THE ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS

BY

CENTRIFUGAL ACTION.

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Contents.

Contents (Con.)

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[1]. In electrolytic
conductors, however, the experiments of Hittorf have shown
that there is an actual transfer of matter through the so-
lution, accompanying the passage of a current. As an ex-
ample of the electrical effects which may accompany such a
motion of the carriers of electricity or ions, let us con-
sider a solution of silver 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 ap-
proximately equal lowering of the considerably lighter ni-

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[1] Maxwell, Treatise on Elec.&Mag.,3rd edition,1892,Vol.II.
p.211 et seq.
Lodge,Modern Views of Elec.&Mag.erd edition,1907,p.89
Nichols,Phys.Zeitschr. $\underline{7}$, 640, 1906.

trate 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[1], and have also been considered by various other investigators[2]. 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 undetect_{able} 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 theoretically 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.

[1] 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;Weid.Ann,17 55, 1882.

[2] Lodge, Phil.Mag.(5) 2, 367, 1876. Hertz, Wied.Ann. 14, 590, 1881. Des Coudres, Wied.Amm.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 is given below. As to experimental results it may be said that the work of van Calcar and de Bruyn is in complete disagreement with the theory. The result reported by the Earl of Berkeley and Dr. Burton is, however, of the predicted order of magnitude.

Gay Lussac, Ann.chim.phys.(2) 11, 306, 1819
Gouy et Chaperon, Ann.chim.phys.(6) 12, 384, 1887.
Nernst, Zeitschr.f.phys.Chem.2, 637, 1888.
Duhem, Journ.de phys.7, 391,1888.
T.v. Turin, Journ.der russ.Geschichte(1) 24,90,1892.Wied.
                                          Beibl.17,16,1893.
Des Coudres, Wied.Ann.49, 284, 1893.
Ibid. Wied.Ann.55, 213,1895.
Van der Waals,Zeits.f.phys.Chem.5,157,1890.
Bredig,Zeitscher.f.phys.Chem.17,459, 1895.
Lobry.de Bruyn et van Calcar,Red.d.travaux chim.d.Pays-Bas,
                                          23, 218, 1904.
Franklin & Freudenberger, Trans.Am.Electrochem.Soc.8,29,1905.
Earl of Berkeley & C.V. Burton,Phil.Mag.17,606,1909.
Gibbs, The Scientific Papers of, Longmans,Green & Co.,1906,
                                          Vol.I, p.144.

The experimental problem was next attacked by Des Coudres who substituted centrifugal force for the weaker action of gravity. He made use of a notating apparatus in which were placed two tubes with electrodes connected in series, containing cadmium iodide solution. The electrodes were placed 31 cms. and 9 cms. 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% from the mean. Although the substitution of centrifugal force for the force of gravity greatly increases the size of the effect which can be 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 num-
ber greater than unity, and hence gives a large electro-
motive 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 analy-
tical 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 tubes 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 in-
cluding a comparison between the value T_a for the transfer-
ence 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.")	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 microvolts.

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 10^7E.F. 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 extenral energy 10^7 E.F 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_x 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 $T_c M_s$ gms. of salt will

have apparently been transferred from the anode to the cath-

ode, where T_c is the ordinary or Hittorf transference number

of the cattion 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

$T_c M_s$ gms. 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 <u>through</u> the solution it

is evidaht that they will be buoyed up by force equal to the

weight of the voluem 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 $g \, T_c \, M_s \left(1 - v_s \, d \right)$ and

$g \, M_x \left(1 - v_{x_1} d \right)$ where $v_s \, \dashv \, v_{x_1}$ are the "partial"

specific volumes[1] of the substances. Equating the external

[1)]

For a definition of "partial" volumes, see page <u>33</u>

electrical work to the work done against these forces in

transferring the substance from one electrode to the other

we have the desired relation[1]

$$10^7 E F = h \, g \left\{ T_c M_s (1 - v_s d) - M_x (1 - v_{x} d) \right\} \quad ----(1)$$

If instead of using a gravity cell we should rotate

our solution ω times per second, with electrodes at h_1 and h_2

, since the centrifugal force acting on one gram at any radius h is $4 \pi^2 \omega^2 h$

the work done in carrying one gram from h_2 to h_1 would

evidently be $\int_{h_1}^{h_2} 4 \pi^2 \omega^2 h \, dh = 2 \pi^2 \omega^2 \left(h_2^2 - h_1^2 \right)$ [2]

and our equation for electromotive force becomes

$$10^7 E F = 2 \pi^2 \omega^2 \left(h_2^2 - h_1^2 \right) \left\{ T_c M_s (1 - v_s d) - M_x (1 - v_{x} d) \right\} ---(2)$$

We see that the value of the electromotive force which

is to be measured is proportional to the factor $h \, g$ or

$2 \pi^2 \omega^2 \left(h_2^2 - h_1^2 \right)$. In the experiments of Des Coudres on

gravitational cells, the factor $h \, g$ was 360,000, while with

his rotating apparatus the value of the corresponding factor

was 585,000. In the centrifugal experiments which are to

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[1]
   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.

