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Chemistry. -- "*On some Particular Cases of Current Potential Lines*".

II. By Dr. A. H. W. ATEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of October 28, 1916.)

In the preceding paper¹⁾ an equation was derived which represents the ratio between the quantity of silver chloride which is deposited on the anode in case of anodic polarisation of a silver electrode in a solution of a chloride, and that which is deposited in the liquid. This equation now enables us to indicate in what way the electrolytical determination of halogens as silver halides takes place with the smallest error possible.

In these determinations the conditions must be satisfied that the halogen is deposited as completely as possible on the anode as silver halide and that as little silver as possible goes into solution from the anode.

During the analysis the halogen content of the liquid diminishes continually. The course of the process can therefore not be indicated by a single current potential line, but only by a number of current potential lines for all concentrations which the halogen ion passes through from the beginning to the end of the analysis. If e.g. we electrolyse a 0.01 *n* solution of NaCl, the course is in the beginning represented by line 1 in Fig. 2 of the preceding paper. If in course of time the solution has become 0.001 *n*, line 2 is applicable, later on, when the concentration has become 0.0001, line 3 applies, etc. As was demonstrated on p. 668 the points on the leftside of *AB* give current densities which chiefly yield AgCl on the anode. If $C_1 = 0.01$ we can, therefore, work with a comparatively large current density, without Ag appreciably going into solution. For $C_1 = 0.001$ this current density is ten times smaller, for $C_1 = 0.0001$ a hundred times smaller, etc.

If we now wanted to execute the electrolysis with a constant current density, till C_1 had become = 0.0001, we should have to work with a very small current density from the very beginning, for which with $C_1 = 0.0001$ no appreciable quantity of Ag goes into solution. In consequence of this the analysis would last very long. It is more advisable to work with a greater current density, as long as C_1 is still great, and diminish it according as C_1 descends. This may be done by measuring the anode potential during the analysis, and by regulating the intensity of the current so that the

1) These Proc. Vol. XIX, p. 653.

anode potential, hence the concentration of the silver ions at the anode, keeps a definite value, or varies in a definite way.

When during the electrolysis the concentration of the chlorine ions at the anode is kept at a constant value c_{1a} , the ratio $\frac{d_2}{d_1}$ is constant during the electrolysis, and equal to:

$$\frac{d_2}{d_1} = \frac{D_2}{D_1} \frac{L}{c_{1a}^2} \quad \dots \quad (1)$$

For silver chloride L is about 10^{-10} . If c_{1a} is kept at 10^{-4} , $\frac{d_2}{d_1}$ will be about 0.01, D_1 and D_2 differing little. Hence 1% of the total quantity of chlorine will precipitate in the liquid as AgCl. This quantity is lost for the analysis. The error made in the analysis, is, however, greater than 1%, for the increase in weight of the anode is determined. This is 1% too small, because AgCl precipitates in the liquid, but this causes a quantity of Ag of the anode to go into solution, which is equivalent to 1% chlorine, hence about three times the quantity. The total error amounts, therefore, to about 4%. This error would be smaller, if the analysis was carried out for $c_{1a} = 10^{-3}$. In this case $\frac{d_2}{d_1}$ would be $= 10^{-4}$. But now there remains in the solution a quantity of chlorine ions equal to 10^{-3} ; to reach, therefore, an accuracy of 1% we should have to start from a solution which is 0.1 normal. The total quantity of AgCl that must separate from this solution, is pretty large, for which a large silver surface is necessary, as the quantity of AgCl that can be deposited on a given anode surface, is comparatively small. It appears, therefore, that an accurate determination of Cl presents difficulties. More favourable are the circumstances for Br and I, as the solubility products of AgBr and AgI are 10^{-12} and 10^{-16} . We can, therefore, work for AgBr with $c_{1a} = 10^{-4}$, and for AgI with 10^{-6} , without an appreciable loss taking place.

The loss of silver chloride becomes slightly smaller when c_{1a} is not kept at a constant value from the beginning, but allowed to diminish during the electrolysis, so that c_{1a} has a greater value at the beginning of the experiment than at the end.

