ON THE MIGRATION OF IONS DURING ELECTROLYSIS

BY

W. HITTORF

(Poggendorff's *Annalen*, **89,** 177, 1853 ; Ostwald's *Klassiker der Exakten Wissenschaften*, No. 21)

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THE explanation which we now give of the process of electrolysis was first proposed, in its general outlines, by Grotthuss in 1805. According to it, the two ions which are simultaneously set free do not come from the same molecule* of the electrolyte, but belong to different ones—namely, those which are in immediate contact with the electrodes. The other components of the compound from which they separate unite at once with the opposite components of the next adjacent molecules; this process takes place between the opposite components of all adjacent molecules in the interior of the electrolyte, and holds them together.

"I conclude from this," remarks Grotthuss,† "that were it possible to produce in water a galvanic current flowing in a circle, without the introduction of metallic conductors, all water particles lying in this circle would be decomposed and immediately after recombined; whence it follows that this water, although it actually undergoes galvanic decomposition in all of its particles, would nevertheless always remain water."

This conception of electrolysis was so natural that it could not fail to supersede the other more or less far-fetched hypotheses which assumed both liberated ions to arise from the same molecule of the electrolyte. It explained without further assumption, the numerous experiments which H. Davy‡ published soon afterwards on the transference of components to the electrodes.

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* [*For greater clearness the term "atom," used throughout by Hittorf, has been translated "molecule" whenever the concept of molecule is intended.*]

† *Phys. Chem. Forsch.*, p. 123.

‡ *Gilb. Ann.*, **28**, 26.

The tardy appearance of the ions of an electrolyte which is not in direct contact with the poles, and their failure to appear at all when separated from the electrodes by a liquid with which they form an insoluble compound, were excellent proofs of the theory furnished by Davy.

Notwithstanding the clear conception of electrolysis which Grotthuss had up to this point, as indicated in the remark which I have given above in his own words (we easily realize to-day, as is well known, the premise of the conclusion by an induction current), he fell into serious error in attempting to further fathom the phenomenon. He conceived it to be produced as follows: the metals between which the electrolyte is placed are the seat of two forces, which vary inversely as the square of the distance, and which, acting oppositely on the two components, repel the one and attract the other. All physicists who turned their attention to this subject favored this view more or less for a long time; the name of the poles which was given to the immersed metals corresponded to it. Grotthuss was, however, herein so far in advance of others that he considered (contrary to his hypothesis, to be sure) the forces acting on each particle of the electrolyte everywhere equal in the circle, an assumption which, as is known, is correct for the simplest conditions of the experiment.

Faraday was the first to penetrate deeper into the phenomenon. He conceived the cause of it in exactly the reverse manner, and was thereby led to the great discovery of the fundamental electrolytic action of the current, which now forms the basis of all investigations in electrolysis. By means of this change he brought the theory into harmony with Ohm's law, without knowing the latter.

"I conceive," he says, in § 524 of his *Experimental Researches,** "the effects to arise from forces which are *internal,* relative to the matter under decomposition, and not *external,* as they might be considered, if directly dependent on the poles. I suppose that the effects are due to a modification, by the electric current, of the chemical affinity of the particles through or by which that current is passing, giving them the power of acting more forcibly in one direction than in another, and consequently making them travel by a series of successive decom-

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* Pogg. *Ann.*, **32**, 435.

positions and recompositions in opposite directions, and finally causing their expulsion or exclusion at the boundaries of the body under decomposition, in the direction of the current, *and that* in larger or smaller quantities, according as the current is more or less powerful. I think, therefore, it would be more philosophical, and more directly expressive of the facts, to speak of such a body, in relation to the current passing through it, rather than to the poles, as they are usually called, in contact with it; and say that whilst under decomposition, oxygen, chlorine, iodine, acids, etc., are rendered at its negative extremity, and combustibles, metals, alkalies, bases, etc., at its positive extremity.

"The poles, § 556,* are merely the surfaces or doors by which the electricity enters into or passes out of the substance suffering decomposition. They limit the extent of that substance in the course of the electric current, being its *terminations* in that direction; hence the elements evolved pass so far and no further."

In this way Faraday, for the first time, explains chemical decomposition with definiteness, as the conduction of the electric current through the electrolyte. He proves the important relation that† "*the sum of chemical decomposition is constant* for every section taken across a decomposing conductor, uniform in its nature, at whatever distance the poles may be from each other or from the section; . . . provided the current of electricity be retained in constant quantity. . ."

Our conception even to-day of the process of electrolytic decomposition is embraced in these laws. In a later paper ‡ Faraday expressed the belief that they would need modification. The chemical theory of the galvanic cell, which he so energetically sought to defend, inclined him, primarily, to make this statement, as well as the fact that electrolytes often conduct weak currents without any decomposition being perceptible. Both points, however, have since been satisfactorily explained by science, without in any way affecting the postulated laws. On the contrary, every more exact investigation has only furnished a new confirmation of them.

We usually picture the process to ourselves by means of a row

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* Pogg. *Ann.*, **32**, 450.

† Ibid., **32**, 426.

‡ Ibid., **35**, 259.

of adjacent molecules, as shown in Fig. 1. It is assumed in the figure that the distance between the neighboring molecules of the electrolyte is greater than that between the chemically bound ions of each individual molecule. This assumption is certainly permissible in those cases which we shall alone have to consider later — namely, those in which the electrolyte is brought into the liquid state by means of a solvent.

The first action of the current consists* in bringing the particles of the body to be decomposed into such a position that the cation of each molecule is turned towards the cathode, and

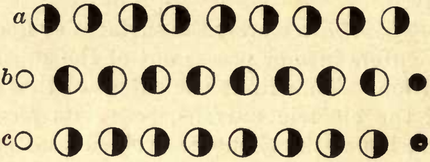

Fig. 1

the anion towards the anode. The two ions then separate from each other, move in opposite directions, and thereby meet with the neighboring ions likewise migrating (Fig. 1, *b*). By this process, however, they have arrived in a position where each anion is turned towards the cathode, and each cation towards the anode. There must therefore result a rotation of each molecule, and the reverse position be established, if the same constituent is to be continuously liberated at the same electrode (Fig. 1, *c*).

It would certainly be of great importance if we could represent these motions, to which the smallest particles of an electrolyte are subjected during the passage of the current, more definitely than in these most general outlines. They would not only throw light on the nature of electricity, but also on the chemical constitution of bodies.

In many cases it seems possible to determine by experiment the relative distances through which the two ions move during electrolysis. As we shall be concerned only with this point in what follows, we will give prominence to it alone in the figure.

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* See *Faraday*, § 1705; Pogg. *Ann.; Ergänzungsband*, I., 263.

For this purpose let us adopt the method of representation given by Berzelius in his works, in which the two ions are represented one below the other, and supposed to move by each other in a horizontal direction (Fig. 2). It is assumed that the electrolyte is brought into the liquid state by means of an indifferent non-conducting solvent.

If we can divide the liquid at any definite place, we shall find that the ions in each portion are in a different proportion after electrolysis has taken place than before. This proportion is determined by the distance through which each ion moves during the passage of the current.

If, for example, we make the assumption, tacitly made in former presentations, that these distances are equal, in which case both migrating ions meet half way between their original positions, a glance at Fig. 2 shows, that after electrolysis, that portion of liquid which borders on the anode will contain half an equivalent less cations than before. The converse is of course true for the other portion which is in contact with the cathode. By equivalent is understood the quantity of the component liberated.

If the two ions do not move through equal distances—that is, if they do not meet each other half way—then the side of the liquid in which the more rapidly moving ion makes its appearance will be increased by more than half an equivalent of it, and diminished by less than half an equivalent of the other ion. Fig. 3 shows this for the case when the anion moves $\frac{1}{3}$, the cation $\frac{2}{3}$ of the distance. The anode side of the liquid contains $\frac{1}{3}$ of an equivalent more anions and $\frac{2}{3}$ of an equivalent less

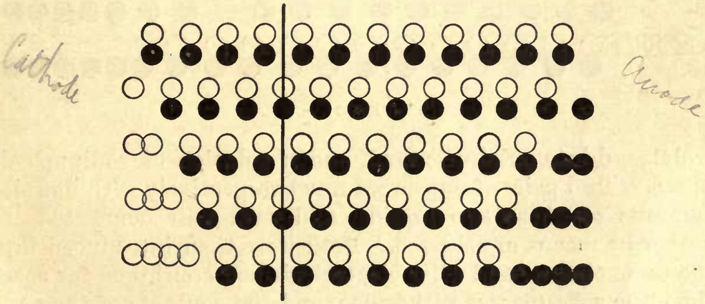

Fig. 2

cations after the decomposition than before. The other side shows the converse relation.

This result evidently holds generally. If one ion moves through $^1/_n$ the distance, and the other $\frac{n-1}{n}$, then the side of the liquid in which the former appears will contain $^1/_n$ equivalent more of it and $\frac{n-1}{n}$ equivalent less of the other ion. The converse relation will hold for the other side of the electrolyte.

The first experiments to determine the transference of ions quantitively, were made by Faraday.* He took up the subject, however, only as a side issue, and confined himself to two electrolytes, dilute sulphuric acid, and a solution of sodium sulphate. Two pairs of cups were filled respectively with definite amounts of these two liquids, and each pair connected together by means of asbestos. Both were then introduced into the same circuit, and after electrolysis had continued for some time, the asbestos was withdrawn, and the contents of the cups subjected to analysis. It is clear that this method is very defective, and that no accurate results are to be expected with it. The results which Faraday obtained in two series of experiments show this sufficiently. In the case of the sodium salt, he determined only the sulphuric acid set free, and tacitly assumed that half of it had been transferred.