[2]
   It may also be pointed out that the expression $2 \pi^2 \omega^2 \left(h_2^2 - h_1^2 \right)$
is the increase in kinetic energy when one gram of material
is transferred from h_1 to h_2 .

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 and especially of Washburn[1] 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 electromotive force was derived, it is obvious that the Hittorf transference number is the one which has been determined in this research.

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[1] Washburn,Tech.Quart.21,164, 1908,Journ.Amer.Chem.Soc.31, 322, 1909.

Buchböck Z.physik.Chem.55, 563, 1906.

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 themmodynamic reasoning. The method of proof is similar to that used by Nernst in his consideration of the diffusion cell.

Consider an iodide$\left(C^+I\right)$of molecular weight M_s dissociating into the ions C^+ and I^- of atomic weights M_c and M_I. Let v_g be the partial specific volume of the salt in solution and $v_c + v_I$ be the same eqantities 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 poduce a potential gradient in the solution $- dE/dh$. 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 $(g\, M_c)$, minus the buoyant force exerted by the solution$(g\, M_c\, v_c\, d)$, minus the electrical repulsion $(10^7 F\, dE/dh)$ corresponding to the potential gradient. If $w + v$ 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 Ohms 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)]

$$u \left\{ g \, M_c \left(1 - v_c d \right) - 10^7 F \frac{dE}{dh} \right\} = v \left\{ g \, M_I \left(1 - v_I d \right) + 10^7 F \frac{dE}{dh} \right\}$$

Solving for dE_1/dh and integrating between the limits 0 and h, where h is the difference in height between the electrodes, we have

$$10^7 E_1 F = h g \left\{ \frac{u}{u+v} M_c \left(1 - v_c d \right) - \left(1 - \frac{u}{u+v} \right) M_I \left(1 - v_I d \right) \right\} \quad -- \quad (3)$$

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 $\frac{1}{2} I_2 + \ominus = I^-$. Since this reaction is accompanied by the change in volume $M_I \left(v_I - v_{I_2} \right)$ and takes place under the difference in pressure between the upper and lower electrodes which is equal to $h g d$, we must add to the electromotive force E_1 as given in equation (3),

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[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.

below

the electromotive force E_2 given by the equation, which is

derived by equating the external electrical work to the work

produced by the change in volume .

$$10^7 \, E_2 \, F \;=\; M_I \left(v_I - v_{I_2} \right) l_{og} \, d$$

Noticing that $\dfrac{w}{w + v} = T_c$ we obtain

$$10^7 \left(E_1 + E_2 \right) F = l_{og} \left\{ T_c \, M_c \left(1 - v_c d \right) + T_c \, M_I \left(1 - v_I d \right) - M_I \left(1 - v_{I_2} d \right) \right\}$$

$$10^7 \, E \, F = l_{og} \left\{ T_c \, M_S \left(1 - v_S d \right) - M_I \left(1 - v_{I_2} d \right) \right\}$$

which is the same equation we originally obtained by thermo-

dynamic reasoning.

The real interest attached to this kinetic considera-

tion is the almost absolute proof it offers that some degree

of dissociation or at least polarization of the salt molecules

exists in aqueous solutions. 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

centrifugal separation. The method gives, of course, no

idea of the magnitude of the degree of ionization.

4.   DESCRIPTION OF APPARATUS.

The general arrangement of the rotating apparatus is shown in Fig. 1.   It consists of a steam turbine 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.

The Steam Turbine:

The turbine used was a thirty horse-power de Laval loaned for this investigation by the General Electric Co. The turbine 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 turbine wheel.   The holes F. are opposite 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 turbine 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 re-designed 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.

The Thrust Bearing:

The thrust bearing used was contained in the case K,
Fig.I. The details are shown in Fig.II. 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 bear-
ing at the proper height. The lateral bearings A and H as
well as the top bearing of the turbine, itself, consists 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.

