

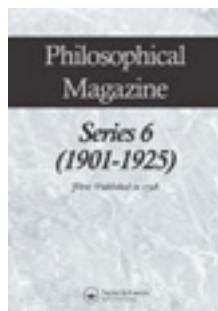
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III. On the concentration at the electrodes in a solution, with special reference to the liberation of hydrogen by electrolysis of a mixture of copper sulphate and sulphuric acid

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the spectrum as sufficiently accurate to make this point certain. The work in this region will have to be repeated under more favourable conditions.

It was our intention to apply the results of the work to a proof of the Ketteler-Helmholtz dispersion formula, but the discovery of the second absorption-band makes this impossible until the extent of the band has been determined, and the extinction coefficient measured, a matter of considerable difficulty. Some of the discrepancies found by Pflüger between his calculated and observed curves, he thought might be explained by the possible presence of an absorption-band in the remote ultra-violet.

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III. *On the Concentration at the Electrodes in a Solution, with special reference to the Liberation of Hydrogen by Electrolysis of a Mixture of Copper Sulphate and Sulphuric Acid.*
By HENRY J. S. SAND, *Ph.D.*, *Bowen Research Scholar at Mason University College, Birmingham* *.

CONTENTS :—Historical introduction.—Theoretical consideration of the Liberation of Two Constituents at an Electrode.—Calculation of the Concentration in a Solution contained in a cylindrical vessel, across one end of which a constant flow of salt is taking place.—Application of results to obtain Values for the Concentration at the Electrode of the Solution of a single Salt and of a Mixture.—Experimental determination of the Time required till Hydrogen appears during Electrolysis of an Acid solution of Copper Sulphate.—A new method for determining the Diffusion-Coefficient of Copper Sulphate.—Experiments to show the great influence of Convection-Currents on the quantity of Hydrogen given off in the Electrolysis of an Acid Solution of Copper Sulphate.—Summary of results.

SINCE the electrolysis of mixtures first attracted the attention of scientists, three distinct views have been held about the processes which take place at the electrodes.

In 1857 Magnus† put forward the theory that in the solution of a mixture of two salts, only one is decomposed if a current of small density be employed ; if, however, the current-density exceeds a certain definite value, the second salt also suffers from decomposition. He attempted to find this definite value in the case of a mixture of copper sulphate and sulphuric acid, ascribing it to a current-density which produced a visible amount of hydrogen at a vertical cathode within fifteen seconds. The result obtained was, that the

* Communicated by the Physical Society : read Oct. 26, 1900.

† Pogg. *Ann.* cii. p. 17.

value was roughly independent of size, distance, &c. of the electrodes, and only a function of the composition of the electrolyte.

About the same time Hittorf was engaged in his fundamental researches on the processes which take place within the electrolyte. His experiments, as is well known, proved that in the interior of the solution of a mixture of two salts, both take part in the conduction of the current at all current-densities. Regarding the process which takes place at the electrode, he at that time assumed that the ions of both salts were primarily deposited in the same proportion in which they had taken part in the conduction of the current within the liquid. In most cases, however, one of the components would act chemically upon the solution with a definite reaction-velocity; and it was only when this velocity was exceeded by the rate at which it was being primarily deposited at the electrode that its liberation would become perceptible*. Thus in a mixture of copper sulphate and sulphuric acid, hydrogen would be primarily liberated at all current-densities; but it would only become visible when the velocity with which it was supposed to decompose copper sulphate in the nascent state was exceeded by the rate at which it was being primarily set free.

It appears that it was Le Blanc who first insisted sufficiently on the fact that the mode of conduction of the current within any part of the interior of the electrolyte does not necessitate the same mode at the electrodes. His investigations having proved that the same minimum electromotive force must be applied to various acids and bases in order to cause the continuous passage of a current of appreciable magnitude through them, Le Blanc framed his well-known theory, that whereas conduction through the interior of an acid or a base is due in almost exclusive preponderance to its own ions, the transmission from the solution to the electrolyte must be ascribed primarily to the ions of water. Generalizing this statement, he expressed the view † that in a mixture of ions at an electrode those exclusively are set free which require the smallest E.M.F. for their liberation; and it is only when their concentration at the electrode has gone down to zero, that those requiring a higher E.M.F. for their liberation also appear. Thus in a mixture of copper sulphate and sulphuric acid, copper only should be deposited till its concentration at the electrode has gone down to zero, after which hydrogen also would be liberated.

* Pogg. *Ann.* ciii. p. 46.

† *Zeitschr. phys. Chem.* xiii. p. 172.

The decomposition of mixtures has recently been examined theoretically by Nernst*. We shall consider the same subject from a slightly different point of view.

For this purpose we adopt the view, probably best adapted for the treatment of chemical problems, that the energy expended by the current in passing through the drop of potential at either electrode is the equivalent of the free energy required to effect the change from ionic to free state, or *vice versa*, taking place there, plus the energy expended on any other processes which may accompany the passage of the current, and which finally result in an irreversible heating-effect. For our purposes we are justified in considering each electrode separately, as we can always suppose the electrode not under consideration so large that the nature of the processes taking place there and the energy expended there per g.-ion do not vary appreciably with the current-strength. We shall suppose a mixture of two salts given, and consider the deposition of n_1 g.-equivalents of the cation most easily deposited. For the present we shall assume that if processes occur which irreversibly cause the production of heat, this quantity of heat shall be proportional to the number of g.-equivalents liberated, so that it can be represented by hn_1 , h being a constant. Under these conditions, if w_1 be the quantity of free energy required to liberate one g.-equivalent, the amount of work done in the deposition of the n_1 g.-equivalents will be independent of the current-density and equal to $n_1(w_1 + h)$. Now the quantity of electricity which causes this will, according to Faraday's law, have the value fn_1 , f being Faraday's constant of $96540 \frac{\text{amp.} \times \text{sec.}}{\text{g.-equiv.}}$. Therefore, if the

drop of potential from the electrode to the liquid be E , the work done by the current in passing through it will be En_1f , and this according to our assumptions is equal to $n_1(w_1 + h)$, or $Ef = w_1 + h$.

This means that the difference of potential between the electrode and the liquid is independent of the current-density employed, and is always the same as the minimum E.M.F. necessary to deposit those ions which are most easily set free. If therefore there be ions of a second substance present, which require for their liberation a minimum E.M.F., $E_2 > E$, none of them will be liberated so long as any of the ions first considered are left in contact with the electrode. It is only when $E_2 = E$ that simultaneous deposition of both occurs. Our suppositions have thus proved equivalent to Le Blanc's view.

* *Zeitschr. phys. Chem.* xxii. p. 541.

It should be noted that our assumption that any heating effect which may take place is proportional to the number of ions deposited, excludes the liberation of heat owing to anything in the nature of electrolytic resistance in the vicinity of the electrode, being bound up with the deposition of the ions—electrolytic heating in a given electrolyte being, as is well known, proportional to the square of the current. In arriving at our result, we also excluded the supposition that at high current-densities ions of the two salts should enter into chemical combination, forming complex ions.

As is well known, the E.M.F. necessary to deposit an ion from a solution on a given electrode varies within certain limits with its concentration in the solution. In the case of reversible processes it can be calculated in volts by Nernst's formula: $E = 0.860 \times 10^{-4} \frac{1}{n} T \ln \frac{P}{p}$, T being the absolute temperature, n the valency of the ion, p its osmotic pressure in the solution, and P its so-called solution-tension. When two monovalent metals of solution-tension P_1 and P_2 are being simultaneously deposited as a mechanical mixture, this equation in connexion with $E_1 = E_2$ leads to

$$0.860 T \ln \frac{P_1}{p_1} = 0.860 T \ln \frac{P_2}{p_2} \text{ or } \frac{p_1}{p_2} = \frac{P_1}{P_2},$$

a formula which is given by Nernst in the paper quoted*.

* *Note.*—In his paper Nernst also gives a formula for the ratio γ of the quantity of the metal (1) deposited in g.-equivalents to the total number of equivalents liberated, the conditions being as above. This formula is based on the consideration which follows from the results just obtained, that if we have a solution containing the salts of two metals in a proportion in which they are not simultaneously deposited, the metal which is in excess of this proportion will at first be deposited alone until the proportion for simultaneous deposition be again attained. If we therefore start with a solution which contains the salts of two monovalent metals in the proportion given by the equation $\frac{p_1}{p_2} = \frac{P_1}{P_2}$, or, assuming complete dissociation and indicating concentrations by c ,

$$\frac{c_1}{c_2} = \frac{P_1}{P_2}; \dots \dots \dots (A)$$

then if we stir in such a manner as to keep the concentration uniform as nearly as possible, the ratio of concentrations which before stirring varied throughout the electrolyte, will have the tendency to become again uniformly

$$\frac{c_1'}{c_2'} = \frac{P_1}{P_2} \dots \dots \dots (B)$$

According to Neumann *, when copper is deposited from the normal solution of its sulphate on a copper electrode, it produces an E.M.F. aiding the current of 0.515 volt hydrogen; on the other hand, when it is reversibly deposited on a platinized platinum hydrogen electrode an E.M.F. of only 0.238 volt, *i. e.* a voltage higher by 0.277, is required to liberate hydrogen reversibly from a normal solution of its sulphate than is required to liberate copper under the same conditions.