Let us suppose the intensity of the current to be so regulated that c_{1a} always remains equal to nC_1 , n being a constant smaller than 1.

Now:

$$\frac{d_2}{d_1} = \frac{D_2}{D_1} \cdot \frac{L}{n^2 C_1^2}$$

At the beginning of the analysis, where C_1 is great, $\frac{d_2}{d_1}$ is, therefore, smaller than at the end, where C_1 has descended to a small value. If we call this initial and this final value C_{1b} and C_{1e} , the mean value of $\frac{d_2}{d_1}$ during the analysis is:

$$\frac{d_2}{d_1} = \frac{\int_{C_{1b}}^{C_{1e}} \frac{D_2}{D_1} \cdot \frac{L}{n^2 C_1^2} dC_1}{C_{1b} - C_{1e}}$$

or

$$\frac{d_2}{d_1} = \frac{D_2}{D_1} \cdot \frac{L}{n^2} \cdot \frac{1}{C_{1b} C_{1e}} \dots \dots \dots (2)$$

For a given value of C_{1b} and C_{1e} the value of $\frac{d_2}{d_1}$ is now determined by n .

If we assume $n = 0.5$, $C_{1b} = 0.01$, $C_{1e} = 0.00004$, then $\frac{d_2}{d_1} = 10^{-3}$.

As a quantity of silver of the anode dissolves which is about three times the value of the deficit of chlorine, the diminution of weight of the anode is found 0.4×10^{-2} too small. Moreover the concentration of the chlorine ions in the solution remains 0.00004 at the end of the determination, hence 0.4 % of the original quantity. Hence with this mode of working the total error is 0.8 %.

If n is taken greater, e. g. = 1, and $C_{1e} = 0.00002$, the shortage of AgCl on the anode becomes 0.2 %, 0.2 % of the chloride remaining in solution, so that the total error amounts here to 0.4 %.

With the given value of C_{1b} a smaller error cannot be reached. This would only be possible by making C_{1b} greater, but this requires a very large silver surface. Nor is the above given value for $n = 1$ practically to be realized, as in this case the current density would become = 0.

In general the current density becomes greater, hence the time required for the execution of the analysis shorter, as n is smaller. The accuracy of the analysis, is however diminished by this.

The duration of the analysis can be calculated in the following way.

When we work with a current density smaller than the critical,

as in practice is always the case, the current density is given with great approximation by:

$$d = 1.117 \frac{D_1}{\delta} (C_1 - c_{1a}), \quad \text{or as } c_{1a} = nC_1$$

$$d = 1.117 \frac{D_1}{\delta} (1 - n) C_1.$$

If the total quantity of halogen is M gramme equivalents, the diminution of this per time unit is equal to the current strength, divided by 96500, hence:

$$-\frac{dM}{dt} = \frac{Od}{96500} \quad \text{if } O \text{ is the surface of the anode.}$$

If further the volume of the solution is V , then $M = VC_1$, and consequently:

$$-\frac{dC_1}{dt} = \frac{Od}{96500V} = \frac{OD_1}{86400\delta V} (1-n) C_1$$

from which follows:

$$t = \frac{86400\delta V}{OD_1(1-n)} \times 2.3 \log \left(\frac{C_{1b}}{C_{1e}} \right). \quad \dots \quad (3)$$

It appears from this equation that for a given value of C_{1b} and C_{1e} the analysis will proceed the more rapidly as δ is smaller, consequently as the stirring is more vigorous, the volume is smaller, n is smaller, and O and D_1 are greater. D_1 may be increased by rise of temperature. A large area of the anode is particularly desirable here because the deposited silver chloride covers the metal, and the effective area becomes, therefore, smaller during the analysis.

