	....
11.12	0	—0.10	....	...	....
.23	0	—0.50	....	...	....
.25	0	—0.55	....	...	....
.28	60.0	+2.58	62.9	652	— 5
.29	58.5	2.47	61.4	655	— 2
.30	59.0	2.52	61.9	658	+ 1
.30$^1/_2$	59.8	2.55	62.8	647	—10
.31$^1/_2$	0	—0.15	....	...	....
.32	0	—0.30	....	...	....
.34	0	—0.18	....	...	....
.36	0	—0.14	....	...	....
.40	0	—0.17	....	...	....
.41$^1/_2$	71.5	+3.65	75.0	649	— 8
.42	71.2	3.73	74.7	668	—11
.43$^1/_2$	72.0	3.73	75.5	655	— 2
.44	72.7	3.90	76.2	672	+15
.45	73.1	3.93	76.7	668	+11
.46	0	—0.25	....	...	....
.47	0	—0.18	....	...	....
.49	0	+0.05	....	...	....
.50$^1/_2$	0	0.17	....	...	....
.52$^1/_2$	0	0.25	....	...	....
.55	78.0	4.38	81.9	653	— 4
.55$^1/_2$	77.5	4.35	81.3	658	+ 1
.56	77.0	4.25	80.8	651	— 6
.57	....	4.25	....	...	....
			Average,	657.1	±6.3

ments, we see a tendency for the individual measurements of the *first* run to show the largest deviations from the mean. There is probably some connection between this and the fact that the value reached by the residual electromotive force is also largest after the first run in a series. In many of the individual runs there is a tendency for the electromotive force to decrease somewhat during the run. This would correspond to the gradual production of a negative residual electromotive force. As already pointed out, the nature of these residual potential differences is too uncertain to permit of a trustworthy correction.

8. The Partial Volumes of Iodine and the Iodides.

Before making a calculation of the transference numbers from the electromotive force data which we have just considered, a knowledge

TABLE II.

(Dec. 23, 1909.)

Solution: Molal NaI, $^1/_{100}$ molal I_2. r_2 = 29.45 cm., r_1 = 4.2 cm.

Standardization of Magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}}$ = 0.8695 (8 exp. av. dev. ±0.0035).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8695$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
10.12	0	—0.16	....	...	....
.15	0	—0.04	....	...	....
.22	0	—0.35	....	...	....
.25½	66.2	+3.00	57.6	904	+15
.26½	65.9	2.95	57.3	898	+ 9
.27	65.9	2.83	57.3	862	—27
.28	65.9	2.83	57.3	862	—27
.28½	66.2	2.92	57.6	880	— 9
.30	0	—0.24	....	...	....
.30½	0	—0.28	....	...	....
.31¼	0	—0.17	....	...	....
.32½	0	0.00	....	...	....
.35	73.2	+3.61	63.7	889	0
.35½	74.2	3.70	64.5	889	0
.36½	74.8	3.75	65.1	885	— 4
.37	75.1	3.79	65.3	888	— 1
.38	76.0	3.88	66.1	887	— 2
.39½	0	—0.26	....	...	....
.40	0	—0.26	....	...	....
.41	0	—0.17	....	...	....
.42	0	—0.07	....	...	....
.43½	0	—0.00	....	...	....
.45	0	+0.03	....	...	....
.46	0	0.05	....	...	....
.48½	74.5	3.70	64.8	881	— 8
.49	74.2	3.72	64.5	893	+ 4
.50	74.8	3.72	65.1	877	—12
.50½	74.5	3.71	64.8	883	— 6
.51	74.5	3.70	64.8	881	— 8
.52	74.0	3.66	64.4	882	— 7
.53½	0	—0.15	....	...	....
.54½	0	—0.10	....	...	....
.55½	0	—0.06	....	...	....
.57	0	—0.05	....	...	....
.58½	0	—0.06	....	...	....
.60½	0	—0.10	....	...	....
11.03	80.0	+4.37	69.5	905	+16
.03½	81.2	4.53	70.6	910	+21
.04½	82.8	4.60	72.0	888	— 1
.05	83.2	4.65	72.3	889	0
.06	84.0	4.77	73.0	895	+ 6
.06½	84.1	4.80	73.1	899	+10
.07½	0	—0.23	....	...	....
.08	0	—0.23	....	...	....

Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8695$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
.10	0	—0.04	....	...	....
.11 1/2	0	+0.12	....	...	....
.14	0	0.17	....	...	....
.16	0	0.17	....	...	....
.18 1/2	74.1	3.73	64.5	897	+ 8
.19 1/4	75.0	3.85	65.2	905	+16
.20	74.8	3.76	65.1	887	— 2
.20 3/4	74.2	3.73	64.5	896	+ 7
.21 1/2	73.9	3.68	64.2	892	+ 3
.22 1/2	0	—0.24	....	...	....
.23 1/2	0	—0.18	....	...	....
.28	0	+0.18	....	...	....
			Average,	889.0	±8.5

TABLE III.

(Dec. 10, 1909.)

Solution: Molal LiI, $^1/_{100}$ molal I_2. $r^2 = 29.45$ cm., $r_1 = 4.2$ cm.

Standardization of Magneto: $\dfrac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 0.8605$ (6 exp. av. dev. ± 0.0040).

Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8605$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
10.10	0	—0.2	....	....	....
.24	0	—0.20	....	....	....
.29	0	—0.15	....	....	....
.33	0	—0.30	....	....	....
.36	59.2	+3.25	50.9	1253	+70
.36 1/2	60.2	3.26	51.8	1217	+34
.37	61.2	3.30	52.6	1192	+ 9
.37 1/2	61.5	3.30	52.9	1179	— 4
.38 1/4	61.9	3.31	53.3	1163	—20
.39	0	—0.20	....	....	....
.40	0	—0.5	....	....	....
.41 1/2	0	—0.4	....	....	....
.44	0	—0.13	....	....	....
.45 1/2	64.1	+3.65	55.1	1202	+19
.46	64.8	3.72	55.8	1193	+10
.46 1/2	65.1	3.68	56.0	1172	—11
.47 1/2	66.0	3.76	56.8	1165	—18
.48	66.3	3.77	57.1	1157	—26
.49	0	—0.15	....	....	....
.49 1/2	0	—0.2	....	....	....
.50	0	—0.25	....	....	....
.51	0	—0.25	....	....	....
.51 1/2	0	—0.25	....	....	....
.53	0	—0.22	....	....	....
.56	0	—0.25	....	....	....
.58 1/2	69.5	+4.23	59.8	1182	— 1
.59	69.3	4.22	59.6	1188	+ 5
.60	69.2	4.18	59.5	1180	— 3
11.00 1/2	68.7	4.13	59.1	1183	0

Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8605$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
.01	68.4	4.05	58.8	1171	—12
.01¾	68.3	4.04	58.75	1170	—13
.02¾	0	—0.14	....	....	....
.03¼	0	—0.18	....	....	....
.04	0	—0.14	....	....	....
.05½	0	+0.10	....	....	....
.07½	0	0.15	....	....	....
.09½	0	0.16	....	....	....
.11	0	0.09	....	....	....
.13	73.8	4.80	63.5	1190	+ 7
.13¼	74.0	4.80	63.7	1182	— 1
.14	74.0	4.75	63.7	1169	— 4
.14½	74.1	4.77	63.75	1173	—10
.15½	74.5	4.84	64.1	1178	— 5
.16	74.8	4.85	64.4	1170	—13
.17	0	—0.19	....	....	....
.17½	0	—0.27	....	....	....
.18	0	—0.30	....	....	....
.19	0	—0.30	....	....	....
.20½	0	—0.28	....	....	....
.24	0	—0.32	....	....	....
.39	0	—0.36	....	....	....
...	....	....	....	....	....
...	....	....	....	....	....
...	....	....	....	....	....
.44	0	—0.20	....	....	....
.46	0	—0.03	....	....	....
.48	80.1	+5.62	68.9	1184	+ 1
.48½	79.8	5.61	68.7	1189	+ 6
.49	79.3	5.48	68.25	1177	— 6
.49½	79.1	5.47	68.1	1179	— 4
.50½	78.5	5.38	67.5	1180	— 3
.52	0	—0.16	....	....	....
.52½	0	—0.25	—..	....	....
.53½	0	—0.30	....	....	....
.55	0	—0.25	....	....	....
.56½	0	—0.25	....	....	....
.58	0	—0.25	....	....	....
12.00	84.1	+6.30	72.4	1202	+19
.00½	84.5	6.33	72.7	1198	+15
.01	84.1	6.18	72.4	1180	— 3
.02	84.0	6.15	72.25	1178	— 5
.02½	84.1	6.16	72.4	1175	— 8
.03	0	—0.18	....	....	....
.04	0	—0.35	....	....	....
.04½	0	—0.35	....	....	....
.05½	0	—0.25	....	....	....
.06¾	0	—0.07	....	....	....
.09½	0	+0.15	....	....	....
			Average,	1183	±11.7