Now according to Caspari's experiments †, a 0.23 volt higher electromotive force is required to set hydrogen free on a copper than on a platinized platinum electrode; *i. e.*, in order to deposit hydrogen on a copper electrode from a normal solution of sulphuric acid 0.507 volt more is required than to deposit copper on the same electrode from the normal solution of its sulphate. If we employ Nernst's formula to calculate the concentration of a copper solution, to deposit

It is easy to see that from the two equations (A) and (B) the ratio γ mentioned above can be calculated to be $\gamma = \frac{P_1}{P_1 + P_2}$. This is the formula given without explanation by Nernst. It should, however, be particularly noted that this ratio γ is not the result of simultaneous, but of successive deposition of the two metals, depending on the rate of stirring, and that, as will be seen later (note, p. 60), the ratio of simultaneous deposition, *e. g.* at the beginning of the experiment, has a different value, irrespective of the fact whether the current employed be large or small.

In order to obtain formulæ referring to simultaneous deposition, when no stirring takes place we assume the electrolysis to take place in a cylindrical vessel bounded by its cathode, and indicate distances from it by x , times by t , and name the quantity of each ion crossing any section in the differential of time in the direction towards the electrode, *i. e.* from greater values of x to less, $F_1 dt$ and $F_2 dt$ respectively; then, assuming complete dissociation, we have for simultaneous deposition of the two (monovalent) metals as above,

$$c_1 = \frac{P_1}{P_2} c_2 \text{ for } x=0;$$

from which follows :

$$\frac{\partial c_1}{\partial t} = \frac{P_1}{P_2} \frac{\partial c_2}{\partial t} \text{ for } x=0;$$

and as in every cross section $\frac{\partial F}{\partial x} = \frac{\partial c}{\partial t}$, this gives :—

$$\frac{\partial F_1}{\partial x} = \frac{P_1}{P_2} \frac{\partial F_2}{\partial x}, \text{ for } x=0.$$

(See also note on p. 60.)

* *Zeitschr. phys. Chem.* xiv. p. 222.

† *Ibid.* xxx. p. 93.

copper from which would require the same voltage as to liberate hydrogen from a normal solution of sulphuric acid at 15° , we find a value of about 2×10^{-18} normal. This means, according to the theoretical considerations advanced, that hydrogen will not be given off from an acid solution of copper sulphate till the concentration of the copper has practically gone down to zero at the electrode.

In apparent opposition to this, the experimental liberation of hydrogen from a not too concentrated acid solution of copper sulphate is a matter which can be accomplished by comparatively low current-densities, and doubt might well arise, whether the suppositions on which our deductions are based were not at fault. It might be supposed that diffusion of the copper sulphate in the liquid would effectually hinder its concentration from going down to zero at the electrode with the rapidity which the experiments require in order to justify the theory. Indeed, as far as I can see, the idea that the concentration of the copper is zero at parts of an electrode from which hydrogen is being given off has not been entertained by any of the experimenters who have published work on a mixture of copper sulphate and sulphuric acid.

It must be remarked here that changes of concentration in a liquid are in most cases no doubt effaced to a much greater extent by convection-currents than by diffusion. But in order to test the theory, it is possible experimentally to do away with convection-currents almost entirely by the methods described in the experimental part; besides from its very nature convection must be an erratic phenomenon, not amenable to calculation and which could not be depended on, continuously and uniformly, to neutralize changes of concentration arising on the total surface of an electrode. In order to test the theory experimentally, it would be necessary to calculate the concentration of the copper ions at the electrode of an acid solution of copper sulphate from which copper alone was being deposited, under the supposition that only diffusion, and no convection, neutralized differences of concentration brought about by the current. Unfortunately neither the laws of conduction of the current nor those of diffusion in a mixture are completely known, and if they were, their application would probably involve extremely great mathematical difficulties. It is therefore not possible accurately to solve the problem just stated. As will be seen later on, we can, however, solve it within certain limits by first turning our attention to the following simpler case.

Problem : Let us suppose electrolysis to take place in

a cylindrical vessel bounded at both ends by its electrodes. Let F g.-equivalents of salt be uniformly and constantly removed at one end, per unit of surface and time, and let the distance from the electrode forming the other end be so great that changes of concentration occurring there do not affect the concentration at the electrode under consideration. Further, let the initial concentration be uniform and equal to c_0 g.-equivalents per unit of volume. Find the concentration in the interior of the liquid and at the electrode at any given time t under the suppositions, that changes of concentration are neutralized by diffusion only, that this takes place according to Fick's law, and that it is not affected by the passage of the current through the liquid*.

As the concentration at any point of the liquid cannot be influenced by the nature of the cause producing the removal of the salt, it will be the same as that in a similar liquid in which a flow F was produced by a suitable gradient of concentration being artificially kept up immediately behind the electrode. In such a solution, and therefore also in the one under consideration, we have for the determination of the state of the liquid the first equation :

$$F = K \frac{\partial c}{\partial x}, \quad (1)$$

for $x=0$,

if concentrations at any point are indicated by c , distances from the electrode by x , and the diffusion-coefficient of the salt by K .

The uniformity of the concentration at the beginning of the experiment affords us the second equation :

$$c = c_0, \quad (2)$$

between $x=0$ and $x=l$ for $t=0$,

and the general expression of Fick's law gives us the third :

$$\frac{\partial c}{\partial t} = K \frac{\partial^2 c}{\partial x^2}, \quad (3)$$

Equations 1 and 3 are satisfied by the following general solution :

$$c = \frac{F}{K} x + \sum_{n=0}^{n=\infty} a_n \cos \left(\frac{n\pi}{l} x \right) e^{-\frac{n^2\pi^2 Kt}{l^2}} ; \quad . . . (4)$$

* *Note.*—The equations given here as far as No. 5 have already been given by H. F. Weber in the elaboration of his beautifully conceived method for the determination of the diffusion-coefficient of $ZnSO_4$ (*Wied. Ann.* vii. p. 539). Concentrations in a solution subjected to alternating currents have been recently examined by Warburg (*Wied. Ann.* lxxvii. p. 495).

and in order that equation 2 may be fulfilled, viz. that

$$c_0 - \frac{F}{K} x = \sum_{n=0}^{n=\infty} a_n \cos\left(\frac{n\pi}{l} x\right),$$

between $x=0$ and $x=l$,

we must, according to Fourier, make

$$\frac{1}{2} a_0 = \frac{1}{2} \int_0^l \left(c_0 - \frac{F}{K} x\right) dx = \frac{1}{2} l c_0 - \frac{1}{4} \frac{F}{K} l^2,$$

$$\frac{1}{2} a_n = \int_0^l \left(c_0 - \frac{F}{K} x\right) \cos\left(\frac{n\pi x}{l}\right) dx = -\frac{l^2 F}{\pi^2 n^2 K} (\cos n\pi - 1),$$

which is equal to 0 or

$$\frac{2l^2 F}{\pi^2 n^2 K}$$

according as n is even or odd.

Substituting these values in equation (4), we obtain

$$c = \frac{F}{K} x + c_0 - \frac{1}{2} \frac{F}{K} l + \frac{4lF}{\pi^2 K} \left(\cos \pi \frac{x}{l} e^{-\frac{\pi^2}{l^2} Kt} + \frac{1}{9} \cos 3\pi \frac{x}{l} e^{-9 \frac{\pi^2}{l^2} Kt} + \dots \right) \quad (5)$$

or

$$c = \frac{F}{K} x + c_0 - \frac{4lF}{\pi^2 K} \left(\frac{1}{8} \pi^2 - \cos \pi \frac{x}{l} e^{-\frac{\pi^2}{l^2} Kt} - \frac{1}{9} \cos 3\pi \frac{x}{l} e^{-9 \frac{\pi^2}{l^2} Kt} - \dots \right)$$

and remembering that :

$$\frac{\pi^2}{8} = \frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \dots$$

we find

$$c = \frac{F}{K} x + c_0 - \frac{4F}{\pi K} \sum_{n=1}^{n=\infty} \frac{l}{\pi (2n-1)^2} \left[1 - \cos (2n-1) \pi \frac{x}{l} e^{-(2n-1)^2 \frac{\pi^2}{l^2} Kt} \right].$$

The infinite series in the above expressions for c converge so slowly for large values of l , as to make them useless for numerical application. For $l = \infty$ all the single members of the series in the last equation become infinitely small, and the series assumes the nature of a definite integral. We

* This equation also fulfils the condition $F = K \frac{\partial c}{\partial x}$ for $x=l$. It can therefore be taken accurately to represent the concentration in a cylinder of length l , filled *e.g.* with CuSO_4 into which F g.-equivalents are introduced per unit of surface and time at the anode and the same amount is being taken away at the cathode, a fact which is utilized by Weber.

shall convert it into a definite integral and make l infinite by the substitutions :

$$n = \frac{q}{dq}, \quad \frac{l}{\pi} = \frac{\kappa}{dq},$$

dq being the differential of the variable q which assumes successively the values $dq, 2dq, \dots, q, \dots, \infty$, and κ an arbitrary positive constant. We thus obtain :

$$c = \frac{F}{K} x + c_0 - \frac{4F}{\pi K} \int_0^\infty dq \frac{\kappa}{4q^2} \left(1 - \cos \left(\frac{2q}{\kappa} x \right) e^{-\frac{4q^2 K t}{\kappa^2}} \right).$$

The value of κ being arbitrary, we can make :

$$\frac{4Kt}{\kappa^2} = 1, \quad \text{i. e. } \kappa = 2\sqrt{Kt},$$

and we find

$$c = \frac{F}{K} x + c_0 - \frac{2F}{\pi K} \sqrt{Kt} \int_0^\infty \frac{dq}{q^2} \left(1 - \cos \frac{xq}{\sqrt{Kt}} e^{-q^2} \right).$$

This expression is further simplified in the following manner: we differentiate twice according to x and obtain

$$\frac{\partial^2 c}{\partial x^2} = - \frac{2F}{\pi K \sqrt{Kt}} \int_0^\infty dq \cos \frac{xq}{\sqrt{Kt}} e^{-q^2}.$$

The value of the integral occurring here being known to be $\frac{\sqrt{\pi}}{2} e^{-\frac{x^2}{4Kt}}$, we have :

$$\frac{\partial^2 c}{\partial x^2} = - \frac{F}{K \sqrt{\pi Kt}} e^{-\frac{x^2}{4Kt}},$$

and making use successively of equations (3) and (2) we find

$$c = c_0 - \frac{F}{\sqrt{\pi K}} \int_0^t \frac{dt}{\sqrt{t}} e^{-\frac{x^2}{4Kt}}; \quad \quad (6)$$

an equation from which it is not difficult to obtain numerical values for c by one of the approximation methods. For the concentration at the electrode for which $x=0$, this equation assumes the extremely simple form

$$c = c_0 - 2F \sqrt{\frac{t}{\pi K}} = c_0 - 1.1284F \sqrt{\frac{t}{K}} \quad . . \quad (7)$$

Experimental application of equation (7).—(a) Application to the Solution of a Single Salt.