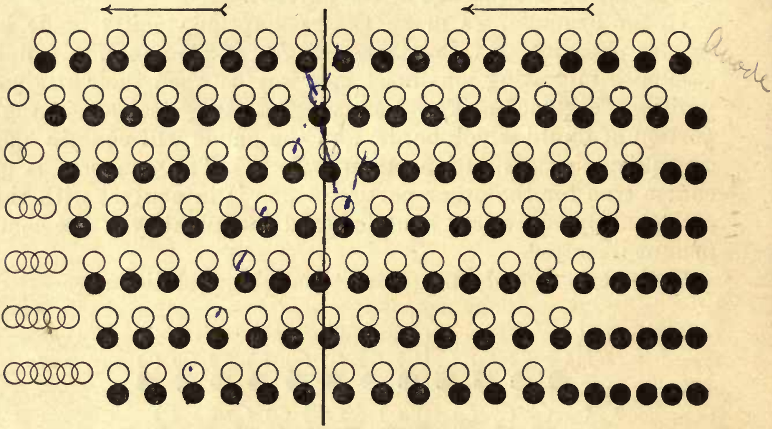

Fig. 3

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* *Exp. Research.*, § 525–530; Pogg. *Ann.*, **32**, 436.

Messrs. Daniell and A. Miller,* in their beautiful investigations on the electrolysis of salts, were led to devote greater attention to the subject of transference. They effected the separation of the liquid by the introduction of a membrane. They filled the two cells into which the vessel was divided with accurately determined quantities of the aqueous solution of the electrolyte, and investigated each after the galvanic decomposition had taken place.

The results which they obtained are very striking. When, namely, copper or zinc sulphate was chosen as electrolyte, they found after electrolysis, exactly the same amount of metal in the cell containing the cathode as they had originally introduced. The quantity of reduced metal, increased by the quantity still dissolved in the liquid, amounted to exactly as much as was present before the electrolysis. According to this, copper and zinc do not migrate at all during electrolysis. Their anion $\ddddot{S}$ traverses the whole distance. An ammonium salt (salammoniac) gave the same result; the complex cation NH_4 is to be classed with the two preceding. They found a transference of the cation with the salts potassium sulphate, barium nitrate, and magnesium sulphate. For potassium it amounted to $\frac{1}{3}$, for barium $\frac{1}{6}$, and for magnesium $\frac{1}{12}$ equivalent. The authors conclude from their experiments that those metals which decompose water at ordinary temperature, or whose oxides are easily soluble in water, are subject to a progressive transference in the voltaic cell from anode to cathode during electrolysis, while those which do not possess so strong an affinity for oxygen retain their place. They found a transference of all anions, even the weakest ones, such as WO_4 and CO_3.

In the translation of their article in Poggendorff's *Annalen*, the direct numerical results of the individual experiments are not given completely. The accuracy of the method cannot therefore be judged. It would appear, however, that it was not satisfactory, as the results are given only in round numbers. Furthermore, it is expressly stated that the experiments are not strictly comparable, and that the figures given cannot be regarded as absolute determinations of the transferred quantity of each metal in the cell.

The introduction of the membrane entails of necessity two

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* Pogg. *Ann.*, **64,** 18.

evils. The lesser lies in the fact that the contents of each cell cannot be completely removed after the electrolysis, as some of the solution remains either in the diaphragm or comes through from the other cell. The more serious is a result of the inexplicable phenomenon, that the quantity of liquid in the negative cell increases, and in the positive cell diminishes, in these experiments. This was frequently noticed by Daniell, and has been very recently more carefully investigated by Wiedemann.* The latter regards it as a motion of the liquid mass as a whole from anode to cathode, and finds it very marked in copper and zinc vitriol solutions. It seems doubly striking, therefore, that Daniell and Miller found the quantity of copper unchanged in the negative cell, since an increase should have occurred as a result of this motion.

As proof that the diaphragm offers no obstruction to the progress of the ions, the authors cite the phenomenon familiar to electrotypers, that, in a copper vitriol solution, the liquid about the negative pole becomes weaker in copper and finally exhausted, when the negative pole is placed in the upper and the positive pole in the lower layers of the solution. They tried a similar experiment by filling a long tube, provided with two upright arms, with a strong solution of copper sulphate, and connected it by means of copper strips to a battery. The liquid in the negative arm became noticeably lighter colored, while, on the other hand, that in the positive arm became darker. From this they concluded that the oxysulphur ion $(\ddddot{S})$, which separated out at the latter place, dissolved copper from the anode, but that this copper could not migrate to the cathode so as to replace the metal precipitated there.

This same phenomenon was reported at nearly the same time by numerous physicists, and introduced into discussions on the process of electrolysis. Pouillet† describes it in a gold solution which was contained in a U-shaped tube. After a current had passed a sufficiently long time, he found the solution in the negative arm almost completely deprived of its gold, while that in the positive arm still contained its original gold contents. He concludes from this "that in the decomposition of gold chloride, and therefore all metal salts, the positive pole has no

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* Pogg. *Ann.*, **87**, 321.

† *Ibid.*, **65**, 474.

decomposing action, that all chemical force resides in the negative pole, that this takes up the gold and sends the chlorine by a series of successive decompositions and recombinations to the positive pole, to be there set free." "If both poles acted," he adds, "the metal separated at the negative pole would be of double origin; one-half would be directly precipitated, the other would come from the positive pole; both arms of the tube would then become weaker in gold to the same extent during the whole duration of the process."

Besides the physicists mentioned, Smee * also discusses the phenomenon.

It is astonishing how this simple experiment has been so generally misunderstood. The dilution which the solution undergoes at the negative pole proves in no way that the metal does not migrate during electrolysis. We can convince ourselves of this at once by glancing back at Fig. 2 or 3. The cation, in the above case, is a solid body in the free state, and, as such, leaves the solvent by the separation produced by the current. Fig. 2 is drawn on the assumption that the ions move through equal distances, and shows that the cathode side is increased after electrolysis by ½ equivalent of cations. Now as one equivalent becomes solid, the solution is thereby diminished by ½ equivalent—that is, diluted by ½ equivalent of the salt. Dilution must therefore occur at the negative pole, even if the cation migrates; and it must evidently do so in all cases, as long as the cation does not migrate alone and the anion remain at rest. Only in this one case will the original concentration remain the same at the cathode.

This very dilution which the cation suffers at the negative pole where the cation leaves the solution, can be very advantageously used to determine the transference quantitatively. An exact separation of the electrolyte is easily effected without the introduction of asbestos or of a diaphragm.

Fig. 4 represents a simple apparatus which I have constructed for this purpose, and which was used in the experiments described below.

A glass cylinder, which contains the solution of the electrolyte, is composed of two parts—a larger, *a*, and a smaller, *b*. The former is cemented to a vessel, *c*, preferably of porcelain,

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* Pogg. *Ann.*, **65**, 473.

and contains the anode *d*. This has the form of a circular perforated plate, and is made of metal, the salt of which is to be electrolyzed. The support fastened to its centre passes through a small cork in a glass plate and permits connection with the galvanic cell. This plate forms the base of the cylinder, and is held in place by a cover which screws on. The anode is not permitted to lie on the bottom, but is placed a little higher up, so that the concentrated solution, which forms at its surface during electrolysis, can flow down through the holes. The smaller part of the cylinder *b* is closed above by a similar perforated glass plate, provided with a cork, and contains the cathode *e*, likewise fastened to a support which projects outward. The cathode must be given a different form from the anode. If it consists of a horizontal plate, the metal deposited by the current on the under surface cannot hold. It falls down and sets the liquid in motion. In order to prevent this, a metal cone is used as cathode, which is fixed with its apex at the centre of a horizontal circular glass plate. The glass plate is much smaller than the cross-section of the cylinder, and so chosen that points in its circumference are approximately equally distant from the base and from the apex of the cone. By this device all parts of the surface of the cone are nearly the same distance from the anode, and the deposited metal distributes itself nearly uniformly over the whole. The base of the cone presses closely against the plate forming the cover. Its height is so chosen that the glass plate *f* comes about in the middle of the cylinder. The cone and support are made preferably of platinum or gold. Failing these, silver may be used, which is what I was obliged to use.

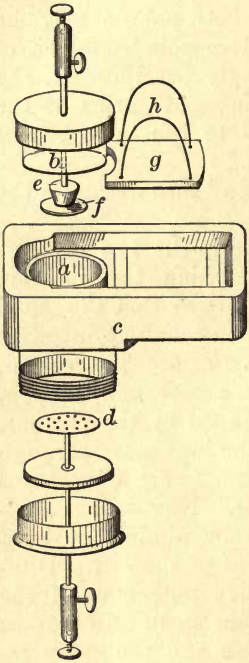

Fig. 4

When an experiment is to be made, the lower cemented part of the cylinder, together with the vessel *c*, is first filled with the solution. The same is done with the upper part in which the cathode is placed, care being taken that no air-bubbles remain in the inside. By means of a glass plate, *g*, which is ground on the open end of this cylinder, a definite quantity of liquid can be measured off. When this has been done the cylinder is inverted and, together with the glass plate, placed in the vessel *c* beside the cylinder *a*. For convenience of manipulation, a silver wire, *h*, passes through four holes in the corners of the plate, thereby forming two handles. The vessel *c* is just large enough to permit the cylinder *a* and the glass plate *g* to rest side by side on the bottom. The cylinder *a*, moreover, is so cemented in, that its upper edge projects above the bottom by just the thickness of the glass plate, so that it lies in the same plane with the upper surface of the latter. The smaller cylinder filled with solution can, therefore, be easily slid along from the plate on to the lower cylinder, thus forming a single cylinder. In this position its contents are supported by the atmospheric pressure.

