*Iridium.*—The atomic weight of iridium has been determined by Holzmann[1] by reduction of ammonium chloroiridiate in a current of hydrogen. The following weights are reduced to the vacuum standard. H = 1.008. N = 14.01. Cl = 35.46.

| Weight $(NH_4)_2IrCl_6$. | Weight Ir. | At. wt. Ir. |
|---|---|---|
| 1.09292 | 0.47809 | 193.50 |
| 1.15060 | 0.50299 | 193.27 |
| 0.80293 | 0.35126 | 193.52 |
| 0.78021 | 0.34119 | 193.39 |
| | | Mean, 193.42 |

Guye[2] compares critically the various methods employed in atomic weight investigations, and pleads for a more systematic attack on the problem from many quarters. Guareschi[3] calls attention to the universal presence of bromine in compounds of chlorine and iodine. Several articles have appeared dealing with the relations between the different atomic weights.[4]

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## THE ACCELERATION OF ELECTRICAL CONDUCTORS.

By Richard C. Tolman, Earl W. Osgerby and T. Dale Stewart.

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CONTENTS.



### PART I. ACCELERATED ELECTROLYTES.

(Experimental Work Performed in the Chemical Laboratory of the University of Cincinnati by R. C. Tolman and E. W. Osgerby.)

### 1. Introduction.

The force of gravity has been found to produce a difference in electrical potential between the two ends of a vertical tube of salt solu-

[1] *Sitzungsb., Phys.-med. Soz. Erlangen,* 44, 84 (1912).

[2] *J. chim. phys.,* 11, 275 (1913).

[3] *Atti accad. sci. Torino,* 48, 128 (1913).

[4] Bilecki, *Z. physik. Chem.,* 82, 249; Borodovskii, *Chem. Ztg.,* 36, 198; Büry, *Z. physik. Chem.,* 80, 381; Dambier, *J. chim. phys.,* 11, 260; Guye, *Ibid.,* 267; Feilmann, *Chem. News,* 107, 15; Katayama, *Sci. Rep'ts Tohoku Imp. Univ. Sendai,* 1, 171; Loring, *Chem. News,* 107, 193; 108, 95; Moir, *J. Chem. Met. Soc. S. Africa,* 13, 544; Wilde, *Chem. News,* 108, 52.

tion.[1] This difference in potential evidently arises from the unequal weights of the positive and negative carriers of electricity in the solution. Thus the lower end of a tube of potassium iodide solution becomes negatively charged, since the negative iodide ions are heavier than the positive potassium ions.

In a similar way we should expect a tube of solution, when subjected to *acceleration*, to show a difference in potential between the two ends. For example, the rear end of a tube of potassium iodide solution should show a negative charge as long as the tube is being accelerated.

The purpose of Part I of this article is to describe some measurements made on accelerated solutions of potassium, sodium and lithium iodides, and to show that the results obtained are in satisfactory agreement with those predicted on a theoretical basis. In Part II of the article we shall apply similar theoretical considerations to the case of accelerated metals and describe the progress that has been made towards an experimental solution of the problem.

## 2. The Theory of an Accelerated Solution.

If a tube of liquid which has the density $d$ grams per cubic centimeter be given an acceleration $a$, it is evident that the force acting on any cubic centimeter of the liquid must be $f = da$ in order to produce the acceleration. Since this force is transmitted to the cubic centimeter in question by the surrounding liquid, it is evident that this space might be filled with a cubic centimeter of any other material without changing the magnitude of the force. Hence for a solution, the force acting on one equivalent of solute during acceleration would be $A\bar{v}da$, where A is the equivalent weight of the solute, $\bar{v}$ its partial specific volume, $d$ the density of the solution and $a$ the acceleration of the solution as a whole. We shall call this force, whose magnitude depends merely on the displaced volume, the *buoyant force* acting on the solute.

If the solute in question carries an electrical charge there may be an additional *electrical force* acting on the solute. If F is the charge in coulombs carried by one equivalent, the electrical force acting on each equivalent of solute will be $10^7 F\, dE/dl$ dynes where $dE/dl$ is the potential gradient in which the solute finds itself.

In general, besides the above forces, there will be a *frictional force* acting on each equivalent of dissolved substance. The fact that Ohm's law holds for electrolytes shows that for ionic solutes this frictional force is proportional to the velocity of the ionic substance through the rest of the solution. If U is the velocity which one equivalent of ionic constituent attains under unit force, then, when the relative velocity of solute and solution is $u$, the frictional force acting will be $u/U$.

[1] See Tolman, THIS JOURNAL, 33, 121 (1911), for a review of the work in this field.

Consider now, a tube filled with a solution of potassium iodide. The tube is provided at the two ends with platinum electrodes and a small amount of iodine is also dissolved in the solution so that the electric current will enter and leave the solution at anode and cathode according to the reactions:

$$\oplus + \dot{\bar{I}} = {}^1/_2 I_2 \qquad\qquad {}^1/_2 I_2 = \bar{I} + \oplus$$

An external connection is made between the two electrodes through a galvanometer.

Let $l$ be the distance between the electrodes,

$q$ the uniform cross section of the tube,

$a$ the acceleration of the tube (in the direction of the line connecting the electrodes),

$d$ the density of the solution,

C its concentration in equivalents per cc.,

$\bar{v}_K$, $\bar{v}_I$, $\bar{v}_{KI}$ and $\bar{v}_{I_2}$ the partial specific volumes of the respective solutes,

K, I, KI and $I_2$ their atomic or molecular weights,

$U_K$ and $U_I$ the velocities which the positive and negative ion constituents attain in a stationary solution when acted on by unit force per equivalent weight of ion,

$n_c = \dfrac{U_K}{U_K + U_I}$ the transference number of the cation,

$u_K$ and $u_I$ the velocities with which the positive and negative ion constituents are lagging behind the solution as a whole,

**R** the resistance of the solution,

$\mathbf{R}_e$ the resistance of the external circuit,

$I_c$ the current flowing,

$f_K$ the force acting on one equivalent of potassium,

$f_I$ the force acting on one equivalent of iodine.