If we electrolyse the solution of a single salt, for example that of pure copper sulphate, we know that the value of F at the cathode in $\frac{\text{g.-equiv.}}{\text{cm.}^2 \text{ sec.}}$ is

$$\frac{in_a}{96540} = \frac{i(1-n_c)}{96540},$$

i being the current-density in $\frac{\text{amp.}}{\text{cm.}^2}$, n_a the transport value of the anion SO_4 , and n_c that of the cation Cu in the solution. The concentration at the electrode after electrolysing for t seconds will therefore be

$$c = c_0 - \frac{1 \cdot 1284}{96540} in_a \sqrt{\frac{t}{K}} = c_0 - \frac{1 \cdot 1284}{96540} i(1-n_c) \sqrt{\frac{t}{K}}. \quad (8)$$

This formula can be employed for the determination of K if coordinate values of c and t are known. Before, however, further attempting to apply it to electrolysis, it will be necessary to consider to what extent the conditions on which it is based can be fulfilled in electrolytic experiments.

Let us suppose electrolysis of a pure copper-sulphate solution to take place in a cylindrical vessel of length l , bounded at the top by a horizontal cathode, at the bottom by a horizontal copper anode. In such a vessel, kept at constant temperature, convection-currents will be reduced to a minimum, as the lighter layers of less concentrated solution are continually being produced at the top, and the more concentrated ones at the bottom.

Our formula being based on the assumption of an infinitely distant anode does not comprise the fact that the anode of the real vessel we are now considering is causing a continuous flow of salt into the liquid at the distance l below the cathode, which is equal to the flow out of it. It is, however, not difficult to see that the following statements are correct:—(1) The real concentration at the anode and in the solution is greater than that given by the formula. (2) The difference between the real concentration and the calculated value is a maximum at the anode, and decreases continually as we approach the cathode. These first two statements can be inferred from the principle of superposition. (3) The real concentration at the distance $\frac{l}{2}$ below the cathode is (either according to Weber's formula (5) or from considerations of

symmetry) constantly c_0 ; the difference between real and calculated values therefore is

$$\frac{F}{\sqrt{\pi K}} \int_0^t \frac{dt}{\sqrt{t}} e^{-\frac{l^2}{16Kt}}$$

It is easy to see that as long as $t < \frac{l^2}{8K}$ the value of this function is smaller than

$$F \sqrt{\frac{t}{\pi K}} e^{-\frac{l^2}{16Kt}}$$

and from statement No. 2 we can conclude that the expression just given is also an upper limit for the difference between the real and calculated values at the cathode. In all the experiments carried out, this quantity is absolutely negligible.

We now come to the reconsideration of our assumption that diffusion in a solution is unaffected by the passage of a current through it. This question was first tested experimentally by H. F. Weber in the case of a zinc sulphate solution, and answered by him in the affirmative. It has recently been very thoroughly examined theoretically by Kohlrausch*. As shown by him, changes of concentration are in general brought about by the passage of a current through a solution of non-uniform concentration. These changes are in the case of a cylindrical vessel given for each ion in our notation by the formula

$$\frac{\partial c}{\partial t} = \pm \frac{i}{96540} \frac{\partial}{\partial x} \left(\frac{ac}{\kappa} \right), \quad \dots \quad (9)$$

in which c is the concentration of the ion under consideration, a is its mobility, and κ the conductivity of the solution. The positive or negative sign must be taken according as the ion is positive or negative (in contrast to Kohlrausch's notation, where the positive ions move from smaller values of x to greater). As is known, $\frac{ac}{\kappa} = n$ is Hittorf's transport value of the ion under consideration, and we can write the above equation in the form

$$\frac{\partial c}{\partial t} = \pm \frac{i}{96540} \frac{\partial n}{\partial c} \frac{\partial c}{\partial x}, \quad \dots \quad (10)$$

from which it can be concluded that in the interior of a solution of a single salt in which the transport values are

* Wied. *Ann.* lxii. p. 209 (1897).

independent of concentration, no change of concentration is ever brought about by the passage of the current. In the case of copper sulphate, however, n_c , the transport value of the copper, is not independent of the concentration. It is given according to Kohlrausch by Hittorf and Kirmis as

$$\frac{\partial n_c}{\partial c} = -0.047 \frac{\text{cm.}^3}{\text{mg.-equiv.}}$$

We have, therefore, for differences of concentration brought about by the passage of the current at every point of a copper-sulphate solution:

$$\frac{\partial c}{\partial t} = -\frac{0.047}{96540} i \frac{\partial c}{\partial x}$$

$\frac{\partial c}{\partial x}$ in our solutions being always positive, we can conclude that this effect will cause a general lowering of concentration, and that the value given by equation (8) for c is slightly too large and must be regarded as an upper limit.

We can also find a lower limit for c by the following considerations. The value of $\frac{\partial c}{\partial x}$ for $x=0$ is given by equation (1), we therefore know that at the electrode, owing to the effect we are considering alone

$$\begin{aligned} \frac{\partial c}{\partial t} &= -\frac{0.047 i^2 n_a}{96540^2 K}, \\ \Delta c &= -\frac{0.047 i^2 n_a t}{96540^2 K}. \end{aligned}$$

This value is, however, too large when taken to represent the total lowering of concentration. We see this when we remember that the gradient of concentration is always a maximum at the electrode, decreasing continuously as we depart from it, and that the lowering of concentration due only to passage of the current will therefore, according to the general equation (10), also be a maximum at the electrode, decreasing with increasing distance from it; this in its turn will have the effect of increasing the gradient at all points of the liquid and thus also increasing diffusion. We have therefore as extreme limits for the concentration at the electrodes of a copper-sulphate solution in which diffusion takes place according to Fick's law, the values given by the equation 8 and by the equation

$$c = c_0 - \frac{1.1284}{96540} i n_a \sqrt{\frac{t}{K} - \frac{0.047 n_a i^2 t}{96540^2 \cdot K}} \quad \cdot \quad \cdot \quad (11)$$

It is of importance to know by how much the value of $\frac{i^2 t}{K}$ differs when determined by either the one or the other of these equations. This calculation does not offer sufficient interest to give it in detail, we shall therefore only state the result that the ratio of the difference between $\frac{i^2 t}{K}$ calculated by (11) or calculated by (8) is given sufficiently accurately by the expression

$$- \frac{2 \times 0.047}{1.1284^2} \frac{c_0 - c}{n_a};$$

which for values of

$$c_0 = 0.2096 \frac{\text{mg-equiv.}}{\text{cm.}^3}, \quad \text{and } c = 0,$$

the only ones employed in the experiments, amounts to about $2\frac{1}{2}$ per cent., *i.e.* K , calculated by (8), is $2\frac{1}{2}$ per cent. smaller than calculated by (11).

In concluding these remarks it must be mentioned that, according to Wiedeburg's* careful investigation of the diffusion of copper sulphate, this does not accurately follow Fick's law, the diffusion-coefficient decreasing slightly with increasing concentration. A thorough examination based upon Wiedeburg's law would, however, lead beyond the scope of this paper.

(b) *Application of Equation (7) to a mixture of Copper Sulphate and Sulphuric Acid.*

As has already been stated, we shall in dealing with mixtures be obliged to confine ourselves to obtaining upper and lower limiting values for the concentration at the electrodes, which will enable us to follow the real values in broad lines in their dependence on initial concentration and current density. Great accuracy in these values will not be required, and we shall be justified in wholly neglecting influences which only slightly affect the results. We shall thus suppose, that in a mixture of copper sulphate and sulphuric acid, the diffusion of the former is not affected by the presence of the latter.

We first proceed to determine limits for the flow F , defined by $F dt$ being the quantity of copper brought by diffusion in the differential of time to each unit of surface of the electrode, when copper alone is being deposited on it. Using the same

* Wied. Ann. xli. p. 675.

notation as above, the flow of copper out of the solution at the electrode is

$$\frac{i \text{ g.-equiv.}}{96540 \text{ cm.}^2 \text{ sec.}}$$

and the flow towards the latter, due to electrolysis

$$\frac{ac \text{ } i \text{ g.-equiv.}}{\kappa 96540 \text{ cm.}^2 \text{ sec.}}$$

The flow F due to diffusion is therefore

$$\frac{i}{96540} \left(1 - \frac{ac}{\kappa}\right).$$

This quantity is variable, increasing continually from its original value to the value $\frac{i}{96540}$, which it assumes when c has gone down to 0. The quantity $\frac{ac}{\kappa} = n_c$, which we may call the transport value of the copper in the solution, can, as is known, be determined experimentally for the values of concentration and conductivity which exist at the beginning of the experiment. For this purpose it is necessary to pass an arbitrary quantity of electricity q through the solution, and to determine the decrease in copper in a region bounded on the one side by the anode, on the other by solution still having the original composition of the liquid (making the necessary correction for copper dissolved from the anode).