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 indivi-
dual 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 obli-

gation for an intelligent and sympathetic understanding of the many difficulties involved in the construction of an apparatus of this kind.

The "Spinning Top".

The rotator B, Fig.I, is two feet in diameter and consists of two hollow steel arms, screwed into a central hub P. The rotator is hung on a shaft 13/16 inch diameter and 8-1/2 inches long. This shaft is flexibly connected to the turbine 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. I. but indicated in plan in Fig.III. 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.

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 revoluations 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 rotor 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 vis-
cous 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 mo-
tion which was prevented by the steadying device described
above. It must be noticed in general, in designing rota-
ting apparatus of this kind, that the actual motion may dif-
fer 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 ro-
tating 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 im-
practicable to run this rotator with a shaft 22 inches long.

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1)
  H. Lamb, Proc.Roy.Soc., 80 A 168, 1908.

The Rotator:

Fig. IV 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 1/2 inch in-
side 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 cen-
trifugal force of the plug and that of the contents of the
tube, assuming them to 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 thick-
ness of wall was also great enough to sustain the 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 con-
stantly increasing load. If h is the radius at any point
where the section is s, D the density, f the tensile strength
of the material, and n the number of revolutions, evidently
fds $= 4\pi^2 n^2 rDsdr$. 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.

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 parafine, sulphur, 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.IV. 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° C. 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 onto 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 covered by 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 sur-rounded 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

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

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 gauge 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.

The Electrical Connections:

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

At L in Fig. I is a brass disk about 2-1/2 inches in diameter fastened to the rotating shaft. This disk prevents any leakage of water from the turbine trickling down the Hooke joint and getting into the hollow rotator 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 turbine 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 turbine and from the friction of the steadying cords, which otherwise travel down the shaft and produced bad temperature differences between the central and peripheral electrodes.

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. I and shown in detail in Fig. V. The leads from the electrodes were made fast to the binding posts M and N, and electric connection was made through the 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 inches in diameter, thus reducing the relative veloci-
ty at the point of contact, mercury was chosen as the con-
tact substance, and the whole apparatus was made of the same
material, steel, throughout. Measurements of the electro-
motive 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.

The Magneto:

Returning again to the figures, T is a worm driving the
shaft s through a worm wheel not seen in the drawing. Meas-
urements 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 Cabot 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, how-
ever, 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.

The Electrical Measuring Instruments:

The potential differences obtained were of the order of a few millivolts. For their measurements, a Leeds and Northrup pontentiometer 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 which contained the rotating solutions have already been described. In the experiments as finally performed only one tube was used, an approximate counter-balance 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 incendescence 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 milli-volt 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. The 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 1-1/2 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].

[1] Laurie, Zeits,f.phys.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.

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 x 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. 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 a half a dozen standardizing runs were made at speeds in the neighborhodd 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 volt-meter 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 opposite di-
rection 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
opposite 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 electro-
motive 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 millivolts.

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° C. would have produced a residual electromotive force of about 0.25 millivolts in the direction actually found[1]. This explanation, however, would not account for the fact that the residual electromotive force tends to increase after the machine has been stopped, and the very conditions removed which were supposed to create

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1)
   In order to determine 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.

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

---

[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 junctions of higher thermoelectric power than the iron-nickel combination.

In some earlier experiments very definite temperature effects were produced by heat which traveled down the rotator shaft. These effects were eliminated, however, by the copper radiating disk N, Fig. 5, already described, see p. .

[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.

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 dif-
ferences 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.

Table I.
(Dec. 2, 1909).

Solution: Molal KI, $\frac{1}{100}$ Molal I_2

r_2 = 29.40 cm., r_1 = 4.3 cm.

Standardization of magneto:-

$\dfrac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}}$ = 1.050 (7 expts.av.dev. $\pm$ 0.0145)

Time	V = Voltage of Magneto	E x.10^3. = E.M.F.	n = V x 1.050 = rev. per sec.	$10^6\dfrac{E}{n^2}$	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
.30½	59.8	2.55	62.8	647	-10
.31½	0	-0.15			
.32	0	-0.30			
.34	0	-0.18			
.36	0	-0.14			
.40	0	-0.17			
.41½	71.5	+3.65	75.0	649	-8
.42	71.2	3.73	74.7	668	-11
.43½	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			
.50½	0	0.17			
.52½	0	0.25			
.55	78.0	4.38	81.9	653	-4
.55½	77.5	4.35	81.3	658	+1
.56	77.0	4.25	80.8	651	-6
.57	---	4.25			

Average   657.1 $\pm$ 6.3

Table II.
(Dec.23,1909)

Solution: Molal NaI, $\frac{1}{100}$ molal I_2

$r_2 = 29.45$ cm., $r_1 = 4.2$ cm.