From the preceding discussion, it is evident that the force $f_K$ acting on each equivalent of potassium must be equal to the sum of the buoyant, electrical and frictional forces, leading to the equation:

$$f_K = K\bar{v}_K da - 10^7 F\frac{E_1}{l} + \frac{u_K}{U_K}$$

where $E_1$ is the difference in potential between portions of the solution in the neighborhood of the two electrodes. Multiplying through by $n_c = \dfrac{U_K}{U_K + U_I}$ we obtain:

$$n_c f_K = n_c K\bar{v}_K da - 10^7 F n_c\frac{E_1}{l} + \frac{u_K}{U_K + U_I} \qquad (1)$$

Similarly for the iodide ion constituent we have:

$$f_I = I\bar{v}_I da + 10^7 F \frac{E_1}{l} + \frac{u_I}{U_I}$$

It should be noted that the electrical force is evidently in the same direction as the other forces for the negative ion and in the opposite direction for the positive ion.

Multiplying through by $(1 - n_c) = \frac{U_I}{U_K + U_I}$ we obtain:

$$(1 - n_c)f_I = (1 - n_c)I\bar{v}_I da + (1 - n_c)10^7 F\frac{E_1}{l} + \frac{u_I}{U_K + U_I} \qquad (2)$$

Subtracting (1) from (2), solving for $E_1$, and simplifying, by putting the sum of the forces acting on one equivalent of the positive and negative ion constituents $(f_K + f_I)$ equal to $f_{KI}$, the force acting on one equivalent of potassium iodide, and further noting that $K\bar{v}_K + I\bar{v}_I = KI\bar{v}_{KI}$, we obtain for $E_1$ the value

$$E_1 = \frac{l}{10^7 F}\{f_I - n_c f_{KI} - I\bar{v}_I da + n_c KI\bar{v}_{KI} da\} - \frac{l}{10^7 F}\frac{(u_I - u_K)}{(U_K + U_I)}. \qquad (3)$$

We shall be interested, however, in the total electromotive force which drives the current through the external resistance of the galvanometer, and to this value of $E_1$, which is merely the potential difference between the portions of solution at the two ends of the tubes, we shall add the electromotive force $E_2$, arising from the potential differences between the electrodes and the solution in their neighborhood. This electromotive force $E_2$ arises from the difference in hydrostatic pressure under which the electrode reactions take place at the two electrodes, and can easily be calculated on thermodynamic grounds.

The difference in hydrostatic pressure at the two ends of the tube is $lda$. The electrode reaction is $\oplus + \bar{I} = {}^1/_2 I_2$ and is accompanied by the volume change $I(\bar{v}_{I_2} - \bar{v}_I)$.

The electromotive force $E_2$ is given by the equation

$$10^7 E_2 F = -I(\bar{v}_{I_2} - \bar{v}_I)lda, \qquad (4)$$

which is obtained by equating the external electrical work obtainable when one Faraday of electricity flows through the solution with the corresponding internal work.

Adding $E_1$ and $E_2$ we obtain an expression for E, the total potential difference between the terminals of the external circuit:

$$E = E_1 + E_2 = \frac{l}{10^7 F}\{f_I - I\bar{v}_{I_2} da - n_c f_{KI} + n_c KI\bar{v}_{KI} da\} - \frac{l(u_I - u_K)}{10^7 F\,(U_K + U_I)} \qquad (5)$$

To simplify we may note that $u_I C q$ is the number of equivalents of iodide crossing any boundary in the solution per second, so that the

current flowing through the solution, $I_c = (u_I - u_K)CqF$. Furthermore, $10^7F(U_I + U_K)CF$ is evidently the specific conductance of the solution, since it is the current which would flow through a unit cube of the solution with unit potential drop. We may write:

$$\frac{l(u_I - u_K)}{10^7F\,(U_I + U_K)} = \frac{l(u_I - u_K)CqF}{10^7F\,(U_I + U_K)CqF} = I_cR \qquad (6)$$

We may also write for E the difference in potential between the two terminals of the external circuit,

$$E = I_cR_e \qquad (7)$$

where $R_e$ is the external resistance.

Substituting equations (6) and (7) in (5) and solving for $I_c$ we obtain

$$I_c = \frac{l}{10^7F(R+R_e)}\{f_I - I\bar{v}_{I_c}da - n_cf_{KI} + n_cKI\bar{v}_{KI}da\}$$

where $I_c$ is the instantaneous value of the current flowing in the circuit. If we multiply through by $dt$ and integrate over a time long enough so that the solution comes to its final steady condition, we may substitute for $\int I_c dt$ the total electricity Q in coulombs which passes, for $\int f_I dt$ the total momentum $Iu$ attained by the iodide ion constituent, $u$ being the final velocity of the tube. Similarly for $\int f_{KI}dt$ we may substitute $KIu$, and for $\int adt$ we may substitute $u$ the final velocity. This leads to the final equation which we shall test:[1]

$$Q = \frac{lu}{10^7F(R+R_e)}\{(1 - v_{I_2}d) - n_cKI(1 - v_{KI}d)\} \qquad (8)$$

### 3. The Apparatus.

The apparatus used by the authors for accelerating electrolytes consisted essentially of a glass tube provided with electrodes and bent to fit the rim of an ordinary bicycle wheel. The tube was filled with electrolyte, the wheel given a sudden acceleration, and the current noted which flowed through a galvanometer placed in the external circuit which connected the two electrodes.

(*a*) *The Glass Tube.*—The apparatus is shown somewhat diagrammatically in Fig. 1. The glass tube $A$ was about two feet in diameter and was provided with platinum electrodes $B$ sealed in at different points.

[1] With regard to the theory which we have here developed for accelerated electrolytic solutions, it should be noted that the same final results could be obtained with somewhat less elaborate calculation if we should first start out by assuming that the electromotive force developed by the acceleration is equal to that which would be developed if the same tube were set up vertically in a gravitational field, the strength of the gravitational field being such that each particle is acted on by the force $ma$ where $m$ is its mass and $a$ the acceleration of the tube. Such a method of considering accelerated electrolytes was used by Colley, *Wied. Ann.*, **17**, 55 (1882).

By closing the stopcock *C* the electrolyte could be given the same acceleration as the tube, while by leaving the stopcock open the liquid could be stirred by the acceleration of the tube. Filling was done through the stopcock *D*. The tube was fastened to the rim of the wheel by electric tape. The circumference at the centre line of the tube was 207.3 cm., the distance between the electrodes that were furthest apart 190.8 cm., and between the nearest electrodes 66.4 cm.