This decrease is equal to $\frac{ac}{\kappa} \frac{q}{96540}$ g.-equiv., and has been determined by Schrader* in the case of certain mixtures — the same mixtures which have been employed for this present work. If the value of this decrease in grammes be α , and the quantity of silver deposited in a silver voltameter by the current employed be β , both of these values having been given by Schrader, then

$$\frac{ac}{\kappa} \frac{q}{96540} = \frac{\alpha}{31.59}, \quad \frac{q}{96540} = \frac{\beta}{107.66},$$

and

$$1 - \frac{ac}{\kappa} = 1 - n_c = \frac{\beta}{107.66} - \frac{\alpha}{31.59}, \dots \dots (12)$$

the numbers 31.59 and 107.66 being the equivalent weights of copper and silver respectively.

* *Ztschft. f. Elektrochemie*, iii, p. 502.

We thus find that if we pass a current of constant density i through an acid solution of copper sulphate, until the concentration at the cathode has gone down to zero, the values of F at the beginning and at the end of the experiment can both be calculated, and we shall be justified in assuming that the concentration actually attained at any time t could also

have been attained if a constant flow $F' = \frac{n'i}{96540}$ lying some-

where between the extreme values of F had taken place. Thus, as far as variability of F is concerned, we can express the concentration at the electrode at any time by the formula

$$c = c_0 - \frac{1.1284}{96540} n'i \sqrt{\frac{t}{K}}, \dots \dots \dots (13)$$

n' being contained between 1 and the value of $1 - n_c$ given in equation (12).

We now come to the consideration of the effect of the passage of the current through the liquid on its concentration. As has already been stated, this is expressed for a positive ion by the equation

$$\frac{\partial c}{\partial t} = \frac{i}{96540} \frac{\partial}{\partial x} \left(\frac{ac}{\kappa} \right).$$

In the case we are now considering the concentration c of the copper will vary extremely rapidly as we approach the cathode, the conductivity κ of the solution on the other hand will remain fairly constant, as the solution, while becoming poorer in Cu and SO_4 ions, will at the same time become richer in H ions, which are brought to the electrode without being liberated there. As we only desire to obtain rough values, we shall therefore be justified in assuming κ constant and equal to the conductivity at the beginning of the experiment. The mobility of the copper we also assume constant. We thus have

$$\frac{\partial c}{\partial t} = \frac{ia}{96540 \kappa} \frac{\partial c}{\partial x}.$$

As $\frac{\partial c}{\partial x}$ is always positive, we can conclude that the passage of the current will have the general effect of raising the concentration in parts of the liquid near and at the electrode where $\frac{\partial c}{\partial x}$ is of appreciable magnitude. The value given by equation (13) must therefore be regarded as a lower limit.

Still more must

$$c > c_0 - \frac{1.1284}{96540} i \sqrt{\frac{t}{K}} \dots \dots \dots (14)$$

We can also find an upper limit for c , by determining the increase of concentration Δc at the electrode due only to passage of the current through the solution, by a precisely similar method to that employed for finding the corresponding decrease in the case of pure CuSO_4 on page 56. In the way shown there, it can also be seen here that the value obtained is too large when taken to represent the combined effect of diffusion and passage of the current. As the final result, we obtain

$$c < c_0 - \frac{1.1284}{96540} n' i \sqrt{\frac{t}{K}} + \frac{an'}{96540^2 \kappa} \frac{i^2}{K} t^* ;$$

* *Note.*—If we had made no assumption about a and κ this inequality would be

$$c < c_0 - \frac{1.1284}{96540} n' i \sqrt{\frac{t}{K}} + \int_0^t \frac{dti}{96540} \frac{\partial}{\partial x} \left(\frac{ac}{\kappa} \right),$$

from which, in conjunction with inequality No. 14, can be concluded

$$\frac{\partial c}{\partial t} = - \frac{1.1284 n' i}{2 \times 96540 \sqrt{K} t} + \epsilon \frac{i}{96540} \frac{\partial}{\partial x} \left(\frac{ac}{\kappa} \right),$$

ϵ being a number contained between 0 and 1.

This formula enables us to obtain some further information about the ratio $\frac{F_1}{F_2}$, in which two monovalent metals can be deposited, which is mentioned in the note on p. 49, if we suppose that in the mixture assumed there the two salts diffuse independently of each other. The equation

$$\frac{\partial c_1}{\partial t} = \frac{P_1}{P_2} \frac{\partial c_2}{\partial t}$$

then leads to

$$\frac{P_1}{P_2} = \frac{\frac{1.1284 n_1' i_1}{2 \times 96540 \sqrt{K_1}} + \epsilon_1 \frac{i_1 \sqrt{t}}{96540} \frac{\partial}{\partial c} \left(\frac{a_1 c_1}{\kappa} \right) \frac{\partial c}{\partial x}}{- \frac{1.1284 n_2' i_2}{2 \times 96540 \sqrt{K_2}} + \epsilon_2 \frac{i_2 \sqrt{t}}{96540} \frac{\partial}{\partial c} \left(\frac{a_2 c_2}{\kappa} \right) \frac{\partial c}{\partial x}}$$

from which for $t=0$ we obtain, remembering that for this value of t $n'=1-n_c$; and also that $\frac{i_1}{i_2} = \frac{F_1}{F_2}$:

$$\frac{F_1}{F_2} = \frac{P_1(1-n_{c2})}{P_2(1-n_{c1})} \sqrt{\frac{K_1}{K_2}}$$

This equation for the limiting value of the ratio in which the two metals separate out in the first differential of time is based on no other assumption than that the two salts diffuse independently of each other, according to Fick's law (besides those assumptions stated on p. 47.

$c_0 - c$ being always positive, this inequality can also be written

$$\epsilon(c_0 - c) = \frac{1.1284 n'}{96540} i \sqrt{\frac{t}{K}} - \frac{an'}{96540^2 \kappa} \frac{i^2 t}{K},$$

where ϵ is a number smaller than 1. The values of $i \sqrt{\frac{t}{K}}$ obtained from this quadratic equation are

$$10^{-4} i \sqrt{\frac{t}{K}} = 5.447 \frac{\kappa}{a} \pm \sqrt{\left(5.447 \frac{\kappa}{a}\right)^2 - 93.20 \frac{(c_0 - c)\epsilon \kappa}{n'a}}.$$

Now as we know that for $t=0$, also $c_0 - c=0$, we conclude that only the negative sign before the square root is applicable. Remembering also that $\frac{n'}{\epsilon}$ is always greater than the value $1 - n_c$ of equation (12), we can transform this equation into the inequality

$$10^{-4} i \sqrt{\frac{t}{K}} < 5.447 \frac{\kappa}{a} - \sqrt{\left(5.447 \frac{\kappa}{a}\right)^2 - 93.20 \frac{(c_0 - c)\kappa}{(1 - n_c)a}}; \quad (15)$$

the dimension of the number 5.447 occurring here is $\frac{\text{amp.} \times \text{sec.}}{\text{g.-equiv.}}$ or, which is the same thing, $\frac{\text{milliamp.} \times \text{sec.}}{\text{mg.-equiv.}}$, and the dimension of the number 93.20 is $\left(\frac{\text{milliamp.} \times \text{sec.}}{\text{mg.-equiv.}}\right)^2$.

In the following Table (I.) I have given the concentrations of the solutions examined experimentally in g.-equivalents per litre, or, which is the same thing, in $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$. They have been made to correspond to solutions examined by Schrader*. The concentrations given by him have a slightly different meaning to mine, as his indicate the number of g.-equivalents contained in the copper-sulphate crystals which were dissolved in one litre of pure water. The quantities α , β , and κ , given by Schrader, as well as the values for a taken from Kohlrausch's tables, which have been used, will also be found in the table. Under the headings " $i^2 t_0$ max." and " $i^2 t_0$ min." will be found the maximum and minimum values of $i^2 t_0$, calculated from the expressions (15) and (14) respectively, t_0 being the time required for c to go down to zero. In the column marked " $i^2 t_0$ acc. to (16)" I have given values of $i^2 t_0$ derived from the formula

$$c = c_0 - \frac{1.1284}{96540} (1 - n_c) i \sqrt{\frac{t}{K}}, \dots \dots \dots (16).$$

* *Zeitschr. f. Elektrochem.* iii. p. 502.

1— n_c being found by equation (12). These values are intermediate between those in the other two columns and given merely for comparison with the experimental numbers.

At the end of the table I have also given the concentration of the solution of pure copper sulphate examined, and the value of $\frac{K}{i^2t}$ derived for it from equation (8), n_a having been taken as 0.63*.

TABLE I.