The electro-analytical determination of the halogens has been fully examined by SMITH¹⁾ and his collaborators, and the recorded results are satisfactory. The method for chlorides has appeared to give the best results when the solution contains a sufficient quantity of OH-ions, to form AgOH with the silver, when the chlorine ions are almost consumed. In this way the loss of silver of the anode is prevented. In consequence of the precipitated AgOH the anode weighs too heavy, but the silver hydroxide can be easily decomposed by heating, so that the increase of weight now actually gives the deposited chlorine. There always remains a deficit, however, as not all the chlorine from the solution can be deposited. For the other halogens the error will be smaller than for chlorine, when the same method of working is followed.

The difference between the three halogens appears clearly from a research by REEDY²⁾, who found a deficit of 0.2% for a diluted acid

¹⁾ SMITH, Electroanalysis.

²⁾ Amer. Journ. of Science. (4) 40 (1915) 281, 400.

solution of iodide, of 0.8 % for bromide, and of 20 % for chloride.

That the error for chloride is so exceedingly large, larger than is necessary, is owing to REEDY'S method of working. He wanted, namely, to precipitate halogen, till no more than 0.1 mgr. was left in 200 cm³ of the solution. For this purpose he calculated the potential which a silver electrode covered with AgCl presents in a solution of 0.1 mgr. per 200 cm³, and then carried out the electrolysis for this constant anode potential. Hence the halogen concentration at the anode was kept constant, and c_{1a} in equation (1) had the value 0.000014 for Cl, the value 0.000007 for Br, and 0.000003 for I.

The ratio of the quantity of silver halide, which precipitates in the liquid to that which precipitates on the anode is according to (1)

$$\frac{d_2}{d_1} = \frac{D_2}{D_1} \cdot \frac{L}{c_{1a}^2}$$

As now L_{AgCl} is about 1.4×10^{-10} , L_{AgBr} 5×10^{-13} , and L_{AgI} 10^{-16} , $\frac{d_2}{d_1}$ becomes 0.7 for chlorine, 0.01 for bromine, and 0.001 for iodine.

The value calculated here for silver chloride is much greater than that of REEDY, which can be explained by this that the values of c_{1a} used are not very accurate. When c_{1a} differs little from \sqrt{L} , a small error in c_{1a} gives a great change in the value $\frac{d_2}{d_1}$. For AgBr and AgI, where c_{1a} is much smaller than \sqrt{L} , an error in c_{1a} brings about only a small absolute change in $\frac{d_2}{d_1}$.

As for 1% bromine that precipitates in the liquid as AgBr, about $1\frac{1}{2}$ times the amount of silver of the anode dissolves, the total error calculated for the bromine determination is about 2.5 %. In the iodine determination it amounts to about 0.2 %. It appears, therefore, that in these latter determinations the calculated error corresponds in order of magnitude with the deficit in REEDY'S determinations.

As was already observed above the determination of chlorine as silver chloride can be made more accurate than was done by REEDY. For this purpose the concentration of the chlorine ions at the anode must be kept at a higher value, e.g. 1 mgr. instead of 0.1 mgr. per 200 cm³.

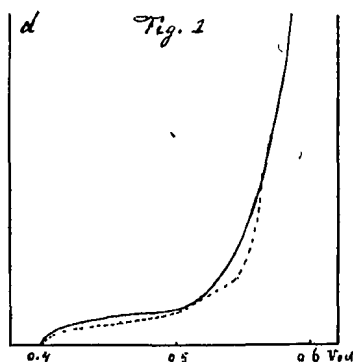
Further REEDY has determined some current potential lines, as they have been drawn in fig. 2 of the first paper, among other things for KI (fig. 3 p. 286 REEDY). A quantitative comparison of the theo-

retical and the experimental line is not possible. Qualitatively the agreement is perfect. It appears from the course of the lines 1 and 2 in fig. 2 that the middle of the horizontal part of these lines lies at a concentration equal to \sqrt{L} . Hence at $c_{1a} = 10^{-8}$ for AgI, which corresponds with a potential of + 0.34 Volt. It appears from REEDY's line that the middle of the horizontal portion really lies at this potential.