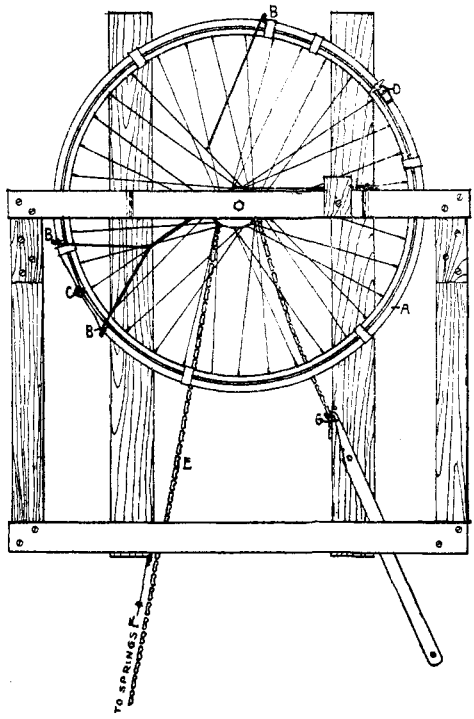

Fig. 1.

(*b*) *The Wheel.*—The wheel was an ordinary, metal rimmed, rear bicycle wheel with sprocket and coaster brake. The sprocket chain *E* passed from a pair of heavy springs *F* around the sprocket to the trigger *G*. The springs could be elongated by "winding up" the wheel and the trigger inserted in the desired link. By releasing the trigger the wheel could be accelerated and later brought to rest, with the coaster brake, by pulling back the free end of the chain. To keep the chain in position a small pull was always kept on its free end by weights attached to a cord which passed over a pulley.

(*c*) *The Springs.*—Two springs were used, connected in parallel. They were close springs, $17\frac{1}{2}''$ long, made of $\frac{1}{4}''$ wire. With the help of a turnbuckle their extension could be adjusted to any desired amount, which was always measured.

(*d*) *The Electrical Connections.*—Connection with the galvanometer was made by small size flexible electric cords, which led from the electrodes to the hub of the wheel, and then passed over suitably placed pulleys to the connections of the galvanometer. Enough slack was allowed so that the cords could wind up on the hub when the wheel was revolving. This slack was kept taut by a suitable weight. It may be specially noted that this method of connection introduces no sliding contacts. Later references will be made to this important point.

(*e*) *The Galvanometer.*—The galvanometer was a Leeds and Northrup, Type H, with a resistance of about 1300 ohms. It was mounted on a

very satisfactory stone pier and showed *absolutely no motion* unless current was passed. It proved much more satisfactory than a suspended magnet galvanometer of presumably greater sensitiveness but much less stability. It was connected directly in series with the electrodes, and was observed with a telescope, at about 1.15 meters distance.

(*f*) *The Speed Measuring Device.*—The speed was measured on a revolving drum provided with smoked paper upon which simultaneous marks were made by a pointer driven by a tuning fork of known period and by a pointer actuated through an electric contact which was made once in each revolution of the bicycle wheel.

## 4. The Experimental Procedure.

In the experiments to be described, measurements were made on solutions of potassium, sodium and lithium iodides. The solutions contained per kilogram of water, one mol of the salt and one hundredth of a mol of iodine. The tube was rinsed with the solution before filling. In carrying out the measurements one experimenter observed the galvanometer through the telescope and the other operated the wheel. With each solution a large number of successive accelerations were made.

(*a*) *The Galvanometer Deflections.*—Owing to unavoidable differences in the conditions at the two electrodes, there was generally some current flowing through the galvanometer even when the tube was stationary, and a reading was always made immediately before releasing the trigger. In the record of experiment results this is called the "*Original Deflection*" of the galvanometer.

Upon releasing the trigger there was a sudden change in the galvanometer deflection. In the record of experimental results this is called the "*Galvanometer Throw.*" This "throw" presumably corresponded to the acceleration of the electrolyte, and for a given electrolyte, acceleration, and distance between electrodes it was approximately constant.

The "galvanometer throw" was in general followed by a slower change in deflection which presumably corresponded to an accidental variation in the conditions around the two electrodes produced by the jar of acceleration. In the record of experimental results this is called the "*Secondary Deflection*" of the galvanometer. As might be expected, the "secondary deflection" tended to be large when the "original deflection" was large. In a series of successive runs, the starting and stopping of the tube usually seemed to equalize the variations at the two electrodes and in a gratifying way decrease the size both of the "original" and the "secondary deflections."

In general, there was not much difficulty in distinguishing between the sudden "galvanometer throw," which was always in one direction, and the slower "secondary deflection" which might be in either direction. If the "secondary deflection" happened to be in the same direction as the

"galvanometer throw" they sometimes merged indistinguishably one into the other. If the "secondary deflection" was in the opposite direction to the "galvanometer throw," it made the end point of the "galvanometer throw" advantageously sharp and distinct. In many cases the "secondary deflection" was absent or indistinguishable from the natural return of the galvanometer to its original position. In all other cases the nature of the secondary throw is stated in the record. Almost never did anything happen to make the "throw" of the galvanometer, even for a single acceleration, in the opposite direction to that predicted on the expectation that the heavy iodide ion would make the rear electrode negative. As complete experimental data are presented in the next section of the article, the reader can judge for himself as to the reality and magnitude of the effect reported.

Under favorable circumstances an effect could, of course, also be observed on suddenly stopping the wheel. This was not, however, suitable for purposes of measurement since, owing to the variable "secondary deflection", the galvanometer was obviously not very stationary when the wheel had to be stopped.

(*b*) *The Standardization of the Galvanometer.*—Since the period of the galvanometer was long compared with the time necessary for accelerating the tube, it was assumed that the "galvanometer throw" was proportional to the quantity of electricity whose measurement was desired. The galvanometer was calibrated by discharging a standard solenoid through it, placing in series varying amounts of resistance to correspond to the varying resistances of the different solutions. Results of the standardization are given in Table I; the value for infinite resistance was obtained by discharging a condenser through the galvanometer. Measurements

TABLE I.