My No.	Schrader's No.	My solutions.		Schrader's solutions.		α in g.	β in g.
		Conc. of Cu in mg.-equiv. cc.	Conc. of H ₂ SO ₄ in mg.-equiv. cc.	Conc. of Cu in mg.-equiv. cc.	Conc. of H ₂ SO ₄ in mg.-equiv. cc.		
A.	4	0.1634	0.0881	0.1670	0.0926	0.1743	0.00828
B.	5	0.2407	0.1327	0.2490	0.1375	0.2057	0.00988
C.	2	0.06618	0.0275	0.06618	0.0275	0.0903	0.00360
D.	10	0.1483	0.1804	0.1483	0.1804	0.2501	0.00860
E.	...	0.2096

Table I. (cont.)

My No.	κ in (ohm × cm.) ⁻¹ .	a in cm ²	i^2t_0 max. (in milamp., sec., cm.)	i^2t_0 min. (in milamp., sec., cm.)	i^2t_0 acc. to 16 (in milamp., sec., cm.)
		ohm × mg.-equiv.			
A.	0.027	15 × 10 ⁻³	1609	836	1246
B.	362 × 10690 × 10 ⁻⁸ .	15 × 10 ⁻³	3330	1773	27.6
C.	79.5 × 10690 × 10 ⁻⁸ .	17 × 10 ⁻³	265	141.0	192.3
D.	391 × 10690 × 10 ⁻⁸ .	15 × 10 ⁻³	1064	691.5	925
E.	$\frac{K}{i^2t_0} = 10^{-9} \times 1.195$ (milamp., sec., cm.).			

Note.—The value of κ for solution A has not been given by Schrader. The number 0.027 is an approximate value, calculated from Kohlrausch's tables.

* According to Kohlrausch's tables, its value at the concentration 0.2 $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$ is 0.643, and at the concentration 0.02 it is 0.62.

In the calculation of i^2t_0 Wiedeburg's value for the diffusion-coefficient of copper sulphate at 18° ,

$$K_{18} = 44.79 \times 10^{-7} (1 - 3.467 c) \frac{\text{cm.}^2}{\text{sec.}}$$

was employed. Here the concentration c is supposed given in $\frac{\text{g. CuSO}_4}{\text{cm.}^3}$; when it is given in $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$ the number 0.2761 must be taken instead of 3.467. The value of K for $c=0$ has been taken in calculating the numbers contained in the columns " i^2t_0 max." and " i^2t_0 acc. to (16)"; and the value of K for the initial concentration in calculating the number i^2t_0 min. From the quantities i^2t_0 given in the table, which are based upon the diffusion-coefficient of copper sulphate at 18° , we should find i^2t_θ at θ degrees by the formula

$$i^2t_\theta = i^2t_{18} [1 + 0.026(\theta - 18^\circ)],$$

in which 0.026 is the temperature-coefficient of diffusion assumed by Wiedeburg.

EXPERIMENTAL PART.

Determination of Time required till Hydrogen appears in the Electrolysis of an acid solution of Copper Sulphate.

A first series of experiments was performed to ascertain the time required till hydrogen first began to appear on electrolysing the mixtures of copper sulphate and sulphuric acid arranged in the preceding table, the solutions electrolysed being contained in cylindrical vessels, bounded at the top by horizontal cathodes. The values obtained are compared with the limits calculated by the formulæ given in the preceding table. Had hydrogen ever appeared before the lowest limit of time was reached, this would have proved conclusively that it was given off before the concentration of the copper at the electrode had gone down to zero. The upper limit could not be exceeded unless there were some considerable error in the experimental numbers employed.

Preliminary experiments were first carried out to study the subject qualitatively. It was found that on electrolysing the solutions with low current densities, horizontal cathodes being employed, which could be lit up for observation, at first only copper was deposited, after a certain time, however, varying greatly with the current density, the total surface

of the electrode would suddenly within about half a minute become uniformly covered with tiny bubbles of hydrogen. The current was at the same time observed, the measuring instrument, as described later on, being either a Weston millivoltmeter or an Ayrton-Mather D'Arsonval galvanometer. When employing the former, the current seemed to remain absolutely constant till shortly before the hydrogen bubbles were visible, when suddenly a considerable drop would take place. In the actual quantitative experiments in which the Weston instrument was employed, the time which passed from the beginning of the experiments till this drop of the current occurred was taken as the time which elapsed until the hydrogen came off.

When employing the D'Arsonval, however, it was seen that the current at first kept slowly decreasing, until it would after a certain time drop considerably and then become fairly constant again. It was seen that after the drop had taken place, the hydrogen bubbles always began to appear. In the experiments in which the D'Arsonval was employed, the time when the sudden drop was completed was taken as that when hydrogen bubbles first appeared. In these experiments a Thomson-Varley rheostat was always introduced into the circuit, by regulating which the current was kept perfectly constant until the large drop occurred. The behaviour of the Weston instrument was probably due to a slight sticking effect.

Three types of apparatus were employed, which will be understood from the accompanying figures 1-3. Tubes of the first type were employed for experimenting on solution A. The cathode consisted of an engravers' plate. It was fixed to the end of the tube, which was ground perfectly flat, by Chatterton cement. As it allowed a spirit-level to be placed on its top, the apparatus could be adjusted so as to make the cathode perfectly horizontal. The anode in this apparatus consisted of copper gauze. As seen from the figure, the tube was closed by a rubber stopper, into which a groove g was cut to allow air-bubbles to be easily removed. The rubber tube r was filled by introducing a long thin glass tube into it, down which the solution was poured by means of a funnel. In the first few experiments tabulated, the original surface of the plate was employed. In the later experiments it was amalgamated in order to secure as uniform a deposit as possible. Apparatus of this type, of which several were made, showed the disadvantage, that the plate forming the cathode occasionally came off, besides it could not be readily removed for examination and cleaning purposes.

All the experiments on solutions B, C, D, and part of those on E were carried out in apparatus 2. It consisted of a polarimeter-tube. The top being originally bevelled had to be ground perfectly flat. The cathode consisted of a copper

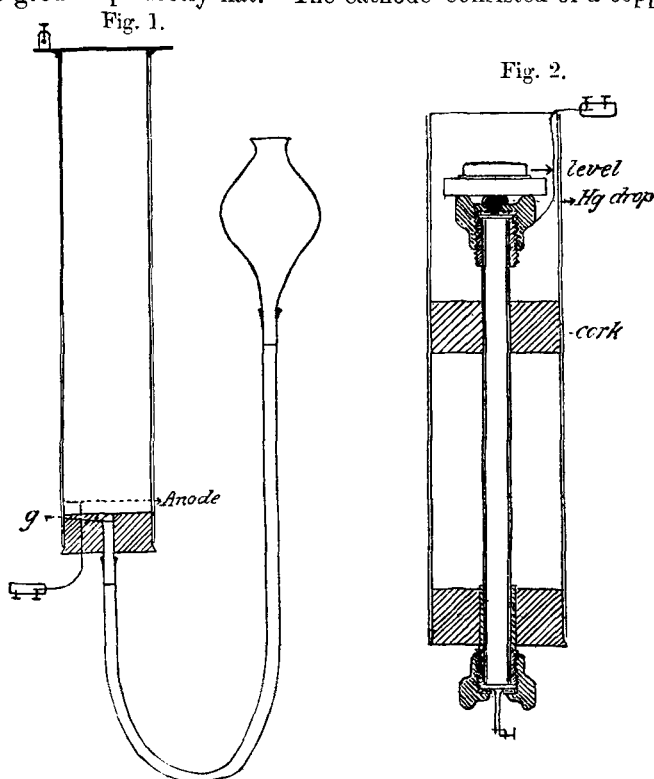
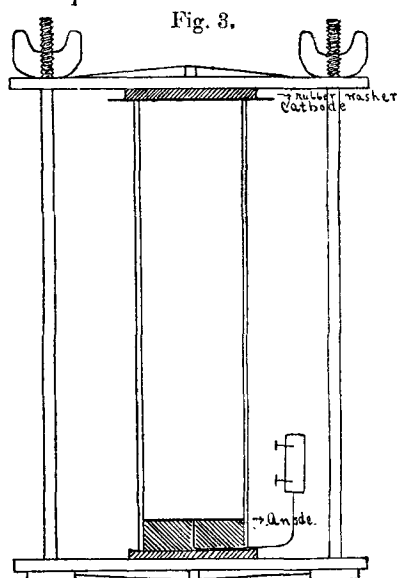


plate which was made perfectly flat, then polished and finally amalgamated. This was done by cleaning it with nascent electrolytic hydrogen, after which it amalgamated extremely readily, on dipping it into mercury. It was then again polished on perfectly clean chamois-leather, excess of mercury being removed from the edges by a pipette, drawn out to a fine point. This process of cleaning and polishing was repeated after each experiment. In order to avoid any liquid coming between the cathode and the surface of the glass forming the end of the tube by capillary action, this was greased with a trace of vaseline, so much only as could not be removed by a piece of dry filter-paper. The cathode was always fixed on the apparatus before introducing the liquid, by placing it in the cap, into which it fitted accurately,

and then screwing down the glass tube on it. By always proceeding in this manner, all risk was avoided of any vaseline being spread on the surface of the electrode. The method of obtaining metallic contact through the cap by means of a drop of mercury will be understood from the figure. On the top of the cap a piece of plate glass was laid and on this a small spirit-level, it having been previously ascertained that it was possible to level the end of the polarimeter-tube by this means. The rest of the apparatus will be sufficiently understood from the figure. As seen, it was jacketed with water. The surface of the cathode was measured by accurately determining the length of the polarimeter-tube, and then weighing it out with mercury. It was found to be 0.699 sq. cm.