The solution contained in the cylinder undergoes a change only at the electrodes during electrolysis. The liquid around the anode becomes more concentrated and, therefore, remains in the lower part; the solution around the cathode becomes diluter and collects on the cover. When the current has decomposed a sufficient quantity, the upper cylinder is slid back again onto the glass plate, and taken out. The outside is cleaned from adhering liquid, and the contents carefully poured into another vessel for analysis. If the upper cylinder be now filled with the original solution and this quantity likewise analyzed, one has, with the quantity of metal deposited, all data necessary for computing the transference.

The cathode projects, intentionally, only to the centre of the upper cylinder in order that the liquid at the opening shall remain unchanged, and the mixing with the liquid in the vessel *c*, which occurs at this place on sliding the cylinder back on to the glass plate, shall occasion no error. To prevent the liquid in *c* from becoming concentrated by evaporation during electrolysis, the apparatus is set into a ground-glass plate, *i*, and covered with a bell-glass during the experiment. Fig. 5 represents in cross-section the apparatus completely set up. The dimensions of my apparatus are as follows: The inside diameter of the cylinder measures 54 mm.; the height of the lower part, 70 mm.; that of the upper part, 25 mm., both inside measurements. The glass is 4½ mm. in thickness, as it must be taken rather thick. As the cathode extends only to the middle of the upper cylinder, the effect of diffusion is destroyed in our experiments. During the comparatively short duration of the electrolysis, this will be active only between the layers in the upper cylinder, and will have no effect on the mass in the lower one; it can, therefore, be the cause of no error. Moreover, the motion, which, according to Wiedemann, the electrolyte as a whole experiences from the anode to the cathode, cannot vitiate our results, as it cannot take place under the above conditions. The only error, so far as I can see, which enters into my method and cannot be avoided, arises from the fact that the metal which is separated out by the current has a different volume from that of the salt which is carried away from the upper part. This change in volume is replaced by liquid flowing in or out. The values which we obtain for the transference will be incorrect by the contents of this quantity of liquid. Our error is, however, very insignificant, and may be at least approximately computed. We shall see that even in the case of very concentrated solutions it does not amount to as much as the unavoidable error of analysis. This will be all the more true in the case of the dilute solutions, for, as is readily seen, the error must, in general, diminish proportional to the dilution.

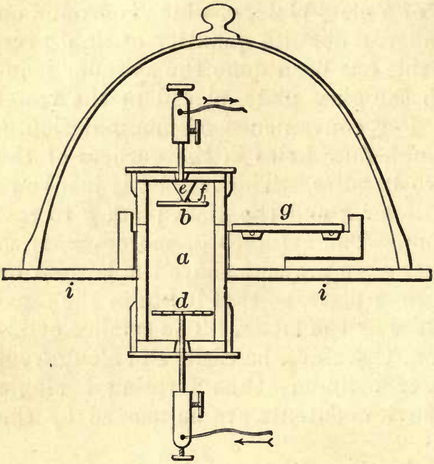

Fig. 5

Besides the apparatus, a voltameter was introduced into the circuit. I chose for this purpose the convenient and accurate arrangement described by Poggendorff, called a silver voltameter. A silver dish, which served as cathode, contained a solution of silver nitrate, into which dipped a silver plate as anode. The latter was wrapped around with a linen cover to prevent little particles, which easily come off during solution of the anode by the liberated anion $\overset{\substack{\cdots\\ \cdots}}{N}$, from falling into the dish, and thus increasing the weight of the reduced silver. The first salt which I decomposed was copper sulphate, with which Daniell and Miller also worked, and which possesses special interest on account of its application in galvanoplasty. It is the most convenient electrolyte for our experiments, for, as is well known, copper deposits coherently, and consequently adheres firmly to the surface of the silver cone.

I. COPPER SULPHATE

The solution which was subjected to electrolysis was prepared by diluting a more concentrated one to about twice its volume. Its specific gravity at 4.9° C. was 1.1036, and it contained 1 part $\dddot{\mathrm{S}}\,\dot{\mathrm{Cu}}$ to 9.56 parts water, or 1 part $(\dddot{\mathrm{S}}\,\dot{\mathrm{Cu}}+5\,\dot{\mathrm{H}})$* to 5.75 parts water.

Experiment A

The electrolysis was carried out at the temperature 4.7° C., and was effected by means of a small Grove cell. The current continued four hours and reduced 1.008 gr. Ag in the voltameter, or 0.0042 gr. Ag per minute.

This quantity of silver is equivalent to 0.2955 gr. Cu.

There was deposited on the silver cone, however, 0.2975 gr. Cu.

The difference, 0.002 gr., arises without doubt from an oxydation of the copper; we base all calculations on values deduced from results obtained by the silver voltameter.

The solution about the cathode contained:

Before electrolysis......... 2.8543 gr. $\dot{\mathrm{Cu}}$
After " .... 2.5897 " "

It was therefore diluted by an amount 0.2646 gr. $\dot{\mathrm{Cu}}$=0.2112 Cu.

The $\dot{\mathrm{Cu}}$ was precipitated in the usual way by caustic potash, from a boiling solution.

The amount of transferred copper is therefore

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* [*Nomenclature introduced by Berzelius. The dots over an element represent the number of attached oxygen equivalents. Gmelin's equivalents; i.e.,* $H=1$, $O=8$, $S=16$, *etc., are used throughout.*]

$$\begin{array}{r} 0.2955 \\ -0.2112 \\ \hline 0.0843 \end{array}$$

0.0843 gr., *i.e.*, $\frac{843}{2955}=28.5$ per cent. equivalent.

Our experiment gives a totally different result from that obtained by Messrs. Daniell and Miller. According to their results, the solution in the upper cylinder should have lost 0.2955 gr. Cu during the electrolysis. .0211

We will next consider whether the transference remains constant for all current strengths. To obtain an answer to this question, the above solution was subjected to the action of a weak and of a strong current.

Experiment B

The current from a Grove cell was so cut down by the introduction of a long thin German-silver wire, that at a temperature of 5.3° C. it reduced 1.2273 gr. Ag in 18 hours and 4 minutes, or 0.00113 gr. Ag per minute.

The quantity of silver corresponds to 0.3597 gr. Cu.

There was deposited on the silver cone 0.3587 gr. Cu.

The solution about the cathode contained :

Before electrolysis....... 2.8543 gr. Ċu
After " .... 2.535 " "

It was therefore diluted...... 0.3193 gr. Ċu, or 0.2549 gr. Cu.

The quantity of transferred copper is therefore

$$\begin{array}{r} 0.3597 \\ -0.2549 \\ \hline 0.1048 \end{array}$$

0.1048 gr., or $\frac{1048}{3597}=29.1$ per cent. equivalent.

Experiment C

The current from three Grove cells reduced at 6.5° C. 1.1503 gr. Ag in 2 hours, or 0.00958 gr. Ag a minute.

This quantity of silver corresponds to 0.3372 gr. Cu.

There was deposited on the silver cone 0.3374 gr. Cu.

The solution around the cathode contained :

Before electrolysis....... 2.8543 gr. Ċu
After " .... 2.5541 " "

It lost therefore............. 0.3002 gr. Ċu, or 0.2396 gr. Cu.

The quantity of transferred copper is therefore

$$\begin{array}{r} 0.3372 \\ -0.2396 \\ \hline 0.0976 \end{array}$$

0.0976 gr., or $\frac{976}{3372}$=28.9 per cent. equivalent.

If we tabulate the results of these experiments :

Current		Transference
113		29.1
420		28.5
958		28.9 per cent.
	Mean..	28.8 per cent.

there can be no doubt that the transference is independent of the intensity of the current. I have always avoided using very large currents, as the rise in temperature which they produce in the solution is disturbing. The immediate effect of this on our data is easily obviated by not removing the electrolyzed solution for analysis immediately after breaking the current, but allowing it to first return to the temperature of the surroundings. On the other hand, an indirect disturbance of the rise of temperature cannot be so easily overcome. This consists in the evolution of a quantity of little air-bubbles which usually cover the surface of the glass plate under the cathode, and which cannot be removed. That these little bubbles are not hydrogen gas is clear from the place where they appear. If large currents are to be used, it is judicious to free the solution as far as possible from absorbed air, before filling the apparatus ; this is most easily done under an air-pump.

The second question which we must consider has reference to the influence of the concentration on the transference. Six solutions of copper sulphate of very different concentration were subjected to electrolysis.

Solution I

A concentrated solution was diluted just sufficiently so that a separation of salt on the anode was not to be feared. It had at 4.5° C. a specific gravity of 1.1521, and contained 1 part $\dddot{S}\dot{C}u$ to 6.35 parts water, or 1 part $(\dddot{S}\dot{C}u+5\dot{H})$ to 3.69 parts water.

The current from a Grove cell deposited, at 5.5° C., 1.0783 gr. Ag in 4 hours. This corresponds to 0.3161 gr. Cu.

On the silver cone there was 0.3168 gr. Cu.

The solution around the cathode contained:

Before electrolysis.......	4.2591 gr. $\dot{C}u$
After "	3.9725 " "
It lost......................	0.2866 gr. $\dot{C}u$, or 0.2288 gr. Cu.