*Standardization of the Galvanometer.*

May 27 and 28, 1913.

| Resistance in series with galvanometer. Ohms. | Quantity of electricity discharged through galvanometer. Coulombs $\times 10^{-8}$. | Galvanometer throw. Millimeters. | Sensitiveness. Coulombs $\times 10^{-8}$ per millimeter. |
|---|---|---|---|
| 15 | 25.65 | 29.0 | 0.885 |
| 315 | 20.95 | 27.6 | 0.759 |
| 515 | 18.66 | 26.6 | 0.701 |
| 715 | 16.82 | 25.5 | 0.660 |
| 1015 | 14.66 | 24.2 | 0.605 |
| 1215 | 13.50 | 23.3 | 0.579 |
| 1415 | 12.50 | 22.6 | 0.553 |
| 1515 | 12.07 | 22.1 | 0.546 |
| 1715 | 11.27 | 21.5 | 0.524 |
| 1915 | 10.57 | 20.9 | 0.506 |
| 2015 | 10.26 | 20.4 | 0.503 |
| $\infty$ | 10.19 | 39.7 | 0.257 |

were also made which showed that the galvanometer throw, with a given resistance in the circuit, was at least approximately proportional to the quantity of electricity discharged.

(*c*) *Determination of the Speed.*—Corresponding to each series of accelerations, and in many cases both before and after the series, a number of determinations were made of the speed attained by the wheel with the same extension of the springs as that employed for the electrical measurements. It was found in general that the speed attained was always

TABLE II.

*Standardization of Tuning Fork.*

(About May 4, 1912)..... 135 1/2 134 1/2 131 133 130 vibrations per second
(May 29, 1912)..... 133 1/4 134 132 128 1/4 134 1/4 vibrations per second

Average, 1 second = 132.6 vibrations.
1 vibration = $7.55 \times 10^{-8}$ seconds.

TABLE III.

*Standardization of Spring.*

| Date. | Extension of spring. | No. tuning fork vibr., 1st revol. | No. tuning fork vibr., 2nd revol. |
|---|---|---|---|
| May 23, 1912..... | 5 3/8 | 21 | 21 1/4 |
| | 5 3/8 | 20 1/2 | .. |
| | 5 3/8 | 20 3/4 | 21 |
| | 5 3/8 | 21 | 21 |
| May 27, 1912..... | 5 3/8 | 20 1/2 | 20 3/4 |
| | 5 3/8 | 20 1/2 | 20 1/2 |
| | 5 3/8 | 20 1/2 | 20 1/2 |
| | 5 3/8 | 20 1/2 | 20 1/2 |
| May 28, 1912..... | 5 3/8 | 21 | 21 |
| | 5 3/8 | 20 1/2 | 21 |
| | 5 3/8 | 20 3/4 | 21 |
| May 30, 1912..... | 5 3/8 | 20 1/2 | 21 |
| | 5 3/8 | 20 3/4 | 21 |
| | 5 3/8 | 20 1/2 | .. |
| May 27..... | 2 3/4 | 35 1/2 | .. |
| | 3 | 33 1/4 | .. |
| | 2 1/4 | 41 1/4 | 44 3/4 |
| | 2 1/4 | 42 | 46 |
| | 2 1/4 | 42 1/4 | 46 1/2 |
| | 2 1/4 | 41 3/4 | 45 |
| May 28..... | 2 1/4 | 44 1/2 | 50 1/2 |
| | 2 1/4 | 43 3/4 | 47 |
| | 2 1/4 | 45 | .. |
| May 31..... | 6 | 19 | 19 |
| | 7 | 16 1/4 | 16 1/2 |
| | 7 | 16 1/4 | 16 1/2 |
| | 7 | 16 1/2 | 16 1/2 |

Extension of spring, 2 1/4", 3.09 revolutions per second.
Extension of spring, 5 3/8", 6.42 revolutions per second.
Extension of spring, 7", 8.11 revolutions per second.

closely the same when the spring was given the same extension. In all the runs the "wound up" wheel was so set as to make nearly a complete revolution before making the first electrical contact, with its corresponding mark on the cheimograph. By counting the number of tuning fork vibrations between marks, it was found in general that the first of the successive revolutions was the fastest, although the speed usually fell off but slowly. For our calculations we shall consider the maximum speed as that obtained from the first recorded revolution.

The tuning fork was standardized against a seconds pendulum belonging to the Physics Department of the University of Cincinnati and the data therefore is presented in Table II. Table III presents the data for the speed attained with different extensions of the spring.

## 5. The Experimental Results.

The main part of the experimental work consisted in a series of measurements with molal solutions of potassium, sodium and lithium iodides, all made with the same deflection of the springs $5^3/_8''$, and with the pair of electrodes which were furthest apart (190.8 cm.). *All* of these measurements are given in Table IV, V, and VI, and the only measurements excluded from the final average are those enclosed by brackets in these tables. It seems desirable to present this complete statement of the data, so that there shall be no question as to the absolute reality of the very minute effect which was measured. The final average deflections obtained from these tables can now be compared with the values that can be predicted from equation (8).[1]

(*a*) *Comparison of Deflections with Values Predicted from Equation (8).*— Equation (8) gives us for the number of coulombs of electricity, Q, sent through the external circuit when a column of a solution of alkali iodide, AI, is accelerated,

$$Q = \frac{lu}{10^7 F(R+R_e)} \{ I(1 - \bar{v}_{I_2} d) - n_c AI(1 - \bar{v}_{AI} d) \}$$

where ($l$) is the distance between the electrodes in centimeters, $u$ is the final velocity in centimeters per second attained by the column of solution (equals 6.42 revolutions per second $\times$ 207.3 cm., the circumference of the wheel), F the value of the faraday in coulombs (96540), $R + R_e$ the total resistance in the circuit in ohms (equals the resistance of the solution + 1315 ohms for the galvanometer), I the atomic weight of iodine, $\bar{v}_{I_2}$ the partial specific volume of iodine in the solution, $d$ the density of the solution, $n_c$ the transference number of the cation, AI the molecular weight of the iodide, and $\bar{v}_{AI}$ the partial specific volume of the iodide in the

[1] In the calculations no allowance has been made for the effect of the slight change in temperature which would be produced at the rear electrode by the compression of the liquid incident upon acceleration.

TABLE IV.