TABLE IV.

(Nov. 20, 1909.)

Solution: Molal HI, approx. M/50 I_2. r_2 = 29.43 cm., r_1 = 4.51 cm.

Standardization of Magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}}$ = 1.0125 (6 exp. av. dev. ±0.0095).

Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 1.0125$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
10.53	0	—0.38	....	....	....
11.10	0	—0.45	....	....	....
.17	0	+0.50	....	....	....
.18½	63.0	1.55	63.8	380	+ 4
.19½	70.0	1.83	70.8	365	—11
.20	70.2	1.90	71.0	377	+ 1
.20¼	70.0	1.90	70.8	379	+ 3
.21½	0	—0.17	....	....	....
.22½	0	—0.25	....	....	....
.24	0	—0.22	....	....	....
.25	0	—0.15	....	....	....
.26	0	—0.1	....	....	....
.28	0	—0.08	....	....	....
.29½	73.5	+2.13	74.4	385	+ 9
.30½	76.0	2.17	76.9	367	— 9
.30	76.1	2.25	77.0	379	+ 3
.31½	75.5	2.25	76.4	385	+ 9
.32	75.8	2.25	76.7	382	+ 6
.33	0	—0.12	....	....	....
.33½	0	—0.20	....	....	....
.35	0	—0.16	....	....	....
.36½	0	—0.12	....	....	....
.38(?)	0	—0.01	....	....	....
.45	78.5	+2.35	79.4	373	—3
.46	79.0	2.33	79.9	365	—11
.46½	78.5	2.40	79.4	381	+ 5
.47	78.2	2.35	79.1	376	0
.48	0	—0.10	....	....	....
.48½	0	—0.15	....	....	....
.49½	0	—0.15	....	....	....
.50½	0	—0.10	....	....	....
.52	0	—0.07	....	....	....
.53	0	—0.02	....	....	....
.54½	79.0	+2.45	79.9	384	+ 8
.55	80.5	2.45	81.4	370	— 6
.56	81.0	2.45	81.9	366	—10
.57	0	—0.10	....	....	....
.57½	0	—0.15	....	....	....
.58	0	—0.15	....	....	....
.60	0	—0.07	....	....	....
12.03	0	+0.06	....	....	....
			Average,	375.9	±6.1

of the partial volumes of iodine in iodide solutions and of the iodides in aqueous solution is necessary.

The partial specific volume of any constituent of a solution may be defined as the increase in volume of the solution when one gram of the constituent in question is added to a quantity of the solution so large that the addition causes no appreciable change in concentration. In the language of mathematics, if the addition of Δm grams of the constituent at the concentration under consideration produces an increase of Δv cc. in the volume of the solution, the partial volume of the substance may be defined as the limit approached by $\Delta v/\Delta m$ as Δm approaches zero.

The quantity $\Delta v/\Delta m$ and its limit the partial volume dv/dm may be obtained by the same experimental methods used for the determination of the specific gravity of solutions, or, indeed, may be calculated from specific gravity data if such are available.

In the author's more complete article,[1] a method is presented of calculating partial volumes from specific gravity data, and calculations are made from existing data of the partial volumes of the salts used. Determinations which were made of the partial volume of iodine are also described. The values used in calculating the transference number are given in the table in the next section.