The amount of transferred copper is therefore

$$\begin{array}{r} 0.3161 \\ -0.2288 \\ \hline 0.0873 \end{array} \text{ gr., or } \frac{873}{3161}=27.6 \text{ per cent.}$$

The solution first electrolyzed, which gave 28.8 per cent. transference, served as Solution II.

Solution III

Specific gravity at 3.6° C.: 1.0553.

It contained 1 part $\dddot{S}\dot{C}u$ to 18.08 parts water, or 1 part $(\dddot{S}\dot{C}u+5\dot{H})$ to 11.19 parts water.

The current from one Grove cell deposited 0.8601 gr. Ag in 5 hours, 45 minutes, at 5.5° C. This corresponds to 0.2521 gr. Cu.

There was 0.2520 gr. Cu on the silver cone.

The solution around the cathode contained:

Before electrolysis.....	1.5026 gr. $\dot{C}u$
After "	1.2895 " "
It lost.....................	0.2131 gr. $\dot{C}u$., or 0.1701 gr. Cu.

The amount of transferred copper is therefore

$$\begin{array}{r} 0.2521 \\ -0.1701 \\ \hline 0.0820 \end{array} \text{ gr., or } \frac{820}{2521}=32.5 \text{ per cent.}$$

Solution IV

Specific gravity at 3° C.: 1.0254.

It contained 1 part $\dddot{S}\dot{C}u$ to 39.67 parts water, or 1 part ($\dddot{S}\dot{C}u+5\,\dot{H}$) to 24.99 parts water.

The current from two Grove cells deposited at 4.5° C., 0.6969 gr. Ag in 5 hours: this is equivalent to 0.2034 gr. Cu.

The copper which covered the silver cone could no longer be weighed, as in this dilute solution the larger part of it was spongy.

The solution around the cathode contained:

Before electrolysis..... 0.6765 gr. $\dot{C}u$
After " ..... 0.5118 " "

It lost.................... 0.1647 gr. $\dot{C}u$, or 0.1315 gr. Cu.

Hence the transference of the copper is

$$\begin{array}{r} 0.2043 \\ -0.1315 \\ \hline 0.0728 \end{array}\ \text{gr., or } \frac{728}{2043}=35.6 \text{ per cent.}$$

Solution V

Specific gravity at 4.8° C.: 1.0135.

It contained 1 part SCu to 76.88 parts water, or 1 part ($\dddot{S}\dot{C}u+5\,\dot{H}$) to 48.75 parts water.

The current of one Grove cell reduced 0.3592 gr. Ag at 4.3° C. This corresponds to 0.1053 gr. Cu.

The copper on the silver cone was spongy. The solution about the cathode contained:

Before electrolysis..... 0.3617 gr. $\dot{C}u$.
After " ..... 0.2758 " "

It lost.................... 0.0859 gr. $\dot{C}u$, or 0.0686 gr. Cu.

Hence the transference of copper is

$$\begin{array}{r} 0.1053 \\ -0.0686 \\ \hline 0.0367 \end{array}\ \text{gr., or } \frac{367}{1053}=34.9 \text{ per cent.}$$

Solution VI

Specific gravity at 4.4° C.: 1.0071.

It contained 1 part $\ddot{S}\dot{C}u$ to 148.3 parts water, or 1 part $(\ddot{S}\dot{C}u+5\dot{H})$ to 94.5 parts water.

The current from one Grove cell reduced 0.3850 gr. Ag in 16 hours, 25 minutes, at 4.4° C. This corresponds to 0.1131 gr. Cu.

The copper on the silver cone was spongy.

The solution around the cathode contained :

Before electrolysis.....	0.1867 gr. $\dot{C}u$
After "	0.0964 " "
It lost.....................	0.0903 gr. $\dot{C}u$, or 0.0721 gr. Cu.

The transference of copper is

$$\begin{array}{r} 0.1131 \\ -0.0721 \\ \hline 0.0410 \end{array} \text{gr., or } \frac{410}{1131}=36.2 \text{ per cent.}$$

Let us tabulate the separate results together for inspection.

NO.	SP. GR.	CONTENTS OF SOLUTION		TRANSFERENCE OF COPPER	
I	1.1521	1 pt. $\ddot{S}\dot{C}u$ to	6.35 pts. $\dot{H}$	27.6	per cent.
II	1.1036	" " "	9.56 " "	28.8	" "
III	1.0553	" " "	18.08 " "	32.5	" "
IV	1.0254	" " "	39.67 " "	35.5	mean, 35.6 per cent.
V	1.0135	" " "	76.88 " "	34.9	
VI	1.0071	" " "	148.3 " "	36.2	

The transference numbers still require the small correction which I pointed out above. We can only estimate this approximately, as we cannot determine with our method, throughout how large a portion of the solution the dilution extends. The dilute solution, which can be easily followed with the eye during the electrolysis, forms directly on the surface of the silver cone, glides upward along it, and collects under the cover. To obtain at least an idea of the amount of this correction, I will calculate it for Solution I, under a definite assumption which will not be far from the truth.

The liquid at the cathode lost 0.2866 gr. $\dot{\mathrm{C}}\mathrm{u}$, or 0.5762 gr. $\dddot{\mathrm{S}}\dot{\mathrm{C}}\mathrm{u}$. Suppose this loss extends over such a mass, x, of the liquid that a solution of concentration II thereby results. Before electrolysis the quantity x contains

$$\frac{6.35}{7.35}\,x \text{ water, and } \frac{1}{7.35}\,x\ \dddot{\mathrm{S}}\dot{\mathrm{C}}\mathrm{u}.$$

After electrolysis it will contain

$$\left(\frac{1}{7.35}\,x - 0.5762\right) \text{gr. } \dddot{\mathrm{S}}\,\dot{\mathrm{C}}\mathrm{u},$$

and be of concentration II; it will therefore contain.

$$\frac{6.35}{7.35\times 9.56}\,x\ \dddot{\mathrm{S}}\ \dot{\mathrm{C}}\mathrm{u} \text{ to } \frac{6.35}{7.35}\,x \text{ water.}$$

The mass sought is therefore obtained from the equation

$$\frac{6.35}{7.35\times 9.56}\,x = \frac{1}{7.35}\,x - 0.5762,$$

and equals $x = 12.616$ gr. Before electrolysis this mass has the volume

$$\frac{12.616}{1.1521} = 10.9504 \text{ c. cm.}$$

It loses 0.5762 gr. $\dddot{\mathrm{S}}\ \dot{\mathrm{C}}\mathrm{u}$ by electrolysis, and the volume becomes $\frac{12.0398}{1.1036} = 10.9095$ c. cm. Hence the withdrawal of 0.5762 gr. $\dddot{\mathrm{S}}\ \dot{\mathrm{C}}\mathrm{u}$ causes a diminution of volume of 0.0409 c. cm. According to *Marchand* and *Scherer*,* galvanically deposited copper has a density of 8.914. Hence the reduced 0.3161 gr. Cu occupies a volume of 0.0355 c. cm. The diminution exceeds the increase in volume by $0.0409 - 0.0355 = 0.0054$ c. cm. This volume is replaced by the solution flowing in. The latter weighs 0.0054×1.1521 gr. $= 0.0062$ gr., and contains 0.00042 gr. $\dot{\mathrm{C}}\mathrm{u}$.

Hence, even in case of this most concentrated solution, the error is of no account. This will be even more true in the other cases.

The effect of the water on the amount of transference is evident from the experimental results. In proportion as the dilution increases, the transference of the cation Cu increases and of the anion ($\dddot{\mathrm{S}}$) decreases. In Solution IV the limit of this influence seems to be reached. From there on the numbers become nearly constant.

There still remains a third condition which can affect the

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* *Gmelin*, iii., 374.

transference; I mean temperature. Our apparatus allows us to work only at temperatures which we can give to the surrounding air.

A solution was prepared which had about the same concentration as Solution II.

Experiment D

During the electrolysis of this solution the temperature of the air varied from 21° to 18° C. The current from one Grove cell reduced 1.4247 gr. Ag in 4 hours 3 minutes. This corresponds to 0.4176 gr. Cu.

0.419 gr. Cu was found on the silver cone.

The solution about the cathode contained:

Before electrolysis..... 2.8921 gr. Ċu
After " ..... 2.5191 " "

It lost.................... 0.3730 gr. Ċu, or 0.2977 gr. Cu.

Hence the transference of the copper is

$$\begin{array}{r} 0.4176 \\ -0.2977 \\ \hline 0.1199 \end{array} \text{gr., or } \frac{1199}{4176} = 28.7 \text{ per cent.}$$

The temperature has no effect between 4° and 21° C.*

Copper vitriol is a salt which crystallizes from aqueous solutions with five molecules of water. The remarkable influence which the amount of water exerts on the transference made the investigation of an anhydrous salt especially desirable. I chose

II. SILVER NITRATE

The salt was melted before dissolving in order to obtain it absolutely neutral. The solution did not react with litmus. It is not as convenient for electrolysis as copper sulphate, as the silver adheres firmly to the cone only when deposited from quite concentrated solutions, and with weak currents. Usually the dendritic crystals grow rapidly over the glass plate underneath the cathode and fall off.

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* [*This conclusion has not been verified by more recent experiments. See Loeb and Nernst, Zeit. für Phys. Chem.*, **2,** 948, 1888; *Bein, Wied. Ann.*, **46,** 29, 1892.]

I chose such currents that a sufficient amount of silver was reduced before it began to drop off. When this threatened to occur the electrolysis was stopped.

Solution I

Specific gravity at 11.1° C.: 1.3079.