Standardization of Magneto:-

$$\frac{\text{Rev. of rotator per second}}{\text{Voltage of Magneto}} = 0.8695 \text{ (8 exp. av. dev. } \pm .0035)$$

Time	V = Voltage of Magneto	E x 10^3 = E.M.F.	n = V x 0.8695 = rev. per sec.	$\frac{E}{n^2}$ x10^6	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			
31-1/4	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

Table II continued should be bound up to fold in.

06½	84.1	4.80	73.1	899	+10
07½	0	-0.23			
08	0	-0.23			
10	0	-0.04			
11½	0	+0.12			
14	0	0.17			
16	0	0.17			
18½	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
21½	73.9	3.68	64.2	892	+3
22½	0	-0.24			
23½	0	-0.18			
28	0	+0.18			

Average 889.0   ± 8.5

Table III
(Dec. 10, 1909).

Solution: Molal LiI, $\frac{1}{100}$ molal I_2.

r_2 = 29.45 cm. r_1 = 4.2 cm.

Standardization of Magneto:-

$$\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 0.8605 \text{ (6 exp. av. dev. } \pm .0040)$$

Time	V = Voltage of Magneto	E x 10^3 = E.M.F.	n = V x 0.8605 = rev. per. sec.	$\frac{E}{n^2}$ x10^6	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
36½	60.2	3.26	51.8	1217	+34
37	61.2	3.30	52.6	1192	+9
37½	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			
41½	0	-0.4			
44	0	-0.13			
45½	64.1	+3.65	55.1	1202	+19
46	64.8	3.72	55.8	1193	+10
46½	65.1	3.68	56.0	1172	-11
47½	66.0	3.76	56.8	1165	-18
48	66.3	3.77	57.1	1157	-26
49	0	-0.15			
49½	0	-0.2			
50	0	-0.25			
51	0	-0.25			
51½	0	-0.25			
53	0	-0.22			
56	0	-0.25			
58½	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
11.00½	68.7	4.13	59.1	1183	0
1	68.4	4.05	58.8	1171	-12
1-3/4	68.3	4.04	58.75	1170	-13
2-3/4	0	-0.14			
3-1/4	0	-0.18			
4	0	-0.14			
5-1/2	0	+0.10			
7-1/2	0	0.15			
9-1/2	0	0.16			
11	0	0.09			
13	73.8	4.80	63.5	1190	+7
13-1/4	74.0	4.80	63.7	1182	-1
14	74.0	4.75	63.7	1169	-4

Table 3 Continued should be bound up to fold in

14-1/2	74.1	4.77	63.75	1173	-10
15-1/2	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
1/2	84.5	6.33	72.7	1198	+15
1	84.1	6.18	72.4	1180	-3
2	84.0	6.15	72.25	1178	-5
2½	84.1	6.16	72.4	1175	-8
3	0	-0.18			
4	0	-0.35			
4½	0	-0.35			
5½	0	-0.25			
6-3/4	0	-0.07			
9-1/2	0	+0.15			

Average   1183   11.7

Table IV.
(Nov. 20, 1909).

Solution: Molal HI, approx $\frac{M}{50}I_2$

$r_2 = 29.43$ cm. $r_1 = 4.51$ cm.

Standardization of Magneto:-

$\dfrac{\text{Rev. of rotator per second}}{\text{Voltage of Magneto}} = 1.0125$ (6 exp. av. dev. $\pm$ .0095)