*Measurements on Potassium Iodide.*

Solution, 1 kilo water, 1 mol. KI, 1/100 mol $I_2$.
Distance between electrodes, 190.8 cm. Resistance, 1110 ohms.
Extension of spring, $5^3/_8''$ = 6.42 revolutions per second.

| Date. | Original deflection in mm. | Galvanometer throw in mm. | Remarks. |
|---|---|---|---|
| May 23, 1912, A.M..... | — 3 | (0.7–1.2) | Throw increased from 0.7 to 1.2 mm. |
| | — 3 | .. | Throw merged into a deflection 3–4 mm. |
| | — 3 | 0.5 | Secondary, —1 1/2 mm. |
| | .. | .. | Solution stirred. |
| | — 2 1/2 | 0.9 | |
| | — 1 1/2 | 1.0 | Difficult to distinguish from secondary of 2 more in same direction. |
| | 0 | 0.9–1.0 | |
| | 0 | .. | Throw merged into a deflection of 4 mm. |
| May 23, 1912, P.M..... | 13 | 0.8–0.9 | |
| | 9 | 0.9 | |
| | 9 | 0.7 | |
| | 7 | 0.9 | |
| | 12 | (0.3) | Quick secondary, —7 mm. |
| | 5 | 0.9 | |
| | 1 | 0.9 | |
| | 6 | 1.2 | |
| | 6 | 0.9 | |
| | 9 | 0.9 | |
| | 9 | 1.0 | |
| | 13 | 1.1 | |
| | 10 | (2.0) | Continued to increase a little, galv. throw and secondary not distinguishable. |
| | .. | .. | Solution stirred. |
| | 3 | .. | Throw merged into a deflection of 3 mm. |
| | .. | .. | Solution stirred. |
| | 3 1/2 | 0.9 | Difficult to distinguish from a secondary of 4–5 mm. more in same direction. |
| | .. | .. | Solution stirred. |
| | 3 | 0.9 | Secondary, —2 mm. |
| | 3 | 0.8 | Secondary, —2 mm. |
| | 5 | 1.2 | Continued to increase a little. |
| | 8 | 1.0 | |
| | 9 | 0.8 | Secondary, —3 to —4 mm. |
| | 7 | 0.9 | Secondary, —3 mm. |
| Average galvanometer throw..... | | 0.91 mm. | |

TABLE V.

*Measurements on Sodium Iodide.*

Solution, 1 kilo water, 1 mol NaI, 1/100 mol $I_2$.
Distance between electrodes, 190.8 cm. Resistance, 1370 ohms.
Extension of spring, $5^3/_8$" = 6.42 revolutions per second.

| Date. | Original deflection in mm. | Galvanometer. throw in mm. | Remarks. |
|---|---|---|---|
| May 27, 1912, A.M..... | 2 | 0.9 | |
| | — 4 | 1.1 | Difficult to distinguish from a secondary 1 more in same direction. |
| | — 5 | (1.5) | Probably partly secondary. |
| | — 9 | 1.0 | Secondary, 5 mm. |
| | .. | .. | Solution stirred. |
| | — 3 | 0.7 | |
| | — 3 | 1.0 | |
| | — 2 | 1.0 | Slight secondary in same direction. |
| | 0 | 1.0 | |
| | 8 | .. | More or less permanent deflection of 12 mm. |
| | 3 | 0.9 | Large negative secondary. |
| | — 3 | 0.8–0.9 | Large negative secondary. |
| | .. | .. | Solution stirred. |
| | 0 | 0.9–1.0 | Large negative secondary. |
| | — 5 | 0.8 | Small, slow negative secondary. |
| | — 6 | 0.9 | |
| | $^1/_2$ | 0.95 | Small negative secondary. |
| | — 2 | 0.9 | |
| | — 2 | 1.0 | |
| | — 1 | 1.0 | |
| | 0 | 1.0 | Secondary, —1 mm. |
| | — 1 | 0.95 | Slight negative secondary. |
| | — 3 | 0.9–0.95 | |
| | — 4 | 0.9–0.95 | |
| | — 3 | 0.9 | Slight negative secondary. |
| | — 5 | 0.8 | |
| | .. | .. | Solution stirred. |
| | — 3 | 0.5 | Small negative secondary after wheel stopped. |
| | .. | .. | Solution stirred. |
| | — 3 | 1.0 | |
| | — 3 | 0.9 | |
| | — $2^1/_2$ | 1.0 | Secondary, 0.1 mm. |
| May 27, 1912, P.M..... | —14 | 0.8 | Difficult to distinguish from secondary 5–6 more in same direction. |
| | .. | .. | Solution stirred. |
| | —12 | 0.9 | Small secondary in same direction. |
| | .. | .. | Solution stirred. |
| | — 9 | 0.8–0.9 | Secondary, —$^1/_2$ mm. |
| | .. | .. | Solution stirred. |
| | — 4 | 0.95 | |
| | .. | .. | Solution, stirred. |
| | — 4 | 0.9 | Secondary, —$^3/_4$ mm. |
| | .. | .. | Solution stirred. |
| | — 9 | 1.0 | Slight secondary in same direction. |
| May 28, 1912, A.M..... | —29 | 0.85 | Followed after a pause by a secondary in same direction. |
| | —23 | 0.95 | |
| | —22 | 0.95 | |
| Average galvanometer throw..... | | 0.91 mm. | |

TABLE VI.

*Measurements on Lithium Iodide.*

Solution, 1 kilo water, 1 mol LiI, 1/100 mol $I_2$.
Distance between electrodes, 190.8 cm. Resistance, 1900 ohms.
Extension of springs, $5^3/_8''$ = 6.42 revolutions per second.

| Date. | Original deflection in mm. | Galvanometer throw in mm. | Remarks. |
|---|---|---|---|
| May 31, 1912, P.M..... | — 6 | (8–10) | One big throw. |
| | — 1 | 1.1 | Secondary, $^1/_2$ mm. |
| | — 3 | 1.0 | |
| | — 6 | 1.1 | |
| | — 6 | 0.95 | |
| | — 7 | 0.95 | |
| | — 7 | 0.95 | |
| | — 6 | 1.0 | |
| | — 5 | 1.0 | |
| | — 5 | 1.0 | Slight negative secondary. |
| | — 5 | 0.9 | Secondary, —1 mm. |
| | — 6 | 0.9 | Secondary, —1 mm. |
| | — 6 | 1.0 | Secondary, —$1^1/_2$ mm. |
| | — 7 | 1.0 | Secondary, —1 mm. |
| | — 8 | 1.0 | Secondary, —$^1/_2$ mm. |
| | — 8 | 1.0 | |
| | — 8 | 1.0 | Secondary, —$^1/_2$ mm. |
| | — 9 | 1.05 | |
| | —12 | 1.0 | Secondary, —1 mm |
| | —12 | 0.9 | |
| Average galvanometer throw..... | | 0.99 mm. | |

solution. The following table (VII) presents the values of the above quantities used in the computations and the values of Q thus calculated. The densities, specific volumes, and transference numbers employed are transcribed from an article[1] on "The Electromotive Force Produced in Solutions by Centrifugal Action" by one of the present authors.