The apparatus 3 was only employed in the series of experiments on pure copper-sulphate solution, and only the last three values of Table VI. have been obtained with it. The cathode here again consisted of an engravers' plate, which reached beyond the surface of the tube and allowed a small level to be placed on its projecting part. In this apparatus the cathode could be easily observed, when suitably illuminated. Its surface was calculated as that of an ellipse from the length of two diameters of the tube, taken at right angles to each other with a screw-caliper. Its value was 3.782 sq. cm.

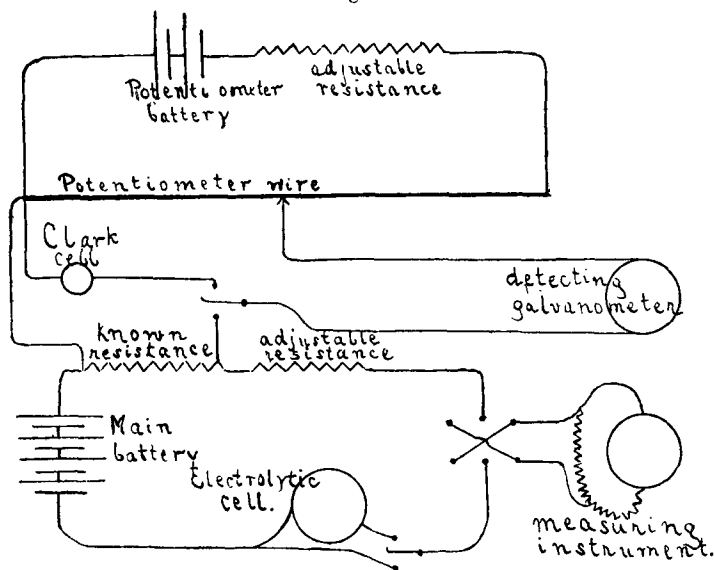
For the experiments the tubes were tightly clamped to a

very heavy tripod stand of $1\frac{1}{2}$ inch iron tubing, which was adjustable by three levelling-screws. As I was anxious to avoid vibrations, which are exceedingly great at Mason College, I followed a suggestion of Prof. Poynting's, and mounted the stand on three 50 kg. weights, each resting on three pieces of rubber. Before each experiment the tubes were allowed to rest for at least twelve hours.

The solutions for electrolysis were prepared by diluting the requisite amount of carefully standardized copper sulphate and sulphuric-acid solution to 1 litre. The former solution, which was prepared from purest commercial copper sulphate, recrystallized twice, was analysed by electrolytic copper determination, the latter by precipitation with BaCl_2 .

The electrical arrangements, which were in principle the same throughout all the experiments described, will be readily understood from the accompanying diagram (fig. 4). The

Fig. 4.



current from a suitable number of accumulators was passed through a known resistance, an adjustable resistance, the electrolytic cell, and the measuring instrument, which, as already mentioned, consisted in all experiments either of an Ayrton-Mather D'Arsonval or a Weston millivoltmeter, in either case suitably shunted. The measuring instrument was carefully calibrated, and also standardized before each experiment by taking its reading when a current of approximately the same magnitude as that employed in the experiment

was passed through it. This current was measured, as will be sufficiently understood from the diagram, by determining the voltage on the ends of the known resistance by means of a separate potentiometer circuit.

As regards the degree of accuracy obtained in the experiments, the upper limit is probably reached by those arranged in Table V. The experiments here having all been repeated, this table shows the degree of coincidence which can be obtained in a series of determinations. The readings have in general been taken to within five seconds. The most serious errors are no doubt brought about by changes of temperature which cause convection-currents in the liquid. The accuracy of the experiments contained in Tables B and C, which were carried out in winter, has certainly been considerably reduced, owing to the heating arrangements of the building. Indeed, differences of as much as 10 per cent. have here in single cases been obtained in successive experiments which could not be accounted for in any other way. I have nevertheless not hesitated to give these earlier values as the ranges of the times obtained are so great that even differences of as much as 10 per cent. do not preclude a comparison with the theoretical values. These being calculated for 18° , should be multiplied by $1 + 0.026(\theta - 18)$ if the experimental values have been obtained at θ° . I have instead made the corrections at the experimental numbers themselves, dividing them by $1 + 0.026(\theta - 18)$. It must be acknowledged that some uncertainty is introduced by this huge temperature correction. The temperature-coefficient for the diffusion of copper sulphate never having been experimentally determined has, as was also done by Wiedeberg, been assumed to be the same as that of other substances.

From the tables it will be seen that the experimental values are in all cases contained between the theoretical limits, and their differences from those calculated by the intermediate formula are in most cases not great. When we consider the extremely great ranges in which the times can be made to vary by varying the current-density, and also the numerous causes of experimental error, I think the medium formula No. 16 will be considered sufficient as an empirical expression of the results. From the fact that the values are always contained between the theoretical limits, and, besides, are far distant from the lower limit, I think we may conclude that these experiments prove within the limits which our theoretical knowledge of the processes taking place in the electrolyte allows, that liberation of hydrogen from an acid solution of copper sulphate takes place only after the concentration of the copper at the electrode has gone down to zero.

A New Method for the Determination of the Diffusion-Coefficient of Pure Copper Sulphate.

A second series of experiments was performed in order to study the behaviour of a pure copper-sulphate solution after the concentration of the copper at the electrode had gone down to zero.

TABLE II.

Solution A, see Table I. Experiments in Apparatus 1.

Experimental Values.							Theoretical Values.		
No.	Current in milliamps.	Surface of electrode in sq. cm.	Current-density in milliamps. cm. ²	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	t acc. to eq. 16.	t minimum.	t maximum.
							$t = \frac{1246}{i^2}$	$t = \frac{836}{i^2}$	$t = \frac{1609}{i^2}$
1 ...	9.33	13.53	0.690	2480	16	2617	2618	1756	3380
2 ...	18.1	16.76	1.081	1010	14	1128	1068	717	1377
3 ...	20.5	13.53	1.515	510	17	524	543	364	701
4 ...	40.9	13.53	3.02	110	15	119	137	92	176
5 ...	51.6	13.53	3.88	75	13	86	85	57	107
6 ...	52.8	13.53	3.905	73	14	81	82	55	105
7 ...	57.4	13.53	4.24	62	15	67	69	47	90
8 ...	78.2	13.53	5.78	28	13	32	37	25	48

TABLE III.

Solution B, see Table I. Experiments in Apparatus 2.
Surface of Cathode .699 sq. centim.

Experimental Values.						Theoretical Values.		
No.	Current in milliamps.	Current-density in milliamps. cm. ²	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	t acc. to eq. 16.	t minimum.	t maximum.
						$t = \frac{2716}{i^2}$	$t = \frac{1773}{i^2}$	$t = \frac{330}{i^2}$
1 ...	0.776	1.111	2025	12.4	2371	2201	1437	2698
2 ...	1.131	1.617	945	13.8	1060	1038	678	1274
3 ...	1.183	1.936	630	13.6	711	725	473	889
4 ...	2.09	2.99	290	13.8	318	304	199	372
5 ...	2.50	3.58	170	14.8	185	212	138	260
6 ...	2.617	3.74	165	13.6	186	195	127	238
7 ...	3.58	5.12	85	12.8	98	103	68	127
8 ...	5.10	7.30	40	13.8	45	51	33	62
9 ...	6.22	8.90	25	13.6	29	34	22	42

TABLE IV.

Solution C, see Table I. Experiments in Apparatus 2.
Surface of Cathode 699 sq. centim.

Experimental Values.						Theoretical Values.		
No.	Current in milliamps.	Current-density in milliamps. cm. ²	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	<i>t</i> acc. to eq. 16.	<i>t</i> minimum.	<i>t</i> maximum.
						$t = \frac{192.3}{i^2}$	$t = \frac{41.0}{i^2}$	$t = \frac{265}{i^2}$
1 ...	0.2123	0.304	1940	12.0	2299	2084	1528	2868
2 ...	0.2202	0.315	1960	13.0	2253	1938	1421	2671
3 ...	0.280	0.400	1040	12.8	1203	1202	881	1656
4 ...	0.406	0.581	550	13.6	621	570	418	785
5 ...	0.502	0.718	330	13.2	378	373	274	514
6 ...	0.768	1.099	150	14.2	166	159	117	219
7 ...	1.133	1.621	67	12.8	78	73	54	101
8 ...	1.801	2.576	23	13.8	26	29	21	40

TABLE V.

Solution D, see Table I. Experiments in Apparatus 2.
Surface of Cathode 699 sq. centim.

Experimental Values.						Theoretical Values.		
No.	Current in milliamps.	Current-density in milliamps. cm. ²	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	<i>t</i> acc. to eq. 16.	<i>t</i> minimum.	<i>t</i> maximum.
						$t = \frac{925}{i^2}$	$t = \frac{691.5}{i^2}$	$t = \frac{1064}{i^2}$
1 ...	0.402	0.575	2560	12.7	2970	2801	2094	3218
1 a ...	0.405	0.780	2600	12.7	3016	2753	2058	3163
2 ...	0.556	0.795	1355	12.5	1580	1463	1093	1684
2 a ...	0.557	0.797	1370	12.0	1604	1457	1089	1675
3 ...	0.734	1.051	750	12.0	888	839	627	963
3 a ...	0.737	1.054	750	12.0	888	833	622	958
4 ...	1.182	1.691	305	12.4	357	323	242	372
4 a ...	1.174	1.680	295	12.3	345	328	245	377
5 ...	1.847	2.64	120	12.4	140	133	99	153
5 a ...	1.885	2.70	120	13.0	138	127	96	146
6 ...	2.82	4.03	55	13.4	63	57	43	66

After this is the case, diffusion can no longer bring sufficient copper to the electrode to carry the current, for the formula shows that if the current were still conducted in the same manner as it was before, the concentration of the copper would become negative. It might therefore be supposed that it would be impossible to keep the current at its former strength. This is, however, found not to be the case.