Time	V = Voltage of Magneto	$E \times 10^3$ = E.M.F.	n = V x 0.0125 = rev.per sec.	$\frac{E}{n^2} \times 10^6$	Dev. from mean
10.53	0	-0.38			
11.10	0	-0.45			
17	0	+0.50			
$18\frac{1}{2}$	63.0	1.55	63.8	380	+4
$19\frac{1}{2}$	70.0	1.83	70.8	365	-11
20	70.2	1.90	71.0	377	+1
$20\frac{1}{2}$	70.0	1.90	70.8	379	+3
$21\frac{1}{2}$	0	-0.17			
$22\frac{1}{2}$	0	-0.25			
24	0	-0.22			
25	0	-0.15			
26	0	-0.1			
28	0	-0.08			
$29\frac{1}{2}$	73.5	+2.13	74.4	385	+9
$30\frac{1}{2}$	76.0	2.17	76.9	367	-9
30	76.1	2.25	77.0	379	+3
$31\frac{1}{2}$	75.5	2.25	76.4	385	+9
32	75.8	2.25	76.7	382	+6
33	0	-0.12			
$33\frac{1}{2}$	0	-0.20			
35	0	-0.16			
$36\frac{1}{2}$	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
$46\frac{1}{2}$	78.5	2.40	79.4	381	+5
47	78.2	2.35	79.1	376	0
48	0	-0.10			
$48\frac{1}{2}$	0	-0.15			
$49\frac{1}{2}$	0	-0.15			
$50\frac{1}{2}$	0	-0.10			
52	0	-0.07			
53	0	-0.02			
$54\frac{1}{2}$	79.0	+2.45	79.9	384	+8
55	$80.\frac{1}{2}$	2.45	81.4	370	-6
56	81.0	2.45	81.9	366	-10
57	0	-0.10			
$57\frac{1}{2}$	0	-0.15			
58	0	-0.15			
60	0	-0.07			
12.03	0	+0.06			
			Average	375.9	$\pm$ 6.1

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 should be a constant. The degree of the constancy of this quantity is illustrated by the fifth column in Tables I - IV which give the values of E/n^2 as calculated from the data. Considering the separate runs in a series of measurements, 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 con-
sidered a knowledge 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 so-
lution 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 mathe-
matics, if the addition of Δ m grams of the constituent at
the concentration under consideration produces an increase
of Δ v 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 Δ m 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.

The purpose of this section is to show the method of
calculating partial volumes from picnometer weighings or from

specific gravity data and also to present the results of some experimental determinations of the partial volume of iodine in potassium iodide solution as well as the partial volumes of potassium, sodium, lithium, and hydrogen iodides in molal solution, as calculated from existing data.

The partial volume for any solute may be determined from successive weighings of a picnometer filled with solutions of different concentrations. Let V be the volume in ccm. held by the picnometer and let it contain M gm. of solution when the percentage concentration of the solute in question is P x 100 and M' gm. of solution of concentration P' x 100. The amount of solvent in the picnometer when it is weighed containing solution of concentration P is (1-P)M, hence the volume of a solution of concentration P' containing the same amount of solvent would be

$\frac{(1-P)M}{(1-P')M'}$ V and the amount of the solute in that solution would

be $\frac{(1-P)M}{(1-P')M'}$ P'M' leading to the relation

$$\frac{\Delta v}{\Delta m} = \frac{\frac{(1-P)M}{(1-P')M'}V - V}{\frac{(1-P)M}{(1-P')M'}P'M' - PM} = \frac{(1-P)MV - (1-P')M'V}{(1-P)MP'M' - (1-P')M'PM} \quad - - - \cdot (3)$$

It is evident that the percentage accuracy in the determination of this quantity $\Delta v / \Delta m$ will be greater the greater the quantities Δv and Δm, in other words the farther apart the concentrations P and P' are taken. On the other hand, if

we are interested in the partial volume of the solute at the concentration P, we must determine the limit of $\Delta v / \Delta m$ as P' is brought nearer and nearer to P. A satisfactory solution of the problem may often be obtained by determining $\Delta v / \Delta m$ for several different values of P', if possible making it in some cases larger and in others smaller than P. These values will then permit a close estimate of the limit of $\Delta v / \Delta m$ at the concentration P.

If a calculation of the quantity $\Delta v / \Delta m$ from specific gravity data is desired, equation (1) has to be changed merely by the substitution of the densities d and d' for the weights M and M' and by placing the volume V equal to unity, giving the formula

$$\frac{\Delta v}{\Delta m} = \frac{(1-P)d - (1-P')d'}{(1-P)d\,P'd' - (1-P')d'Pd} \quad \text{---} \quad (4)$$

For the purpose of determining the partial volume of iodine in iodide solutions picnometer weighings were made of a solution of approximately quarter normal potassium iodide containing varying quantities of iodine. The partial volume was desired in solutions very dilute in iodine ($\frac{M}{100} I_2$), and hence the solutions were made as dilute in iodine as was consistent with a reasonable degree of accuracy in the calculation of $\Delta v / \Delta m$ between pure potassium iodide solution and the iodine

solution in question. It is especially desirable to make
the determinations with solutions as dilute as the accuracy
of the method will permit, since the exact measurements of
Kohlrausch and Hallwachs[1] have shown that for several sub-
stances there is a rapid change in partial volumes when con-
siderable dilutions are reached.