TABLE VII.

| Solution. | $l$. | $v$. | $R + R_e$. | I. | $\bar{v}_{I_2}$. | $d$. | $n_c$. |
|---|---|---|---|---|---|---|---|
| KI..... | 190.8 | 1330 | 2425 | 126.9 | 0.2376 | 1.115 | 0.486 |
| NaI..... | 190.8 | 1330 | 2685 | 126.9 | 0.2376 | 1.110 | 0.385 |
| LiI..... | 190.8 | 1330 | 3215 | 126.9 | 0.2376 | 1.096 | 0.268 |

| Solution. | $AI$. | $\bar{v}_{AI}$. | $Q$. | $Q/D$. | Deflection. Calc. | Deflection. Obs. |
|---|---|---|---|---|---|---|
| KI..... | 166.0 | 0.284 | $0.412 \times 10^{-8}$ | $0.593 \times 10^{-8}$ | 0.7 mm. | 0.9 mm. |
| NaI..... | 149.9 | 0.244 | $0.511 \times 10^{-8}$ | $0.559 \times 10^{-8}$ | 0.9 mm. | 0.9 mm. |
| LiI..... | 133.9 | 0.2605 | $0.557 \times 10^{-8}$ | $0.507 \times 10^{-8}$ | 1.1 mm. | 1.0 mm. |

In the next to the last column of the table we have put values of the expected deflection as calculated from the values of Q, making use of

[1] Tolman, THIS JOURNAL, 33, 121 (1911).

values for the sensitiveness of the galvanometer Q/D, obtained by interpolation from Table I for the particular resistances in series with the galvanometer. These values may be compared with the observed values as given in the last column. We feel that the agreement is within the limit of experimental error, when we consider the difficulties of rapidly estimating tenths of a small scale division. The greatest deviation is in the case of KI solution, the calculated value being 0.7 mm. and the observed value 0.9 mm. The deviation in this direction might be partly due to a tendency to estimate as 0.9 of a division anything slightly under 1 division.

(*b*) *Change in Galvanometer Throw with Speed of Apparatus.*—Further evidence of the correctness of our theory of accelerated conductors may be obtained from the fact that the magnitude of the galvanometer throw was found to increase with the magnitude of the acceleration. According to our theory, the galvanometer throw should be directly proportional to the final speed attained by the wheel. In the case of the *potassium iodide* solution only one isolated acceleration was made with any extension of the spring other than $5^3/_8''$. In the case of the *sodium iodide* solution, eight accelerations were made with an extension of $2^1/_4''$, corresponding to a velocity of 3.09 revolutions per second (see Table III). The average of the eight galvanometer throw for the speed 3.09 was 0.35 mm., while the average galvanometer throw for the speed 6.42 was 0.91 mm.(see Table V), figures which certainly check our theory within the experimental error.

In the case of the *lithium iodide* solution, one isolated measurement was made with a spring extension of about 8″, and nine measurements were made with a spring extension of 7″, corresponding to a velocity of 8.11 revolutions per second (see Table III). The average of the nine galvanometer throws for the speed 8.11 was 1.17 mm., while the average galvanometer throw for the speed 6.42 was 0.99 mm. (see Table VI), figures which again check our theory with the experimental error.

(*c*) *Change in Galvanometer Throw with Distance between the Electrodes.*—Further evidence of the correctness of our theory of these acceleration effects is given by the fact that the galvanometer throw became smaller when the distance between the electrodes was smaller. Both with the sodium iodide and the lithium iodide solution, accelerations were made with $5^3/_8''$ extension of the spring and the pair of electrodes which were nearest together (66.4 cm.). These measurements were not as satisfactory as the other measurements, both the "original deflection" and the "secondary deflection" being oftentimes very large. This was perhaps partly due to the fact that the two electrodes which were connected by the shortest length of conducting solution were in reality much further apart on the wheel, as will be seen from the diagram, than the pair

of electrodes usually employed which were separated merely by a stopcock. This might tend to increase the difference in the conditions around the electrodes.

With the sodium iodide solution 52 accelerations were made. Owing to large "secondary deflections" or other reasons, the values of the measurements were discarded in 17 cases; the remaining 34 measurements gave an average "galvanometer throw" of 0.26 mm.

Allowing for the smaller resistance of the column of solution (515 ohms) when the electrodes nearest together (66.4 cm.) were used, it is possible to calculate the expected galvanometer throw from the value (0.91 mm.) obtained when the electrodes were furthest apart (190.8 cm.), and the resistance of the solution was 1370 ohms. The calculated value is 0.37 mm. which agrees with the above within the probable experimental error. (The change in sensitiveness of the galvanometer with resistance has been allowed for with the data given in Table I.)

With the lithium iodide solution 13 accelerations were made with the electrodes nearest together. The values of the measurements were discarded in 5 cases, the average value of the remaining 8 galvanometer throws being 0.32 mm. The resistance of the short column of LiI solution was 720 ohms.

The expected value of the galvanometer throw, calculated on the basis of a throw of 0.99 mm. with the electrodes furthest apart would have been 0.42 mm., which is again a check within the probable experimental error.

In concluding our account of this experimental work, it should be noted that when the tube of solution was replaced by a single turn of copper wire absolutely no effects were observable in the galvanometer on acceleration, showing that the effects were not of accidental origin, and that the winding upon the hub of the wheel of the flexible connecting wire introduced no error.

## 6. Conclusions.

The data presented in the preceding sections afford conclusive proof that potential differences are developed at the ends of a column of accelerated electrolyte, and, within the necessarily large experimental error, check the requirements of our theory of accelerated solutions. Previous to these determinations, the only work reported on accelerated electrolytes was an experiment of Colley[1] made in 1882 by dropping a tube of cadmium iodide solution. His result was also in approximate agreement with theory.

It might seem as though there were no necessity for carrying out these measurements of the very small potential differences which can be produced in accelerated solutions, since the similar electromotive forces that are produced in solutions by the action of obtainable centrifugal forces

[1] Colley, *Wied. Ann.*, **17**, 55 (1882).

are much larger and have already been thoroughly investigated.[1] The measurements were made, however, with the view of extending such investigations to the much more difficult problem of metallic conductors where, as we shall see, the acceleration method is far better adapted than the centrifugal method. Hence it seemed desirable to obtain some preliminary experience with accelerated electrolytes and get, if possible, a check on the general theory of accelerated conductors.