It contained 1 part $\overset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{N}}\dot{A}g$ to 2.48 parts water.

The current reduced 1.2591 gr. Ag in 1½ hours at a temperature of 11.2° C.

The solution about the cathode gave:

Before electrolysis...	17.4624 gr. ClAg
After " ...	16.6796 " "
It lost....................	0.7828 gr. ClAg, or 0.5893 gr. Ag.

Hence the amount of the transferred silver is

$$\begin{array}{r} 1.2591 \\ -0.5893 \\ \hline 0.6698 \end{array} \text{ gr., or } \frac{6698}{12591} = 53.2 \text{ per cent.}$$

Solution II

Specific gravity at 19.2° C.: 1.2788.

It contains 1 part $\overset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{N}}\dot{A}g$ to 2.735 parts water.

The current from one cell reduced 1.909 gr. Ag at 19° C.

The solution at the cathode gave:

Before electrolysis...	15.9364 gr. ClAg
After " ...	14.7233 " "
The loss is	1.2131 gr. ClAg, or 0.9132 gr. Ag.

The transference of silver is therefore

$$\begin{array}{r} 1.909 \\ -0.9132 \\ \hline 0.9958 \end{array} \text{ gr., or } \frac{9958}{19090} = 52.2 \text{ per cent.}$$

Solution III

Specific gravity at 18.4° C.: 1.1534.

It contains 1 part $\overset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{N}}\dot{A}g$ to 5.18 parts water.

The current from one cell reduced 1.1124 gr. Ag in 1 hour 21½ minutes at a temperature of 18.4° C.

The solution about the cathode gave:

Before electrolysis . . . 8.6883 gr. ClAg
After " . . . 7.9569 " "

The loss is . . . . 0.7314 gr. ClAg, or 0.5506 gr. Ag.

Hence the amount of transferred silver is

$$\begin{array}{r} 1.1124 \\ -0.5506 \\ \hline 0.5618 \end{array} \text{ gr., or } \frac{5618}{11124} = 50.5 \text{ per cent.}$$

Solution IV

Specific gravity at 18.8° C.: 1.0774.

It contained 1 part $\overset{\cdot\cdot\cdot\cdot\cdot}{N}\dot{A}g$ to 10.38 parts water.

The current from two cells reduced 0.4541 gr. Ag in half an hour at 18.8° C.

The solution about the cathode gave:

Before electrolysis . . . 4.4156 gr. ClAg
After " . . . 4.1080 " "

The loss is . . . . 0.3076 gr. ClAg, or 0.2316 gr. Ag.

Hence the amount of transferred silver is

$$\begin{array}{r} 0.4541 \\ -0.2316 \\ \hline 0.2225 \end{array} \text{ gr., or } \frac{2225}{4541} = 49 \text{ per cent.}$$

Solution V

Specific gravity at 19.2° C.: 1.0558.

It contained 1 part $\overset{\cdot\cdot\cdot\cdot\cdot}{N}\dot{A}g$ to 14.5 parts water.

The current from two cells reduced 0.3937 gr. Ag in 25 minutes at 19.2° C.

The solution about the cathode gave:

Before electrolysis . . . 3.1731 gr. ClAg
After " . . . 2.8985 " "

The loss is . . . . 0.2746 gr. ClAg, or 0.2067 gr. Ag.

The amount of transferred silver is therefore

$$\begin{array}{r} 0.3937 \\ -0.2067 \\ \hline 0.1870 \end{array}\text{ gr., or }\frac{1870}{3937}=47.5\text{ per cent.}$$

Solution VI

Specific gravity at 18.4° C.: 1.0343.

It contains 1 part $\overset{\cdot\cdot\cdot\cdot\cdot}{\bar{N}}\dot{A}g$ to 23.63 parts water.

The current from two elements reduced 0.3208 gr. Ag in half an hour at 18.4° C.

The solution at the cathode gave:

Before electrolysis... 1.9605 gr. ClAg
After " ... 1.7358 " "
The loss is.............. 0.2247 gr. ClAg, or 0.1691 gr. Ag.

Hence the amount of transferred silver is

$$\begin{array}{r} 0.3028 \\ -0.1691 \\ \hline 0.1517 \end{array}\text{ gr., or }\frac{1517}{3208}=47.3\text{ per cent.}$$

Solution VII

Specific gravity at 18.5° C.: 1.0166.

It contains 1 part $\overset{\cdot\cdot\cdot\cdot\cdot}{\bar{N}}\dot{A}g$ to 49.44 parts water.

The current from two cells reduced 0.2470 gr. Ag in 45½ minutes at 18.5° C.

The solution around the cathode gave:

Before electrolysis... 0.9485 gr. ClAg
After " ... 0.7758 " "
The loss is.............. 0.1727 gr. ClAg, or 0.1300 gr. Ag.

The amount of transferred silver is therefore

$$\begin{array}{r} 0.2470 \\ -0.1300 \\ \hline 0.1170 \end{array}\text{ gr., or }\frac{1170}{2470}=47.4\text{ per cent.}$$

Solution VIII

Specific gravity at 18.6° C.: 1.0076.

It contains 1 part $\ddot{N}Ag$ to 104.6 parts water.

The current from three elements reduced 0.1888 gr. Ag in 41 minutes at 18.6° C.

In this very dilute solution the silver separated out on the silver cone at first black and spongy, as described by Poggendorff,* and became afterwards yellowish-white and crystalline.

The solution about the cathode gave :

Before electrolysis... 0.4515 gr. ClAg
After " ... 0.3197 " "
The loss is.............. 0.1318 gr. ClAg, or 0.0992 gr. Ag.

The amount of transferred silver is

$$\begin{array}{r} 0.1888 \\ -0.0992 \\ \hline 0.0896 \end{array} \text{ gr., or } \frac{896}{1888} = 47.4 \text{ per cent.}$$

Solution IX

Specific gravity at 9.6° C.: 1.0044.

It contains 1 part $\ddot{N}Ag$ to 247.3 parts water.

The current from four elements reduced 0.0863 gr. Ag in 1 hour 3 minutes at 9.6° C.

The solution about the cathode gave :

Before electrolysis... 0.1916 gr. ClAg
After " ... 0.1316 " "
The loss is.............. 0.0600 gr. ClAg, or 0.0452 gr. Ag.

Hence the transference of the silver is

$$\begin{array}{r} 0.0863 \\ -0.0452 \\ \hline 0.0411 \end{array} \text{ gr., or } \frac{411}{863} = 47.6 \text{ per cent.}$$

We will again tabulate the results obtained with the nine different solutions.

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* Pogg. *Ann.*, **75**, 338.

NO.	SP. GR.	CONTENTS	TRANSFERENCE OF SILVER	
I	1.3079	1 pt. $\ddot{N}\dot{A}g$. to 2.48 pts. $\dot{H}$	53.2	per cent.
II	1.2788	“ “ “ 2.73 “	52.2	“ “
III	1.1534	“ “ “ 5.18 “	50.5	“ “
IV	1.0774	“ “ “ 10.38 “	49.	“ “
V	1.0558	“ “ “ 14.5 “	47.5	47.44 mean per cent.
VI	1.0343	“ “ “ 23.63 “	47.3	
VII	1.0166	“ “ “ 49.44 “	47.4	
VIII	1.0076	“ “ “ 104.6 “	47.4	
IX	1.0044	“ “ “ 247.3 “	47.6	

The correction which ought to be applied to these figures is here again, even for Solution I, so small that it falls within the experimental error. If we make the same assumption as in the case of copper vitriol, it amounts to 0.0005 gr. for the 0.6698 gr. of transferred silver. The effect of water in the case of silver nitrate is opposite to that in the case of copper vitriol. The transference of the cation Ag diminishes, that of the anion $\ddot{N}$ increases, with increasing amount of the solvent. The effect of the water reaches a limit in Solution V. Greater dilution does not further change the value.

In the two above salts, the ions are all different substances. I now investigated compounds of the same cation with different anions, and chose for this purpose silver sulphate and silver acetate. Both of these salts are difficultly soluble in water, but still sufficiently so to give accurate results for our purpose.

III. SILVER SULPHATE

Experiment A

Specific gravity of the solution at 15° C.: 1.0078.

The solution contained 1 part $\ddot{S}\dot{A}g$ to 123 parts water.

The current from four elements reduced 0.1099 gr. Ag in 24 minutes at 15° C.

The solution about the cathode gave :

Before electrolysis... 0.4166 gr. ClAg
After “ ... 0.3358 “ “
The loss is.............. 0.0808 gr. ClAg, or 0.0608 gr. Ag.

The quantity of transferred silver is therefore

$$\begin{array}{r} 0.1099 \\ -0.0608 \\ \hline 0.0491 \end{array} \text{ gr., or } \frac{491}{1099}=44.67 \text{ per cent.}$$

Experiment B

The current from four elements reduced 0.1127 gr. Ag in 25 minutes.

The solution around the cathode gave :

Before electrolysis... 0.4090 gr. ClAg
After " ... 0.3261 " "
The loss is.............. 0.0829 gr. ClAg, or 0.624 gr. Ag.

Hence the amount of transferred silver is

$$\begin{array}{r} 0.1127 \\ -0.0624 \\ \hline 0.0503 \end{array} \text{ gr., or } \frac{503}{1127}=44.63 \text{ per cent.}$$

Experiment C

The current from four elements reduced 0.1108 gr. Ag in 23½ minutes at 19.4° C.

The solution around the cathode gave :

Before electrolysis... 0.3539 gr. ClAg
After " ... 0.2720 " "
The loss is.............. 0.0819 gr. ClAg, or 0.0616 gr. Ag.