In 1844 Smee* described an experiment, in which he electrolysed a solution of pure copper sulphate in a tall vessel, in the upper part of which he placed the cathode. His description of the varying appearance presented by the deposition of the copper as the concentration of his solution went down to zero runs:—"On the action of the galvanic force bright reguline copper first appeared at the negative pole, this was followed by a brittle, this by a sandy, this by a spongy deposit, this by black powder, and finally hydrogen was evolved." I have in general been able to verify Smee's observations as well as the fact, mentioned by him, that copper hydrate is formed at the electrode after the black powder has begun to appear. I have, however, in no case—neither when employing apparatus 3, nor when a form of apparatus was employed in which the solution was not contained in a closed vessel—been able to observe bubbles of hydrogen. It is therefore probable that Smee's copper-sulphate solution was more acid than mine. In my experiments the black spongy deposit always seemed to grow into the solution; in single cases it became intermingled with bright branches of metallic copper. The black deposit is evidently not pure copper, for it disappears when left for some time in dilute sulphuric acid. It is probably a copper hydride†.

The behaviour of the current while electrolysing a solution of pure copper sulphate was quite similar to that when an acid solution was examined. The black deposit always appeared after the large drop had taken place. The completion of the drop in the current was taken as the time when the concentration of the copper had gone down to zero. From a knowledge of this time and of the current-density employed, it is possible to calculate the diffusion-coefficient of copper sulphate by means of the expression given at the end of Table I. This has been done in Table VI. (p. 72).

* *Phil. Mag.* xxv. p. 437.

† See *Pogg. Ann.* lxxv. p. 350.

TABLE VI.

Determination of Diffusion-coefficient K of copper sulphate. Solution E. Experiments 1-3 in apparatus 2; surface of cathode 0.699. Experiments 4-6 in apparatus 3; surface of cathode 3.782 sq. cm.

No.	Current in milliamps.	Current-density in milliamps. $\frac{\text{cm.}^2}$	Time observed in seconds.	Temp. θ in $^{\circ}\text{C}$.	K_{θ} by formula (Table I.) $K = 10^{-9} \times 1.195 \theta^2 t_0$ in $\text{cm.}^2/\text{sec}$.	K_{18}° by formula $K_{18} = \frac{K\theta}{1 + 0.026(\theta - 18)}$	Mean value of K_{18} .
1...	0.75	0.966	3390	14.4	3.79×10^{-6}	4.16×10^{-6}	4.46×10^{-6}
2...	1.004	1.436	1530	14.2	3.79×10^{-6}	4.21×10^{-6}	
3...	1.038	1.485	1515	13.8	3.99×10^{-6}	4.48×10^{-6}	
4...	6.68	1.766	1095	15.4	4.08×10^{-6}	4.38×10^{-6}	
5...	6.41	1.694	1285	15.0	4.41×10^{-6}	4.78×10^{-6}	
6...	6.37	1.683	1275	14.4	4.31×10^{-6}	4.76×10^{-6}	

According to Wiedeburg the diffusion-coefficient of copper sulphate at 18° is $4.479 \times 10^{-6} \frac{\text{cm.}^2}{\text{sec.}}$ at the concentration 0, and $4.220 \times 10^{-6} \frac{\text{cm.}^2}{\text{sec.}}$ at the concentration of solution E (see p. 63 & p. 57). Although the mean value for K_{18} in the above table is about what should be expected from Wiedeburg's determinations, yet the differences between the single experiments, none of which were known to have gone wrong in any respect, is too great to justify the recommendation of the method in its present form for more than a rough determination of diffusion-coefficients.

Experiments on the Effect of Convection currents on the Relative Quantity of Hydrogen given off in the Electrolysis of an Acid Solution of Copper Sulphate.

The following experiments deal with the relative quantity of hydrogen produced by electrolysis of an acid copper-sulphate solution when considerably greater current-densities are employed than those used in the preceding experiments. This subject has been experimentally treated by Schrader in the paper already quoted, and by Houlléville*.

Both investigators employed vertical electrodes and neither promoted nor hindered the natural convection-currents of their electrolyte. They found that their results were roughly expressed by hyperbolic functions.

* *Ann. Chim. et Phys.* [7] ii. p. 351 (1894).

From the results obtained in the foregoing part of this paper, the electrolytic evolution of hydrogen from an acid solution of copper sulphate is explained in the following manner. The concentration of the copper goes down to practically zero with great rapidity, as shown by the formulæ, when current-densities are employed which are considerably larger than those used in the preceding experiments. After this, diffusion no longer brings sufficient copper to the electrode to carry the current, and hydrogen is given off too in ever increasing quantity, until either the concentration of its ions has gone down to practically zero, or convection-currents bring new liquid to the electrode from which copper alone is again deposited. It will thus be seen that convection-currents play as great a part in the determination of the ratio of the two constituents as any of the other conditions of the experiment, and always have the effect of diminishing the relative quantity of hydrogen given off.

A lower limit of this quantity, when sufficient convection takes place, is thus always 0 per cent.; and the question might be asked, Is there an upper limit when we employ a given current-density, and use a large quantity of electrolyte; and what is its magnitude? I do not propose to discuss this question fully, but only to point out that, owing to the fact that convection-currents always have the tendency to diminish the production of hydrogen, such an upper limit can for all practical purposes be taken as represented by the relative quantity of hydrogen produced in a solution in which no convection-currents whatever interfere, at the time when the concentration of both copper and hydrogen ions at the cathode has gone down to practically zero. It is also possible to see from the formulæ given which are the main influences that determine this limit, by determining the lengths of time during which copper only and during which mainly hydrogen have been given off. They are, in the first place, the relative magnitudes of the expressions $\frac{c_0}{1-n_c}$ for the hydrogen and the copper ions, and, to a smaller degree, the relative values of the diffusion-coefficients of sulphuric acid and copper sulphate.

I have discussed this question in view of some experiments that have been quite recently performed by Toepffer*, a short account of which will be found in the *Zeitschrift für physikalische Chemie*, xxx. p. 570. He deposited alloys of iron, cobalt, nickel, and zinc from mixtures of several of their salts, with the result that when his so-called low current-

* Fully described in his thesis kindly sent me by the author.

densities were employed, the metal requiring the higher E.M.F. for its liberation was always deposited in relative quantities which far exceeded its relative concentration in the solutions.

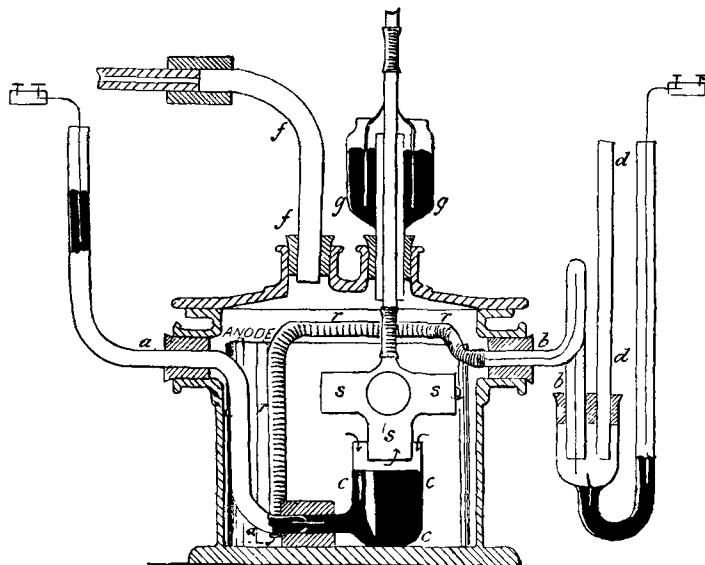
Firstly, as regards the values of the lowest current-densities used by the author, it seems probable that these would have been sufficient to make the concentrations at his cathode go down to zero in times varying from ten to one-tenth of a second if no convection-currents had interfered. This can be taken from the values given for concentrations and current-density in the thesis referred to, if, in order to obtain numerical values, we assume that diffusion-coefficients &c. had been the same in the author's solutions as in mine. None of his current-densities can therefore be described as small in the sense used in this paper; and I do not think there can be any doubt that if sufficiently small values had been used, the metal requiring the lower E.M.F. for its deposition would have preponderated in the alloy formed. As regards the actual preponderance of the baser of the two metals, a great deal of light could no doubt be thrown on this by determinations of transport values in the solutions examined, as will be seen from what has been stated above. If, as Toepffer assumes, the nobler metal has the tendency to form complex anions to a greater extent than the baser, this would certainly greatly influence the transport values in the direction required to explain the results.

The main purpose of the experiments I am now about to describe is to show to how great an extent the relative quantity of hydrogen, given off in the electrolysis of an acid solution of copper sulphate, is influenced by convection-currents; and also to show that when these are artificially increased by stirring, the hydrogen can be made to disappear altogether, even in cases in which otherwise more of its equivalents than of those of copper would have been liberated.