9. Calculation of the Transference Number.

Substituting for π its value, and for F the value 96580, equation (2) may be written:

$$T_c = \left(\frac{4.895 \times 10^{10}}{(r_2^2 - r_1^2)}\frac{E}{n^2} + M_I(1 - v_{I_2}d)\right) \div M_s(1 - v_s d).$$

Using the average values of E/n^2 the transference number of the cation T_c was calculated for each of the salts. The data and results are given below:[2]

Solution.	$E/n^2 \times 10^6$.	$(r_2^2 - r_1^2)$.	M_s.	v_s.	M_I.	v_{I_2}.	d.	T_c.	$P. E.$
$M/1$ KI, $M/100$ I_2....	657.1	846.0	166.0	0.284	126.9	0.2376	1.115	0.486	± 0.001
$M/1$ NaI, $M/100$ I_2...	889.0	849.3	149.9	0.244	126.9	0.2376	1.110	0.385	± 0.001
$M/1$ LiI, $M/100$ I_2...	1183	849.3	133.9	0.2605	126.9	0.2376	1.096	0.268	± 0.0013
$M/1$ HI, $M/50$ I_2....	375.9	846.2	127.9	0.282	126.9	0.2376	1.090	0.816	± 0.001

a. The Accuracy of the Results.—The last column in the table gives the extremely small "probable error" introduced into the value of the transference number, by the deviations between the different measurements of E/n^2. It was obtained by dividing the mean deviations by the square root of the number of observations. It is not a satisfactory measure

[1] *Proc. Amer. Acad. Arts Sci.*, 46, 109–146 (1910).

[2] The values of E/n^2 are, of course, all negative since the current tends to flow from the outer to the inner electrode.

of the reliability of the transference numbers, since there is considerable probability that the "residual" electromotive force existing between the electrodes during rotation were more likely to be in one direction than the other. The value ± 0.010 may be taken as a fairer measure of the probable accuracy of the determinations. In the case of KI, this would correspond to an average error of about 0.1 millivolt in the electromotive force.

b. The Effect of Pressure on the Results.—In deriving the equation in Section 2 for the potential difference of a cell under the influence of centrifugal force, the tacit assumption was made that the quantities v_s, v_{I_2} and d are, throughout the solution, the same as those calculated from density measurements made at atmospheric pressure. This is not strictly true, since there is considerable pressure produced in the solution by the centrifugal force.

In the author's original article[1] an exact equation is derived in which the variation of these quantities with the pressure is allowed for; and it is shown that the error introduced by neglecting the variation is, as would be expected, entirely negligible.

In considering the pressure gradient in the tube, it must also be pointed out that the transference number determined in these experiments is the transference number which exists when the solution is actually under the influence of that particular pressure gradient. Owing to their enormous "internal pressure" the properties of liquids are, however, in general but little affected by changes in the external pressure.

c. The Effect of Dissolved Iodine on the Results.—In the case of the alkali iodides one per cent. of the $\bar{I}$ ion was changed into $\bar{I}_3$ ion by the iodine present. In the HI solution, owing to oxidation, about twice as much iodine was present. The transference number would, however, be only slightly affected by the small admixture of $\bar{I}_3$ ion.[2]

10. Comparison of the Results with Other Transference Measurements.

The available data on the transference numbers of iodides are very few, and, of these, many are vitiated by the use of membranes in the apparatus.[3] The most satisfactory data for comparison are the values determined by Washburn[4] for the Hittorf transference numbers of the alkali *chlorides* (at a concentration 1.2—1.3 molal), and the value for the Hittorf transference number of hydrochloric acid (at a concentration

[1] *Loc. cit.*

[2] For data on the mobility of the $\bar{I}_3$ ion see Burgess and Chapman, *J. Chem. Soc.*, **85**, 1305 (1904); Bray and MacKay, THIS JOURNAL, **32**, 914 (1910).

[3] See McBain (*Proc. Wash. Acad. Sci.*, **9**, 1–78 (1907)), University of Toronto Studies, Papers from the Chem. Laboratories, No. 67, for a complete collection of the experimental data on transference numbers.

[4] Washburn, *Tech. Quart.*, **21**, 164 (1908); THIS JOURNAL, **31**, 322 (1909); Buchböck, *Z. physik. Chem.*, **55**, 563 (1906).