The transference of silver is therefore

$$\begin{array}{r} 0.1108 \\ -0.0616 \\ \hline 0.0492 \end{array} \text{ gr., or } \frac{492}{1108}=44.4 \text{ per cent.}$$

The results of the three experiments :

$$\begin{array}{r} 44.67 \text{ per cent.} \\ 44.63 \text{ `` ``} \\ 44.4 \text{ `` ``} \\ \hline \end{array}$$

give the mean........ 44.57 per cent.

IV. SILVER ACETATE

Experiment A

Specific gravity of the solution at 14° C.: 1.0060.

It contained 1 part Äc Ag* to 126.7 parts water.

The current from four elements reduced 0.2197 gr. Ag in 1 hour 21 minutes at 14° C.

The solution at the cathode gave:

Before electrolysis... 0.3736 gr. ClAg
After " ... 0.2631 " "
The loss is............... 0.1105 gr. ClAg, or 0.0832 gr. Ag.

Hence the transference of silver is

$$\begin{array}{r} 0.2197 \\ -0.0832 \\ \hline 0.1365 \end{array} \text{ gr., or } \frac{1365}{2197}=62.13 \text{ per cent.}$$

Experiment B

The current from four elements reduced 0.1892 gr. Ag in 1 hour 7 minutes at 15° C.

The solution at the cathode gave:

Before electrolysis... 0.3656 gr. ClAg
After " ... 0.2728 " "
The loss is............... 0.0928 gr. ClAg, or 0.0699 gr. Ag.

The amount of transferred silver is

$$\begin{array}{r} 0.1892 \\ -0.0699 \\ \hline 0.1193 \end{array} \text{ gr., or } \frac{1193}{1893}=63 \text{ per cent.}$$

Experiment C

Specific gravity at 15° C.: 1.0045.

The current from four elements reduced 0.1718 gr. Ag in 1 hour 13 minutes at 15° C.

The solution at the cathode gave:

Before electrolysis...... 0.2825 gr. ClAg
After " ..... 0.1977 " "
The loss is................. 0.0848 gr. ClAg, or 0.0638 gr. Ag.

* [*Äc is equivalent to* $C_2H_4O_2$ *minus* $\frac{1}{2}H_2O$ *in modern notation.*]

The amount of transferred silver is

$$\begin{array}{r} 0.1718 \\ -0.0638 \\ \hline 0.1080 \end{array}\ \text{gr., or } \frac{1080}{1718}=62.86 \text{ per cent.}$$

From the results of these three experiments,

$$\begin{array}{lll} 62.13 & \text{per cent.} & \\ 63 & `` & `` \\ 62.86 & `` & `` \\ \hline \end{array}$$

we obtain the mean... 62.66 per cent.

If we glance at the values obtained with the three silver salts, it is at once evident that the same cation migrates by different amounts when in combination with different anions, the condition of the solutions remaining otherwise the same.

With Ag($\overset{\cdot\cdot}{\bar{\mathrm{A}}}\mathrm{c}$) the transference of Ag is 62.6 per cent.
$\overset{\cdot\cdot}{\bar{\mathrm{A}}}\mathrm{c}$ " 37.4 " "
" Ag($\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$) " " " Ag " 47.4 " "
$\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$ " 52.6 " "
" Ag($\overset{\cdot\cdot\cdot}{\mathrm{S}}$) " " " Ag " 44.6 " "
$\overset{\cdot\cdot\cdot}{\mathrm{S}}$ " 55.4 " "

If the explanation of the transference numbers which we gave at the beginning of this paper is correct, then the distances traversed during electrolysis by Ag and $\overset{\cdot\cdot}{\bar{\mathrm{A}}}\mathrm{c}$, Ag and $\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$, and Ag and $\overset{\cdot\cdot\cdot}{\mathrm{S}}$, are in the ratio respectively of,

100 : 59.7
100 : 110.9
100 : 124.2

In these numbers a relation to chemical affinity is unmistakable. Of the three anions with which we are concerned, every chemist regards the $\overset{\cdot\cdot}{\bar{\mathrm{A}}}\mathrm{c}$ as the weakest, the $\overset{\cdot\cdot\cdot}{\mathrm{S}}$ as the strongest.

The same relation is evident if we compare the transference numbers of ($\overset{\cdot\cdot\cdot}{\mathrm{S}}$) Cu and ($\overset{\cdot\cdot\cdot}{\mathrm{S}}$) Ag. In the first of these two electrolytes which contain the same anion, the migration of the $\overset{\cdot\cdot\cdot}{\mathrm{S}}$ is 64.4 per cent. and of the Cu 35.6 per cent., while at the same concentration, the migration of $\overset{\cdot\cdot\cdot}{\mathrm{S}}$ in the second electrolyte is 55.4 per cent. and of Ag 44.6 per cent. The relative distances traversed are therefore:

For $\overset{\cdot\cdot\cdot}{\mathrm{S}}$ and Cu : 100 and 55.3
For $\overset{\cdot\cdot\cdot}{\mathrm{S}}$ and Ag : 100 and 80.5

In order to explain the relation indicated, the following consideration naturally offers itself. Of several anions in combination with the same cation, we will consider that one the most electro-negative which moves the greatest distance towards the anode. The analogous relation holds for several cations present with the same anion. The farther apart two substances stand from each other in the voltaic series, the stronger appears their chemical affinity. We might therefore look for a measure of chemical affinity in the distances through which the anions migrate during electrolysis. At present, however, I am far from ready to assign this significance to the above figures. When we consider that copper appears more positive than silver in its electrical aspect, and that the quantity of water exerts such a decided influence on the transference, a theory is by no means yet to be thought of.

I do not yet attempt to give an explanation of the influence of the water. Whatever hypothesis we propose for this, we must remember that the neutrality of the solution is not disturbed by the electrolysis—that free acid never makes its appearance at the cathode. We can determine the transference equally well in our experiments if we determine quantitively the acid in the solution about the cathode, or if we determine the base. I always prefer the former way in these investigations, when analytical methods permit the acid being more sharply determined.

In my experiments with the four salts, hydrogen was never separated out at the cathode along with the metal, although very dilute solutions have been electrolyzed. I took, of course, great care to make up neutral solutions and to exclude all free acid. Although Smee* obtained a different result in the electrolysis of copper sulphate, yet this is only apparently the case. Smee cites in support of the older view of galvanic decomposition, according to which water only is decomposed, and the metal is a result of the reduction caused by the liberated hydrogen, an experiment in which he decomposed a copper vitriol solution in a tall glass vessel with copper electrodes, the upper of which was negative and the lower positive. He observed copper to separate out on the former, at first in a compact, later in a spongy form, and then hydrogen evolved, while the

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* Pogg. *Ann.*, **65**, 473.

upper portion of the solution gradually became completely colorless, and the lower positive electrode became covered with a thick layer of copper oxide. With the exception of the remark concerning the anode, I have always observed the same results when the cathode in my apparatus had the form of a horizontal plate. If we place it just at the surface, so that only its underside is in contact with the liquid, the copper appears immediately in the spongy form if the current is not too weak; it soon falls off and leaves a surface of pure water in contact with the cathode, whence, of course, hydrogen must appear. This follows so clearly from Figs. 2 and 3 that a further discussion is superfluous. To avoid this result, my cathode was given the form of a cone.

Daniell* has already unquestionably proved the hydrogen which is evolved during the galvanic decomposition of aqueous solutions of the alkali or alkali earth salts, to be secondary. It is known that when salts of iron, manganese, cobalt, and nickel, even in perfectly neutral aqueous solution, conduct the current, hydrogen is set free simultaneously with the metals. Is this hydrogen likewise secondary? Nothing is easier than to answer this question. A solution of $\dddot{S}\,\dot{F}e$, which was purified from free acid by repeated crystallization, was introduced into a circuit with a silver voltameter. An iron plate dipped in the solution as anode, and a platinum plate as cathode. The liquid about the latter is as neutral after the electrolysis as before. If the hydrogen be of secondary origin, it is evolved by a portion of the liberated iron decomposing the water by uniting with its oxygen. Hence ferrous oxide must be mixed with the reduced iron, and the total amount of $\dddot{\bar{F}}e$ corresponding will contain as much iron as is equivalent to the silver.

The two following experiments show this clearly:

Experiment A

The current from three elements reduced 3.672 gr. Ag in the silver voltameter, which is equivalent to 0.9537 gr. Fe. The deposited iron was dissolved in aqua regia and precipitated as $\dddot{\bar{F}}e$ by ammonia.

The $\dddot{\bar{F}}e$ weighed 1.3625 gr.; it contained, therefore, 0.9542 gr. Fe.

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* Pogg. *Ann.*, *Ergãnzbd*, i., 565.

Experiment B

The reduced silver weighed 3.0649 gr., and is equivalent to 0.7960 gr. Fe.

The $\dddot{\bar{\mathrm{F}}}\mathrm{e}$ weighed 1.1375 gr., and contained 0.7966 gr. Fe.

We shall obtain further information of the effect of water on the migration if we substitute another solvent. Unfortunately, our choice in this direction is very limited. Absolute alcohol is the only liquid which can replace water, and this only in a few cases, as it dissolves only a few electrolytes.

only
at ord
temp.

Of our four salts, silver nitrate alone is soluble in absolute alcohol. At higher temperatures it is easily soluble; at lower temperatures, at which alone electrolysis can be carried out on account of the volatility of the alcohol, it is difficultly soluble. A solution saturated at a higher temperature contained at 5° C. only 1 part $\overset{:\!:\!\cdot}{\mathrm{N}}\dot{\mathrm{A}}\mathrm{g}$ in 30.86 parts of alcohol.