For the measurements, two separate solutions were made
up from the same KI solution each containing about 1.5% I_2.
The concentration of the solutions was determined by weigh-
ing the iodine used and transferring it directly from a
glass stoppered weighing tube into the solution. The amount
of solution used was also determined by weight. From each of
these original solutions two more were prepared by dilution
with weighed quantities of the pure potassium iodide solution,
giving in all six iodine solutions whose densities were de-
termined. The density of the original KI solutions was also
determined.

The volume of the picnometer used was about 21 cc., and
was exactly determined by weighing the picnometer filled with
pure water. The picnometer used was of the form recommended
by Ostwald and Luther and the setting of the meniscus in the
capillary was made in a thermostat kept constant at 25° C.
For each solution, at least two weighings were made, the pic-
tometer being replaced in the thermostat and the meniscus

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[1] Wied.Ann.53 14, 1894.

reset between weighings. The weighings were made immediately after removing the picnometer from the thermostat and wiping off the surface. The successive weighings of the same solution usually agreed within two tenths of a milligram. Proper corrections were made for the buoyancy of the air. The iodine was prepared by resubliming with potassium iodide.

The results are presented in the following table:

No.of Sol.	$\%I_2$	Density	$\Delta v/\Delta m$
1	1.630	1.03955	0.2370
2	1.506	1.03842	0.2390
1'	1.099	1.03525	0.2362
2'	1.014	1.03452	0.2410
1"	0.8292	1.03310	0.2385
2"	0.7538	1.03250	0.2374
0	0	1.02660	------

The last column gives the value $\Delta v/\Delta m$ between a solution containing no iodine and one of the concentration indicated. No evidence is present of a systematic variation of $\Delta v/\Delta m$ with the consentration. Omitting the value of $\Delta v/\Delta m$ for solution #2', the average value is $\Delta v/\Delta m$ = 0.2376 ± 0.0004 ($=\dfrac{\text{average dev.}}{\sqrt{5}}$), and this was taken as the partial specific volume of iodine at great dilutions in potassium iodide solution. The specific volume of pure iodine from the data in Landolt and Börnstein is 0.202.

In the following tables the results are given for some calculations of $\Delta v/\Delta m$ for potassium, sodium, lithium and hydrogen iodides in aqueous solution at 20° C. from the data of

Wegner and of Perkin given in Landolt and Börnstein.

Potassium Iodide (Wegner)

P	P'	d (20/4)	d' (20/4)	$\Delta v/\Delta m$
10.27	15,12	1,0784	1.1205	0.283
10.27	20.04	1.0784	1.1665	0.285
15,12	20,04	1.1205	1.1665	0.286

For a concentration of one mol per kg.water

P = 14.2, dv/dm taken as 0.284 cc. for molal solution.

Specific volume of the solid (L & B)   0.326 cc.

Sodium Iodide (Wegner).

P	P'	d (20/4)	d' (20/4)	$\Delta v/\Delta m$
6.25	9.28	1.0483	1.0743	0.240
6.25	14.70	1.0483	1.1239	0.242
9.28	14.70	1.0743	1.1239	0.244

For a concentration of one mol per kg.water P = 13.0, dv/dm taken as 0.244 cc.

Specific volume of the solid (L & B)   0.282

Lithium Iodide (Wegner)

P	P'	d $(20/4)$	d' $(20/4)$	$\Delta v/\Delta$ m
0	5.90	0.9997	1.0437	0.262
0	10.54	0.9997	1.0825	0.2615
5.90	10.54	1.0437	1.0825	0.261

For a concentration of one mol per kg.water P = 11.8,
dv/dm taken as 0.2605 cc.

Specific volume of the solid (L & B) 0.246.

Hydrogen Iodide (Perkin)

P	P'	d $(20/20)$	d' $(20/20)$	$\Delta v/\Delta$ m
0	20.77	1.0000	1.1754	0.2815
0	31.77	1.0000	1.2962	0.2805
20.77	31.77	1.1754	1.2962	0.2795

For a concentration of one mol per kg. water

P = 11.3, dv/dm taken as 0.2815 cc.(20°) or 0.282 true cc.
for molal solution.