For this purpose the apparatus was devised, shown in the accompanying figure (fig. 5), which allowed the course of the electrolysis to be continually followed by measuring the quantity of hydrogen given off, and in which, at the same time, the solution above the cathode could, when desired, be rapidly renewed by vigorous stirring. It will be seen that it resembles a desiccator in general appearance, but has two openings in the side and two in the lid. Through one of the side-openings the tube *a* passes leading to the cup *c*, which is filled with mercury, forming the cathode, uniform deposition of the copper being thus ensured. The glass tube *b* passing

through the other side-opening is continued by the rubber tube *r*. It contains the wire leading to the anode, formed of a piece of pure electrotype copper, which lines the inside of the vessel. This tube also serves to pass hydrogen into the

Fig. 5.



solution before each experiment. The tube *f* leads through the lid to the gas-burette. The gas-tight joint *g*, through which the stirrer passes, will be understood from the figure. It may be described as an inverted cup rotating in a ring of mercury. Glycerine is placed at the top of the mercury, and after the cup had become well moistened with the glycerine it could be made to rotate up to over 500 revolutions per minute without any considerable leakage occurring. When rotating at these very high velocities, a very slight escape of the hydrogen contained in the vessel took place; but this was in the nature of diffusion occurring through a porous cup, for it seemed independent of the pressure of the gas, and a correction could therefore easily be made for it. The stirrer *s* may be described as a modified Witt's stirrer. It has four hollow arms out of which the liquid is thrown by centrifugal force, being replaced by solution drawn from above the cathode. Owing to the great extent to which it causes the liquid in the vessel to rotate, which hinders the

flow to the electrode, its efficiency decreases somewhat after it has been going for some time, and its velocity must be increased in order that the former efficiency may be obtained. The stirrer was fixed at its top to the end of the shaft from which it derived its motion by means of a short piece of rubber tube. It was also in connexion with a speed-counter.

In the experiments the apparatus was nearly filled with 600 c.c. of solution. Before use, a rapid current of hydrogen was passed through it for about half an hour by means of the tubes *d*, *b*, *r*, the gas escaping through a tap in the gas-burette. After this, mercury was poured down the tube *d*, which made a gas-tight joint and besides formed metallic contact for the wire leading to the anode. Either before or after each experiment, the apparatus was tested for leakage, the stirrer always rotating at about the same speed as it did in the experiment. The apparatus was mounted inside a large water-bath, to which also the pulleys &c. for the stirrer were fixed. It was made to order by Messrs. C. E. Müller & Co., of High Holborn, W.C.

The measuring-instrument for the current was in these experiments always the millivoltmeter mentioned above, the electrical arrangements being in principle exactly the same as those employed for the experiments described above.

The solutions employed are Nos. A and B of the previous experiments, which have also been examined by Schrader*; the minimum current-density employed by me being greater than the maximum value of 36 milliamperes per sq. cm. used by Schrader. Some results are given in the following tables. The quantities of hydrogen observed are corrected to 0° and 760 mm. The percentage ratio of the hydrogen given off to the total number of equivalents liberated has been calculated from the current employed. The time required for the concentration of the copper to go down to zero, calculated by means of the empirical equation 16, has been given in each case.

It will be seen from the results that when the solution is not artificially stirred, the quantity of hydrogen liberated decreases rapidly after the experiments have been going on for some time. This is evidently due to the rapid convection-currents brought about in the liquid by the electrolysis, and not to slight changes in the average concentration of the liquid, for when it was allowed to stand for about a day, the

* Taken from his thesis kindly lent me by Prof. Warburg, in whose laboratory the experiments were carried out.

Table of Experiments on Influence of Convection.—Solution A. Surface of cathode 2.14 sq. cm.

No.	Current in amps.	Current-density in milliamps. cm. ²	Time from beginning to end of } to } minute.	Average volume of hydrogen liberated per minute, corr. to 0° & 760 mm., in c.c.	Percentage ratio of equivalents of hydrogen to total equivalents liberated.	Time for concentration at electrode to become zero without convection by eq. 16, in seconds.	Revolutions of stirrer per minute.	Temp. of bath.	
1.	0.120	56.1	1st to 2nd	0.51	61 per cent.	0.4	0	12°	
	"	"	3rd to 8th	0.37	44	"	"	"	
	"	"	9th to 12th	0.23	33	"	"	"	
	"	"	13th to 22nd	0.23	28	"	"	"	
	"	"	23rd to 28th	0.17	20	"	"	"	
	"	"	1st to 4th	0.00	0	"	180	"	
	"	"	1st to 1st	0.64	46	0.14	0	12°	
	"	"	2nd to 6th	0.51	37	"	"	"	
	"	"	7th to 11th	0.43	31	"	"	"	
	"	"	12th to 23rd	0.38	27	"	"	"	
1 _a .	"	"	24th to 38th	0.37	26	"	"	"	
	"	"	1st to 3rd	0.06	4	"	540	"	
	2.	0.240	93.5	1st to 1st	1.44	51	0.035	0	13°
			"	2nd to 2nd	0.90	32	"	"	"
"			3rd to 5th	0.76	27	"	"	"	
2 _a .	"	"	6th to 9th	0.48	17	"	"	"	
			1st to 1st	0.76	27	"	"	"	
			2nd to 2nd	0.47	17	"	325	"	
			3rd to 4th	0.28	10	"	"	"	
			"	"	"	"	"	"	
3.	0.400	187	1st to 1st	1.44	51	0.035	0	13°	
		"	2nd to 2nd	0.90	32	"	"	"	
		"	3rd to 5th	0.76	27	"	"	"	
3 _a .	"	"	6th to 9th	0.48	17	"	"	"	
			1st to 1st	0.76	27	"	"	"	
			2nd to 2nd	0.47	17	"	325	"	
			3rd to 4th	0.28	10	"	"	"	
			"	"	"	"	"	"	
Solution B.									
1.	0.120	76.1	1st to 9th	0.52	62	0.56	0	13°	
			10th to 11th	0.48	57	"	"	"	
			12th to 13th	0.43	51	"	"	"	
			14th to 17th	0.38	45	"	"	"	
			18th to 15th	0.31	37	"	"	"	
			20th to 30th	0.27	32	"	"	"	
1 _a .	"	"	1st to 3rd	0.00	0	"	240	13°	

values found at the beginning of the experiment were again approximately attained. The experiments in which the solution was stirred were performed on different days to those in which no artificial stirring took place. It will be seen that in cases where otherwise over 60 per cent. of the equivalents given off would have consisted of hydrogen, the hydrogen could be made to disappear altogether. When a current-density was employed which would reduce the copper to zero in about 0.035 of a second, the stirrer could not make the hydrogen disappear altogether, but only decrease during the first minute to the extent to which it would have decreased if no stirring had been going on, owing to natural convection alone, after three minutes.

SUMMARY OF RESULTS.

An equation (No. 8) has been derived and rigidly proved or calculating the concentration at the electrode of a solution of a single salt from which the metal is being deposited under the conditions that (1) the solution is contained in a cylindrical vessel bounded by the electrode; (2) that no convection-currents occur; and (3) that the diffusion of the salt obeys Fick's law and its transport values are constant. This formula can be made the basis of a method for roughly determining diffusion coefficients.

In the case of mixtures, it is possible to arrive at limits for the concentration; and it has been experimentally proved (1) that hydrogen always appears at the electrode of an acid solution of copper sulphate in which no currents of liquid are taking place, between the limits of time for the concentration to go down to zero; and (2) that the time when it appears differs only slightly from that calculated by equation 16, which is the same in form as equation 8. It seems, therefore, that this formula can be taken as a sufficient empirical expression for the concentration at the electrode of a mixture too.

Lastly, the great part played by convection-currents in determining the ratio of the two constituents given off at the electrode of an acid copper-sulphate solution has been shown, it having been proved experimentally that by artificial stirring hydrogen can be made to disappear altogether in cases where it would otherwise have presented over 60 per cent. of the equivalents carrying the current from the solution to the electrode.

The experiments described here have been carried out entirely in the laboratories of Prof. P. F. Frankland and

Dr. D. K. Morris, at Mason College, Birmingham, preliminary experiments having been performed in London at University College in the laboratories of Profs. Ramsay and Callendar. I have pleasure in expressing my thanks to these gentlemen, as well as to Mr. A. W. Porter, of University College, London, for friendly interest shown in my work.

IV. *On the Specific Velocities of Ions in the Discharge from Points.* By A. P. CHATTOCK, *Professor of Physics, University College, Bristol*; and WINIFRED E. WALKER, *B.Sc.*, and E. H. DIXON, *B.Sc.*, *Associates of University College, Bristol**.

IN a communication to the Philosophical Magazine for November 1899, it was shown by one of us that under suitable conditions the pressure of the electric wind furnishes a means of determining the specific velocities of the ions concerned in its production; and results obtained in the case of air were given in illustration of the method.

Subsequent experiments on other gases, while leading to values which were roughly in accord with the velocities of ions obtained by α -rays, have remained unpublished on account of the behaviour of hydrogen. The results for the negative ions in this gas were found to vary between the very wide limits 5.7 and 8.3, and in later work 4.7 and 10.0 centimetres per second in a field of one volt per centimetre.

It is true that, owing to the smallness of the wind-pressures for hydrogen, exceptionally large errors were to be expected in the readings of the pressure-gauge, and hence in the deduced velocities; but the magnitude of the observed variations was much too great to be accounted for in this way, and it seemed possible that these might be due to real changes in the specific velocities themselves.

Analysis of the results now obtained, without being absolutely conclusive, leaves little room for doubt that this view is correct.

Specific ionic velocities have been measured in the five substances, *Hydrogen, Carbon Dioxide, Air, Oxygen,* and *Turpentine* according to the formula

$$V = z/cp,$$

where c is the current from the point, and p the increase in the total wind-pressure corresponding with a shift of the discharging point through z along the axis of the discharge-tube (*l. c.*).

* Communicated by the Authors.