The solution which was electrolyzed was somewhat diluter. The glass plate fastened under the cathode by sealing-wax was replaced by an ivory plate which was screwed on, and the cylinder *a* was sealed into the vessel *c* with plaster of Paris. The solution conducted poorly.

Experiment A

The current from six elements reduced 0.2521 gr. Ag in 3 hours 32 minutes at 3.8° C.

The solution about the cathode gave:

Before electrolysis... 0.9181 gr. ClAg
After " ... 0.7264 " "
The loss is.............. 0.1917 gr. ClAg, or 0.1443 gr. Ag.

Hence the transference of silver is

$$\begin{array}{r} 0.2521 \\ -0.1443 \\ \hline 0.1078 \end{array}\text{ gr., or } \frac{1078}{2521}=42.8 \text{ per cent.}$$

Experiment B

The current from six elements reduced 0.1367 gr. Ag in 2 hours 22 minutes at 5° C.

The solution about the cathode gave :

Before electrolysis...	0.8743 gr. ClAg
After " ...	0.7700 " "
The loss is..............	0.1043 gr. ClAg, or 0.0785 gr. Ag.

The transference of silver is therefore

$$\begin{array}{r} 0.1367 \\ -0.0785 \\ \hline 0.0582 \text{ gr., or } \frac{582}{1367}=42.6 \text{ per cent.} \end{array}$$

Hence in alcoholic solution the transference of Ag is 42.7 per cent. ; of $\dddot{\mathrm{N}}$, 57.3 per cent. ; and the relative distances traversed are 100 and 134.2 respectively.

This result, which was not anticipated, indicates the great caution to be observed in the interpretation of our results. I intend next to study such salts as are easily soluble in absolute alcohol at low temperatures, and hope in the next communication to be able to present results on the salts of zinc, cadmium, iron, manganese, etc. With several of these hydrogen separates out at the cathode during the electrolysis. As the solution becomes diluted there, my apparatus can easily be adapted to this investigation by a slight modification. I then also intend to return to Daniell and Miller's method and to their discordant results.

BIOGRAPHICAL SKETCH

JOHANN WILHELM HITTORF was born in Bonn, May 27, 1824. He was made a member of the Philosophical Faculty of the Royal Academy of Münster in 1852, with the title of Professor of Chemistry and Physics, having previously occupied the position of Docent in the same institution. By the reorganization of the faculty in 1876, he was relieved of the instruction in chemistry. As professor of physics he continued work of instruction until 1890, when sickness compelled him to give up active work. He was then made Professor Emeritus, which position he still holds.

The valuable contributions which Hittorf has made to science, have made him an honored member of many societies. He is corresponding member of the Königliche Gesellschaft of Göttingen, Berlin, and Munich; foreign member of the Danish Academy of Copenhagen, and honorary member of the Manchester Literary and Philosophical Society, and of the London Physical Society. The degree of M.D. was conferred on him by the medical faculty of the University of Leipzig, and in 1897 he was honored with the Prussian order *pour le mérite* for science and arts. In 1898 he was elected Honorary President of the German Electrochemical Society.

Of Hittorf's published papers, most of which have appeared in Poggendorff's and Wiedemann's *Annalen* since 1847, the extended series of investigations on electrolysis, of which the above is the first, should first be mentioned. In 1864 the "Multiple Spectra" of the elements was established in an investigation with Plücker. In the years 1869–1874 a series of important papers appeared on the phenomena accompanying the passage of electricity through rarefied gases, and on the remarkable behavior of cathode rays.

In Chemistry may be mentioned an investigation on the allotropic forms of selenium and phosphorus, in which a new black metallic crystalline modification of the latter was discovered. Quite recently Hittorf has contributed several articles to the *Zeitschrift für Physikalische Chemie.*

ON THE CONDUCTIVITY OF ELECTROLYTES DISSOLVED IN WATER IN RELATION TO THE MIGRATION OF THEIR COMPONENTS

BY

F. KOHLRAUSCH
Director of the Reichsanstalt, Charlottenburg

Presented May 6, 1876, before the Göttingen Academy of Sciences

(*Göttingen Nachrichten*, 1876, 213; Carl, *Repertorium*, **13**, 10, 1877)

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ON THE CONDUCTIVITY OF ELECTROLYTES DISSOLVED IN WATER IN RELATION TO THE MIGRATION OF THEIR COMPONENTS

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I TAKE the liberty of presenting, as an appendix to a previous communication (these Proceedings, 1874, 405), a few remarks on the Mechanics of Electrolysis. I have shown with Mr. Grotrian, in the paper mentioned, that dilute aqueous solutions of the chlorides of all the alkalies and alkali earths possess nearly the same conductivity when an equal number of equivalents are dissolved. in equal volumes of water.

If the differences still remaining be compared with the transference numbers of the migrating components, as determined by Wiedemann, Weiske, and especially by Hittorf* in his classical work on *The Migration of Ions During Electrolysis*, an evident connection between the two quantities is at once noticed. By following this matter further, one is led to an assumption, remarkable for its simplicity, regarding the nature of the electrical resistance of dilute solutions, which I will now develop with the aid of the previous examples, as well as by some which I have more recently observed.

* Hittorf, Pogg. *Ann.*, **89**, 177; **98**, 1; **103**, 1; **106**, 513. Wiedemann, ibid., **99**, 182. Weiske, ibid., **103**, 466.

Pure water does not possess an appreciable conductivity, and hence it is most natural to regard current conduction in an aqueous solution of a body as due, not to conduction by the water, but by the dissolved particles. This view is probably held by most physicists at the present time.* According to it the water acts only as a medium in which the electrolytic displacements take place, and the electrical resistance of the solution would be the frictional resistance which the migrating elements of the salt, etc., experience against the water particles and against each other.

If, now, the solution be very dilute, this friction will occur for the most part on the water particles. Hence one will be further tempted to conclude—and this is a conclusion which to my knowledge has never previously been drawn — *that in a dilute solution every electrochemical element* (*e.g.*, hydrogen, chlorine, or also a radical, as NO_3) *has a perfectly definite resistance pertaining to it, independent of the compound from which it is electrolyzed.* As we know little concerning the nature of a solution, however, it is clear that such an assumption is justified only by experimental verification.

I think I can now prove that the facts correspond very nearly to the above law for a large group of substances—namely, for all the univalent acids and their salts whose conductivity has been investigated.

For this purpose let us consider dilute solutions which contain an equal number of electrolytic molecules in equal volumes. I shall call such solutions *electrochemically equivalent.* Of course the electrolytic molecule is not always to be regarded as the molecule now assumed in chemistry, but only that fraction of the latter which is decomposed by the same quantity of electricity as a molecule composed of two chemically univalent components.

Let each solution form a column of unit cross-section, and let it be acted on by an electric force (potential gradient), unity. If the ions have the opposite velocities, u_0 and u, then by Faraday's law, according to which each migrating partial molecule carries with it a quantity of electricity independent of its nature, the current is proportional to u_0+u

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* Compare, *e.g.*, Hittorf; Quincke, Pogg. *Ann.*, **144**, 2; Wiedemann, Galvanismus (2), I., p. 471.

(and to the number of molecules contained in unit length of the column, which, however, shall be the same in all solutions).

On the other hand, the strength of the current through unit cross-section due to an electromotive force unity is, as well known, nothing else than what is called the conductivity, l, of the solution, which must therefore be proportional to u_0+u. The ratio of the velocities u_0 and u has been determined by Hittorf for a large number of solutions. We will call with Hittorf $n=\frac{u_0}{u_0+u}$ the transference number of the component which has the velocity u_0.

Now let two electrochemically equivalent solutions of two compounds, I and II, be given, which have one component in common—*e.g.*, that one having the velocity u_0, while the other components have the velocities u_1 and u_2 respectively. Let the corresponding conductivities of the solutions be l_1 and l_2. Then from the above

$$\frac{l_1}{l_2}=\frac{u_0+u_1}{u_0+u_2}=\frac{\left(\frac{u_0}{u_0+u_2}\right)}{\left(\frac{u_0}{u_0+u_1}\right)}=\frac{n_2}{n_1}.$$

Hence our hypothesis requires *that the conductivity of electrochemically equivalent solutions of two electrolytes, having a component in common, shall vary inversely as the transference numbers of the common component;* or, *that the product of the conductivity of each solution and the corresponding transference number of the common component shall be equal.*

This conclusion is verified in the following compilation of all material on electrolytes of univalent acids at my disposal.

TABLE

	l_1	n_1		l_2	n_2	$\frac{l_1}{l_2}$	$\frac{n_2}{n_1}$
KCl	977	0.510	NaCl	807	0.63	1.21	1.23
“	“	“	NH_4Cl	949	0.51	1.03	1.00
“	“	“	$Ca\frac{1}{2}Cl$	742	0.68	1.32	1.33
“	“	“	$Mg\frac{1}{2}Cl$	712	0.69	1.37	1.35
“	“	“	$Ba\frac{1}{2}Cl$	800	0.62	1.22	1.22
“	“	“	$Sr\frac{1}{2}Cl$	777	0.65	1.26	1.27
“	“	“	HCl	3230	0.161	0.302	0.316
KNO_3	927	0.495	$AgNO_3$	810	0.53	1.14	1.07
“	“	“	HNO_3	3360	0.142	0.275	0.287
KBr	1044	0.514	HBr	3100	0.178	0.329	0.346
KI	1048	0.50	HI	3190	0.258	0.328	0.516
KCl	977	0.490	KBr	1044	0.486	0.94	0.99
“	“	“	KI	1048	0.50	0.93	1.02
“	“	“	KNO_3	927	0.505	1.05	1.03
“	“	“	$KClO_3$	843	0.55	1.16	1.12
“	“	“	KAc	699	0.676	1.40	1.38

In the whole table there is but one considerable difference between the ratios of n and of l—namely, in the case of HI. But in this very case it is probable, from the values of the transference numbers which Hittorf gives, that u has been found too large for iodine. Such an error is easily possible, as only one observation was made, and as control experiments cannot be made at both electrodes in the case of acids as in the case of salts.