It is interesting to note in the cases of potassium and
sodium iodides that the specific volume of the pure substance
is greater than the partial specific volume of the substance
in solution, and in these cases there is a slight but definite
increase in the partial volume as the solution becomes more
concentrated, that is as it approaches the pure salt. More-
over, in the case of lithium iodide, although here the par-
tial volume in solution is greater than the volume of the pure
substance it also approaches the latter as the solution becomes
more concentrated.

9. CALCULATIONS OF THE TRANSFERENCE NUMBER.

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

$$ T_c = \left\{ \frac{4.895 \times 10^{10}}{(h_2^2 - h_1^2)} \frac{E}{n^2} + M_I \left(1 - v_{I_2} d \right) \right\} \div M_s \left(1 - v_s d \right) $$

Using the average values of E/n^2 the transference
number of the cathion T_c was calculated for each of the salts.
The data and results are given below[1]:

Salt	$\frac{E}{n^2} \times 10^6$	$(h_2^2 - h_1^2)$	M_s	v_s	M_I	v_{I_2}	d_s	T_c	P.E.
KI	657.1	846.	166.0	0.284	126.9	0.2376	1.115	0.486	±0.001
Na I	889.0	849.3	149.9	0.244	"	"	1.110	0.385	±0.001
Li I	1183	849.3	133.9	0.2605	"	"	1.096	0.268	±0.0013
H I	375.9	846.2	127.9	0.282	"	"	1.090	0.816	±0.001

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

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

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 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.

The Effect of Pressure on the Results:

In deriving the equation on page 9 for the potential difference of a cell under the influence of centrifugal force, the tacit assumption was made that the quantities σ_S, σ_{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. The following equation in which the quantities are considered as variables is exact.

$$10^7 \, EF = \int_{n_1}^{n_2} 4\pi^2 u^2 n \left\{ T_c \, M_S \left(1 - \sigma_S d\right) - M_I \left(1 - \sigma_{I_2} d\right) \right\} dn \qquad (5)$$

The derivation of the equation is obvious. 10^7 E.F. is the external work obtained when one faraday of electricity flows through the solution under the potential difference E produced by the centrifugal action. This energy quantity is equal to the work required to restore the solution to its original condition. To accomplish this $T_c M_s$ gms. of salt must be brought back from r_2 to r_1, and this quantity, multiplied by $v_s d$ is the number of gms. of displaced solution which will automatically move in the opposite direction as we move the salt through the solution, M_I and $v_I d$ are the same quantities for the iodine, which has to be transferred from r_1 to r_2. The centrifugal force acting on the material which is to be moved is the product of the mass into $4\pi^2 \mu^2 r$ and the total work done is obtained by multiplying by dr, and integrating between r_2 and r_1. If the integration is made on the assumption that v_s, v_{I_2} and d do not vary with r, that is with the pressure, the equation actually used is obtained. As a matter of fact both the density of the solution and the partial volume of the salt will vary with the pressure, and hence as we move the salt through the solution from one electrode to the other at each level it will displace a different weight of solution and will hence be buoyed up by a different amount. We have no data for the variation of v_s and v_{I_2} with the pressure, but an upper limit for the error which has been intro-

duced by taking them as constant, may be calculated.

Assuming that $\bar{v}_S d$ and $\bar{v}_{I_2} d$ vary linearly with the pressure, since the pressure equals $3\pi^2 \mu^2 h^2 d$ [1], where d is approximately unity, we may write the equations

$$\bar{v}_S \, d = \overline{\bar{v}_S d}_0 \left(1 + 3\pi^2 \mu^2 h^2 \alpha_1 \right)$$

$$\bar{v}_{I_2} \, d = \overline{\bar{v}_{I_2} d}_0 \left(1 + 2\pi^2 \mu^2 h^2 \alpha_2 \right)$$

where $\overline{\bar{v}_S d}_0$ and $\overline{\bar{v}_{I_2} d}_0$ are the values for zero pressure, and α_1 and α_2 are the linear coefficients for the fractional change of $\bar{v}_S d$ and $\bar{v}_{I_2} d$ with the pressure. Substituting into equation 5 and integrating we obtain

$$E = \frac{2\pi^2 \mu^2}{10^7 F}\left(h_2^2 - h_1^2\right)\left\{ T_c M_S \left(1 - \overline{\bar{v}_S d}_0\right) - M_I\left(1 - \overline{\bar{v}_{I_2} d}_0\right)\right\}$$

$$- \frac{2\pi^4 \mu^4}{10^7 F}\left(h_2^4 - h_1^4\right)\left\{ T_c M_S \alpha_1 \, \overline{\bar{v}_S d}_0 - M_I \alpha_2 \, \overline{\bar{v}_{I_2} d}_0\right\}$$