1.0 molal) which can be calculated from Buchböck's determination of true transference number and hydration. This comparison is made in Table V. The transference numbers for the chlorides and iodides at infinit dilution, calculated from conductivity data are also given in the table, and finally, values obtained for $N/10$ KI and $N/10$ NaI by Dennison,[1] using the method of Dennison and Steele and a value by Bein[2] for $N/20$ KI. This last is the only available datum for these iodides obtained by the Hittorf method without the use of membranes.

TABLE V.—TRANSFERENCE NUMBER OF THE ANION.

Halide of	Iodide, centrifugal.	Chloride, Washburn, Buchböck.	Iodide, Infinit dilution.[3]	Chloride, Infinit dilution.[3]	Iodide, Dennison.	Iodide, Bein.
K......	0.514	0.518	0.507	0.503	0.514	0.505
Na.....	0.615	0.634	0.604	0.601	0.624	...
Li	0.732	0.722	0.665	0.66?	...	...
H......	0.184	0.160[4]	0.174	0.172	...	...

The agreement between the results presented in the table for the iodides with those for the chlorides is satisfactory. The greatest deviation occurs in the values for the two halogen acids. Hydrochloric acid,[5] however, is known to be abnormal in its behavior, since the transference number passes through a minimum at a concentration below normal, and the same effect might occur in hydriodic acid solution. Furthermore, since the electromotive force measured was so small in the case of hydriodic acid any constant error in the nature of a residual electromotive force might have had a large effect.

11. Summary.

In this article an apparatus and procedure have been described for determining transference numbers by the centrifugal method, first tried by Des Coudres. The method consists in the measurement of the electromotive force produced between electrodes placed at the central and peripheral ends of a rotating tube containing the electrolyte. An equa-

[1] Dennison, *Trans. Faraday Soc.*, 5, 165 (1909). It has been shown by Lewis, THIS JOURNAL, 32, 862 (1910), that the method of Dennison and Steele gives, after applying a calculable correction, the Hittorf transference number and not the true transference number as stated by Washburn.

[2] Bein, *Z. physik. Chem.*, 27, 1 (1898).

[3] These values for the transference number at infinit dilution were calculated from the latest conductivity data of Kohlrausch. *Z. Elektrochem.*, 13, 333 (1907).

[4] This value for the Hittorf transference number of molal HCl is calculated from Buchböck's determination of true transference number and hydration by the relation connecting those quantities as developed by Washburn. Washburn himself gives 0.18 for the Hittorf transference of HCl, a value which was taken from Kohlrausch's tables, but it is probably considerably too high. For HCl, 0.97 molal, Riesenfeld u. Reinhold, *Z. physik. Chem.*, 68, 440 (1909), obtain the value 0.155, and Hopfgartner, *Z. physik. Chem.*, 25, 115 (1898), obtains 0.159 for 0.9 molal HCl.

[5] Riesenfeld u. Reinhold, *Z. physik. Chem.*, 68, 440 (1909).

tion can be derived, connecting this electromotive force and the transference number of the salt with the speed of rotation, the density of the solution, and the molecular weight and the "partial" specific volume of the substances involved, quantities which can be independently determined.

Some of the details of the construction of the rotating apparatus may have general interest. A distinctive feature of the apparatus was the method of driving the rotator (which had not been specially balanced) as a "spinning top," by hanging it below a fixed point of support. A simple arrangement of cords was devised for steadying the shaft of the rotating top and preventing precessional motion. A thrust bearing suitable for high speeds is also described. It consists of a series of ball bearings which distribute the total relative motion. An equation is given for calculating the dimensions of a rotating arm of uniform strength with the cross section increasing in size towards the center of rotation.

With this apparatus measurements were made of the electromotive force produced by the rotation of molal solutions of potassium, sodium, lithium, and hydrogen iodides. As predicted from the equations, the electromotive force was found to increase proportionately to the square of the speed of rotation. From the data the transference number was calculated for the four solutions, and found to agree as well as could be expected, with the available results of other methods of determination.

It was pointed out in connection with a kinetic derivation of the electromotive force relation, that the production of an electromotive force by centrifugal force is a proof of the presence of free ions in an electrolytic solution or at least of a certain degree of electrical polarization in the molecules.

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