The assumption of the independent migration of ions may also be tested by the transference numbers alone, and hence confirmed or confuted in the case of substances whose conductivity is not yet known. It is easily seen that the following relation must hold between the transference numbers of the four compounds which can be formed from two pairs of electrochemical atoms A A′ and B B′:

Let m_1 n_1, m_2 n_2, m_3 n_3, m_4 n_4 be the transference numbers of the electrolytes A B, A B′, A′ B, A′ B′ respectively, where m refers always to A, n to B, and of course $m+n=1$.

Then our assumption evidently requires that

$$\frac{m_1}{n_1}\frac{m_4}{n_4}=\frac{m_2}{n_2}\frac{m_3}{n_3}.$$

In the following six examples, taken from Hittorf's determinations, together with Wiedemann's values for HNO_3, the deviations from the required relation amount to scarcely more than is to be expected from the uncertainty of the observations themselves.

A	A'	B	B'	KCl n_1	KNO$_3$ n_2	NaCl n_3	NaNO$_3$ n_4	$\frac{m_1 m_4}{n_1 n_4}$	$\frac{m_2 m_3}{n_2 n_3}$
K	Na	Cl	NO_3	0.51	0.495	0.63	0.614	0.60	0.60
Na	Ba	Cl	NO_3	0.63	0.614	0.616	0.61	0.38	0.39
H	Ca	Cl	NO_3	0.161	0.142	0.68	0.62	3.18	2.84
K	Na	Cl	I	0.51	0.50	0.63	0.62	0.59	0.59
K	Na	Cl	Ac	0.51	0.324	0.63	0.443	1.21	1.23
K	Ag	Ac	NO_3	0.324	0.495	0.627	0.626	1.88	1.72

From the experimental confirmation of these two consequences, I am of the opinion that the law here suggested has great probability—that is to say, that we may speak of the mobility* of an electrolytic component in water.

I give below, as provisional, the following numbers for the ~~mobility~~ velocity u, referred to that of hydrogen as unity:

H	Br	Cl	I	K	NH_4	NO_3
1.00	0.19	0.19	0.18	0.18	0.18	0.17

Ag	ClO_3	Ba	Na	Ca	Sr	Mg	Ac
0.15	0.15	0.12	0.11	0.10	0.10	0.09	0.09

The mobility of hydrogen exceeds, therefore, that of the other elements five to eleven times, and it may indeed be asserted with certainty *that the high conductivity of acids is due to the fact that hydrogen is one of their migrating components.* Possibly the same remark also applies to the good conduction of the alkalies in solution.

The above numbers also give the possibility of calculating the conductivity of a dilute solution of an electrolyte the components of which have the mobilities u and u'. If one part by weight of the solution contains p parts by weight of the elec-

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*["*Beweglichkeit.*" *In modern phraseology it is more customary to speak of the "velocity of migration," "Wanderungsgeschwindigkeit" of an ion.*]

trolyte, and if A denotes its electrochemical molecular weight, then the conductivity of the solution at 18° referred to mercury is given approximately by

$$k=0.027\,\frac{u+u'}{A}\cdot p.$$

The factor by which p is multiplied represents, therefore, the specific conductivity.

Finally the force which produces a definite velocity of one of the above components may be expressed in mechanical units, as first shown by W. Weber and R. Kohlrausch* in the case of water, although at that time under assumptions regarding electrolysis which do not correspond to ours. By introduction of the absolute resistance of mercury and of the electrochemical equivalent, one obtains for hydrogen, for example, the velocity $\frac{2.9\text{ mm.}}{10^{12}\text{ sec.}}$, corresponding to an electrical force of separation unity expressed in absolute magnetic measure (millimeter, milligram, and second as fundamental units). From this it follows, that if the electromotive force of a Daniell cells acts on a column of dilute HCl (or HBr, HNO_3, etc.) a millimeters in length, the hydrogen will be moved along with a velocity of $0.33\,\frac{\text{mm.}}{\text{sec.}}$. The velocity of any other ion under the same conditions is obtained by multiplying this number by u.

If the electromotive force be calculated in mechanical units on the assumption that the hydrogen is moved by the force exerted by the electromotive force on the quantity of electricity migrating with it, it is found that in order to force the hydrogen electrolytically through the water with a velocity of $1\,\frac{\text{mm.}}{\text{sec.}}$, a force equal to the weight of 33,000 kg. must act on each milligram of hydrogen.† If 33,000 be divided by the product of the electrochemical molecular weight and the value of u for another component, the corresponding value for that component is obtained.

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* *Abhandlungen der K. Sächs. Ges. d. Wiss.*, v., 270.

† These figures are based solely on resistances to conduction, and have, therefore, nothing to do with the overcoming of the forces of chemical affinity which manifest themselves in the polarization of the electrodes.

Further experiments alone can decide how far the laws here developed may be generalized on the one hand, or must remain limited to certain groups of substances on the other, and to what extent they apply rigidly or only approximately. I must mention here, however, that of the substances whose conductivities were investigated, one—namely, acetic acid—stands quite isolated from the above relations, if it be assumed, from analogy with the acetic acid salts, that hydrogen forms one of its ions. If this be so, acetic acid should be a very good conductor, while in reality, even in aqueous solution, it does not even approach the worst conducting of the solutions here considered. From this quite abnormal behavior it would follow that in acetic acid other conditions are present, either in regard to its chemical constitution, or in the nature of its solution in water,* than in the case of the other acids, or even the acetic acid salts. An exactly similar case occurs in aqueous ammonia, although this does not belong to the examples mentioned in this paper. I expected that aqueous ammonia would conduct particularly well, since ammonia salts conduct exceedingly well, and potassium and sodium hydrate, moreover, conduct much better than their salts. But, on the contrary, this substance, like acetic acid, is such a poor conductor that it evidently belongs to an entirely different class of bodies. This fact lends support to the view of some chemists, that aqueous ammonia does not contain the compound NH_4OH corresponding to the alkali hydrates, but is only a solution of NH_3.

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I defer the further discussion of such cases, as well as my observations on the polybasic acids and their salts, to the future, remarking only in the mean time that their conductivity comes out too large when calculated from the above transference numbers of their components.

In conclusion I wish to call attention to another noteworthy point of comparison between the conductivity and the transference numbers of dissolved electrolytes, to which Mr. Hittorf himself has very kindly called my attention. Most electrolytes investigated show a decreasing value of the transference number of the cation with increasing concentration. A few, how-

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* Hydrocyanic acid appears to act similarly.

ever, retain nearly the same transference relations in strong as in dilute solutions. This is more or less the case with the potassium salts, and next to them ammonium chloride, the only ammonium salt investigated.

Now the conductivities of the last-mentioned substances show a similar agreement, in contrast to the others. In the case of most electrolytes the ratio of the conductivity to the percentage composition of the solutions diminishes continuously and very considerably; so much so, in fact, that not infrequently the known phenomenon of a maximum occurs. In the case of potassium and ammonium salts, however, this ratio is much more constant. From this relation, noticed as stated by Hittorf, it would follow that the resistances to motion which arise in denser solutions affect, in general, the cation more than the anion. But I would add at once, however, that a diminished mobility must also be ascribed to the latter, in order to explain the observed conductivity of stronger solutions.

WÜRZBURG, *May* 1, 1876.

BIOGRAPHICAL SKETCH

FRIEDRICH KOHLRAUSCH, son of Rudolph Kohlrausch the physicist, was born at Rinteln, Germany, in 1840. He was educated at the Polytechnicum at Cassel, and at the Universities of Marburg, Erlangen, and Göttingen, making his doctor's degree at the last-named university, under Wilhelm Weber in 1863. He then acted as assistant in the astronomical observatory at Göttingen, in the laboratory of the Physical Society at Frankfort, and in the University of Göttingen. He held the professorship of physics in the Polytechnicum at Zurich, 1870–71; at Darmstadt, 1871–75; and at the University of Würzburg until 1888, when he succeeded Kundt as director of the physical laboratory at Strassburg. On the death of v. Helmholtz, in 1894, he left Strassburg to accept the appointment of director of the Physikalisch Technische Reichsanstalt at Charlottenburg, which position he now holds.

The numerous contributions of Professor Kohlrausch to physical science have been mostly in the domain of electricity and magnetism, and are characterized by the high degree of precision with which they have been carried out. A number of the best methods and instruments now used in electrical and magnetic measurements are due to him. In addition to the extensive series of researches on the electrical conductivity of electrolytes, begun in 1868 and continued to the present time, may be mentioned his investigations on elasticity in 1866; his series of researches on magnetic measurements, 1881–84; and his determination with W. Kohlrausch, of the electrochemical equivalent of silver in 1886. He is also the author of one of the best-known works on physical laboratory methods, entitled *Leitfaden der praktischen Physik,* which has been translated into four different languages.