## PART II. METALLIC CONDUCTORS.

(Experimental work performed in the Chemical Laboratory of the University of California by R. C. Tolman and T. D. Stewart.)

### 1. Introduction.

At the present time, we have at our command much less definite information concerning the physical-chemical structure of metallic conductors than we have for electrolytes. There have, however, long been theoretical reasons for supposing that the current is carried at least in *solid* metals largely by the negative electron, and of late years there has been increasing experimental evidence in support of such a hypothesis.[2]

If this hypothesis is correct, the carrier of electricity in a metal should have a mass about 1/1800 of that of the hydrogen atom, and it should be possible to obtain evidence of its presence either by a centrifugal method, in which a measurement would be made of the difference in electrical potential between the axis and rim of a rotating metallic wheel, or by an acceleration method similar to the one which we have just described for electrolytic conductors.

The centrifugal method, which is quite successful for electrolytic conductors, is not at all well adapted for metals. In the case of rotating tubes of electrolyte, electrical connection with both the inner and outer electrodes can be made by wires which lead to central mercury cups and connection with these cups can be made to the measuring apparatus. In the case of a rotating disk of metal, however, if a wire connection be taken from the periphery to a central mercury cup, the electromotive force set up in this wire will obviously be just equal and opposite in direction to the potential difference between the periphery and axis of the disk and hence completely neutralize the desired effect.[3] For this reason it is necessary to make connection with the periphery of the wheel with some form of rubbing contact and this will itself produce large and variable electromotive forces. Experiments with a rotating aluminum disk were made by Nichols[4] who found that the variable electromotive forces produced by the

[1] Tolman, THIS JOURNAL, **33**, 121 (1911).

[2] See, for example, Richardson, *Science*, **38**, 57 (1913). Kraus, THIS JOURNAL, **35**, 1732 (1913).

[3] In the case of the electrolyte the electromotive force set up in the wire connection is of course negligible in comparison with that set up in the tube of electrolyte.

[4] Nichols, *Physik. Z.*, **7**, 640 (1906).

contacts were relatively very large, although he was able to conclude from his experiments that the mass of the carrier of electricity in metals must at least be smaller than the mass of the hydrogen atom.

The acceleration method seems much more suitable for metals, and the authors have carried out measurements by this method which show that the mass of the carrier in metals is probably less than 1/200 that of the hydrogen atom. The authors believe, however, that it will be quite possible to modify further the apparatus so as to detect the still smaller effects which would be produced if the carrier is really the electron with a mass 1/1800 that of the hydrogen atom.

## 2. The Apparatus.

The accompanying photograph, Fig. 2, shows the main features of the apparatus which we employed. It consists essentially of an aluminum alloy (Macadamite) disk $11\frac{1}{2}''$ in diameter with a groove cut in the rim $\frac{5}{8}''$ wide and $\frac{3}{4}''$ deep. In this groove was wound 2407 feet of No. 28 silk insulated copper wire making connection at the two ends with the

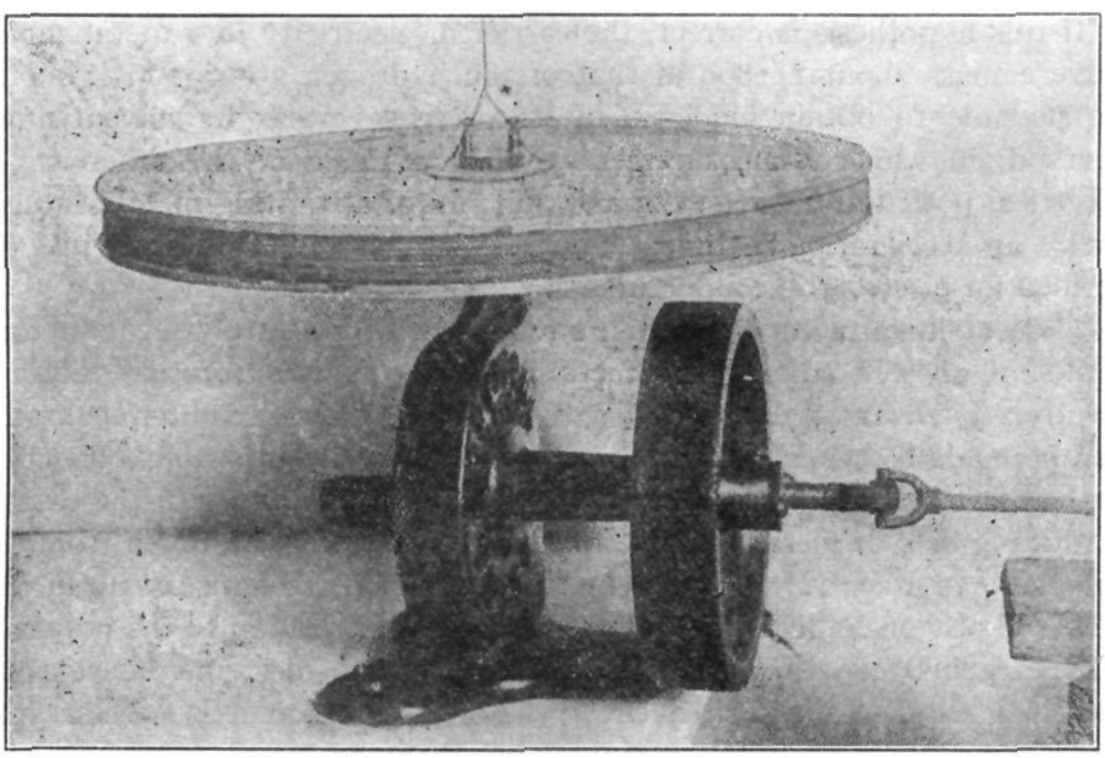

Fig. 2.

insulated binding posts seen at the centre of the disk. The insulation between the wire and the disk was found to be entirely satisfactory, and the lengths of the wire, as determined by weight and by resistance, were found to be the same, showing satisfactory insulation between the different turns of wire.

The disk was mounted on a vertical shaft, connected by enclosed spiral gears (ratio of 3 to 29) with the horizontal shaft carrying the pulley seen

at the right of the picture. This pulley was belted direct to a two horse power motor. It was found necessary to make the pulley out of bronze since the magnetic effect of a rotating iron pulley produced large and fluctuating electromotive forces in the coil on the disk, because of the very large number of turns of wire.