The term $\dfrac{2\pi^4 \mu^4}{10^7 F}\left(h_2^4 - h_1^4\right)\left\{ T_c M_S \alpha_1 \, \overline{\bar{v}_S d}_0 - M_I \alpha_2 \, \overline{\bar{v}_{I_2} d}_0\right\}$

is seen to be the error introduced into the calculation of the electromotive force, by neglecting the change of the density and partial volumes with the pressure. Since the partial volumes will probably decrease with pressure and partly neutralize the increase in density, to obtain an upper limit for the error let us put α_1 and $\alpha_2 = 4 \times 10^{-12}$, the value for the fractional change in the density of water per $\dfrac{\text{dyne}}{\text{cm}^2}$. Making

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[1] This is strictly true only when the liquid reaches way to the center of the rotating apparatus.

this substitution, the value of the above term becomes only
0.00018 millivolts, for the experiment on potassium iodide,
at 80 revolutions per second.   We see that no appreciable
error has been introduced by neglecting the change in the
density and the partial volumes produced by pressure.

Before leaving the consideration of the pressure gra-
dient in the tube, it must be pointed out that the trans-
ference number determined in these experiments, is the trans-
ference number which exists when the solution is actually un-
der 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.

The Effect of the Dissolved Iodine on the Results:

In the case of the alkali iodides one percent 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 I_3 ion [1].

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[1]
   For data on the mobility of the $\bar{I_3}$ ion see Burgess &
     Chapman, J. Chem. Soc. Trans. 85, 1305, 1904, Bray &
     Mackay, Journ. Amer. Chem. Soc.

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[1] The most satisfactory data for comparison are the values determined by Washburn[2] 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 1.0 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 infinite dilution, calculated from conductivity data, are also given in the table, and finally,

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1)
See McBain(Proc.Wash.Adad.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.

2)
Washburn, Tech.Quart.21, 164, 1908, Journ.Amer.Chem.Soc.

Buchböck, Z. physik.Chem.55, 563, 1906.   31, 322, 1909

values obtained for $\frac{N}{10}$KI and $\frac{N}{10}$NaI by Dennison[1] using the method of Dennison and Steele and a value by Bein[2] for $\frac{N}{20}$KI. This last is the only available datum for these iodides obtained by the Hittorf method without the use of membranes.

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1)

Dennison.Trans.Faraday Soc. 5, 165, 1909. It has been shown by Lewis J,Am.Chem.Soc. 32, 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 Zt. phys. Chem. 27, 1, 1898.

TABLE V.

Transference Number of the Anion.

Halide of	Iodide centri-fugal	Chloride Washburn Buchböck	Iodide infinite dilution+	Chloride infinite dilution+	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	0.662		
H	0.184	0.160*	0.174	0.172		

*

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 appears to have been taken from Kohlrausch's tables, but it is probably considerably too high. For HCl, 0.97 molal, Reisenfeld u. Reinhold.(Zts.f.Phys.Chem.68, 440 1909) obtain the value 0.155, and Hopfgartner (Zts.phys.Chem. 25, 115, 1898), obtains 0.159 for 0.9 molal HCl.

+ These values for the transference number at infinite dilution were calculated from the latest conductivity data of Kohlrausch, Zt. f. Electrochem. 13, 333, 1907.

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 [1], 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 equation 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

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[1]
  Riensenfeld u. Reinhold.Zts.f.phys.Chem.68, 440, 1909.

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 rota-
ting apparatus may have general interest. A distinctive
feature of the apparatus was the method of driving the ro-
tator as a "spinning top", which had not been specially
balanced and which was hung below its fixed point of sup-
port. A simple arrangement of cords was devised for steady-
ing the shaft of the rotating top and preventing precession-
al 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 solu-
tions 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 deri-

vation 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.

The writer desires to express his gratitude to Professor A. A. Noyes, the Director of the Research Laboratory, whose interest and support made possible the completion of this research. Thanks are also due to Professor Elihu Thomson and Dr. Sanford A. Moss of the General Electric Company, through whose kind offices was loaned the steam turbine used in this investigation. The writer also had the benefit of Dr. Moss's extensive experience with high-speed rotation, and is indebted to Professor George B. Haven of the Institute for his assistance in checking a large number of calculations of machine design which were made before the final apparatus was constructed.

The construction of the apparatus was made with the help of two grants of money from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences. The Chemical Department of the Institute was also very generous in its support of this costly research.