A brake, not shown in the figure, was arranged for bringing the disk quickly to rest. It functioned by squeezing the rim of the wheel between leather pads and would bring the disk to rest almost instantaneously from a speed of 5000 revolutions per minute.

To measure the speed of rotation the apparatus was made to drive a magneto, which was placed about eight feet away in order to minimize magnetic disturbances. This magneto was driven by the small shaft leading off to the right of the picture. The voltage of the magneto, which was approximately proportional to the speed, was read on a voltmeter placed conveniently near to the operator of the apparatus.

For the apparently difficult problem of making, between the rotating coil and the galvanometer, an electrical connection which would not itself introduce appreciable electromotive forces, a surprisingly simple and satisfactory solution was eventually found. The connection was made through fine silk insulated wires which led directly up from the binding posts and were allowed to twist up when the apparatus started. In order to allow for the shortening produced by the twisting, the wires were led over a pulley providing sufficient slack which was kept tight by a small weight The wires went through a hole in the ceiling to the ceiling of the room above, and this allowed for enough twisting so that two or three runs could be made before the wires broke. The insulation between the twisted wires was found to be entirely satisfactory, and with the galvanometer employed we could not find that any electromotive force was produced by the twisting.

The galvanometer was connected directly in series with the rotating coil through the above connections. It was a Leeds and Northrup high sensibility galvanometer, having a resistance of 36 ohms and was used without damping coils. The galvanometer was mounted on concrete masonry and showed no observable deflections when directly short circuited. Its sensitiveness as a ballistic galvanometer was found by discharging the secondary of a standard solenoid through it, having in the circuit the same total resistance as with the coil of wire on the disk. The distance from the galvanometer mirror to the scale was about fifty inches and the sensitiveness approximately $2.1 \times 10^{-8}$ coulombs per 1 mm. throw.

### 3. The Experimental Work.

The experiments consisted in bringing the apparatus to a high speed of rotation, suddenly stopping the disk and observing whether there was any pulse of electricity through the galvanometer.

Even when the wheel was entirely at rest the galvanometer was usually found to be giving small and variable deflections. These deflections were mostly not very rapid, although sometimes there would be sudden jumps, the total range of deflection usually being inside of 1 mm., and often less for long periods of time. It was found that these variable deflections were apparently caused by variations in the magnetic flux through the large number of turns of wire in our coil, these variations being due to nearness to the disturbances of the city of Berkeley. By going about a mile up the canyon back of the university and setting up the same galvanomteer it was found that these effects disappeared. The deflections were not large enough to interfere seriously with our experiments at their present stage of accuracy, but would have to be eliminated before further progress could be made.

Besides these deflections, which were produced by fluctuations in magnetic field, it was found that the slight tipping which could be given to the disk because of the natural looseness of the vertical shaft in its bearings would cut enough lines of force to produce a galvanometer throw of about 5 mm. Even putting on the brake when the wheel was entirely stationary would usually produce tipping enough to cause perhaps as much as a millimeter throw. For this reason we could not expect the galvanometer to remain absolutely stationary when the rotation of the wheel was stopped by the brake, and in fact on stopping the wheel we obtained throws all the way from zero up to 3 or 4 mm. Before further progress can be made these accidental effects will have to be eliminated.

## 4. Results.

From our experiments, however, we think it pretty safe to conclude that on reducing the speed from the neighborhood of 5000 revolutions per minute to zero there was no systematic galvanometer throw greater than 1 mm. which would correspond to $2.1 \times 10^{-8}$ coulombs.

Consider now equation (8), which connects the quantity of electricity delivered, on accelerating an electrolytic conductor, with the total change in velocity, the length of the conductor, the equivalent weights of the carriers, etc. For the case of metallic conductors we may consider that the only mobile carrier is the electron, and may at least temporarily assume that its partial specific volume is small enough to be negligible, which will give the equation the simple form

$$Q = \frac{(l)u}{10^7 F\,(R + R_e)}\, m \qquad (9)$$

where $m$ is the equivalent weight of the electron. Putting $Q = 2.1 \times 10^{-8}$ coulombs (which corresponds to a galvanometer throw of 1 mm.), $l = 73500$ cm. (the total length of the wire), $u = 7100$ cm./sec., (the rim velocity at 5000 r. p. m.), and $R + R_e = 136$ ohms, the total resistance

of the circuit, we obtain for $m$ the approximate value 0.005, showing that the mass of the carrier in metals is probably less than 1/200 that of the hydrogen atom.

### 5. Conclusions.

We believe that these experiments have set a limit for the mass of the carrier in metals considerably lower than any previous experimental work.[1] We see, moreover, no insuperable difficulties in carrying the sensitiveness of our method to a point where the electron, if it really is the carrier of electricity in metals, with a mass 1/1800 that of the hydrogen atom, should produce an appreciable effect. One of our main purposes in giving this brief description of our work on metallic conductors is the hope that we may be able to obtain funds for carrying this research to completion, a consummation which for many years has been the desire of one of the present authors.[2]

A tenfold increase in the accuracy of the observations would apparently be sufficient for the desired purpose, and it seems probable that this could be obtained if we could eliminate the accidental effects produced by uncontrollable variations in the earth's magnetic field and those produced by the small tipping of the disk which unavoidably occurs when the brake is applied. Probably the best way to accomplish this result will be to try to construct efficient screens for cutting out the earth's magnetic field from the apparatus. With the help of such a magnetic screen and some increase in the sensitiveness of the apparatus, which could be obtained by increasing the length of wire on the disk and its rim velocity, as well as obtaining a more sensitive galvanometer arrangement, it should be quite possible to solve the problem.

BERKELEY, CAL.

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## ON THE TRANSITION TEMPERATURES OF THE HYDRATES OF SODIUM CARBONATE AS FIXED POINTS IN THERMOMETRY.

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Recent investigations conducted in this laboratory, and confirmed elsewhere, have shown that the transition temperatures of hydrated crystalline salts provide excellent means for fixing definite points upon

[1] As far as we know, the only quantitative experiments reported in the literature are those of Nichols of which we have already spoken. Maxwell ["Treatise on Electricity and Magnetism," 3d edition (1892), Vol. II, et seq.] and Lodge ["Modern Views of Electricity" 3rd edition (1907), p. 89] have both attempted, without success, to obtain effects dependent on the mechanical momentum which might be associated with the passage of a current of electricity, but give no figures as to the sensitiveness of their methods.

[2] See Tolman, *Science*, **37**, 192 (1913).