This is different with a line given by REEDY for AgBrO_3 in 0.5 molecular KBrO_3 . Here the middle of the horizontal portion lies at about 0.470 V, corresponding with a silver ion concentration of 10^{-6} . Then the product of solubility of AgBrO_3 would be 10^{-12} . This value is much too small for AgBrO_3 . For the solubility BÖTTGER¹⁾ found 7×10^{-3} mol. per L. As for this dilution AgBrO_3 is almost totally ionized, the product of solubility will be about 5×10^{-5} . The product of solubility found from REEDY's line, is therefore certainly not that of AgBrO_3 . Its value agrees pretty well with that of AgBr , which leads us to the supposition that REEDY's line does not refer to AgBrO_3 in KBrO_3 , but to AgBr in KBr , which might be the case if the bromate used was contaminated with bromide. This supposition is supported by what follows. For the potential of AgBrO_3 in 0.5 molecular KBrO_3 without polarisation REEDY finds 0.400 V., which yields a product of solubility for AgBrO_3 of 10^{-7} .

As was demonstrated above this value is too low. If we assume the measured potential to refer to AgBr in KBr , the solution used would have to contain 10^{-5} KBr , for which it would be therefore necessary that the bromate used was contaminated with 0.002% bromide.

Besides, the length of the horizontal piece in the line of REEDY is slightly more than 0.1 Volt, as is required for a silver salt, for which $\sqrt{L} = 10^{-6}$ in a solution which is 10^{-5} molecular at the anion. For AgBrO_3 in 0.5 molecular KBrO_3 the horizontal portion would have to be about twice as long.



In fig. 1 the line found by REEDY is drawn, the dotted line is the calculated one of AgBr in $10^{-5} n$ KBr , in which the scale of the current densities is chosen so that a point of the calculated line coincides with a point of the found line.

It appears that there exists a satisfactory agreement between these two lines, when it is borne in mind that

¹⁾ Z. f. physik. Chemie. 46 (1903) 602.

the value of 10^{-5} of the bromine ion concentration is correct only in approximation.

If we assume that the product of solubility of AgBrO_3 is 5×10^{-5} , the concentration of the silver ions is 10^{-4} in 0.5 molecular KBrO_3 . The current tension line of AgBrO_3 in KBrO_3 would not begin therefore before 0.57 V., and would therefore be a continuation of the one drawn in figure 1.

5. *Anodic formation of metal compounds in the solution.*

In the preparation of insoluble metal compounds by electrolytical way according to Lückow, we wish to attain that the precipitation does not form on the anode, but in the liquid. The conditions for this follow immediately from figure 3 of the first paper and from equation (43)

It is clear that we shall have to work with a current density greater than the critical density hence:

$$d > \frac{1.117}{\sigma} (D_1 C_1 - D_2 C_2).$$

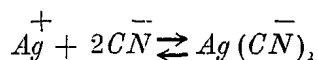
The current density need only be little greater than this value to make all the precipitation form in the liquid. This condition will the sooner be satisfied as C_1 is smaller and σ greater. That is to say that the concentration of the anion, which gives a precipitate with the metalion, must be small, and the liquid should not be stirred or only slightly. These are the very same conditions as Lückow gives for his mode of working.

6. *Electrolysis of solutions of complex salts.*

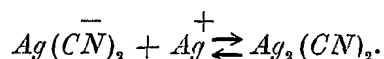
In the electrolysis of solutions of complex salts, e.g. $\text{Ag}_2(\text{CN})_2$ dissolved in KCN, a precipitate can be formed on the anode under some circumstances, in this case of $\text{Ag}_2(\text{CN})_2$.

This very greatly increases the resistance, and enfeebles the current, so that it is necessary to prevent the formation of this precipitate. It is now easy to indicate at what current density this precipitate will be formed.

In a solution of $\text{Ag}_2(\text{CN})_2$ in KCN exist the equilibria:



and



If we call the concentration of $\text{Ag}(\text{CN})_2^-$, Ag^+ , CN^- and $\text{Ag}_2(\text{CN})_2^+$ c_1 , c_2 , c_3 and c_4 , then

$$c_3 c_3^2 = K c_1 \quad \dots \dots \dots (4)$$

and

$$c_1 c_2 = K' c_4 \quad \dots \dots \dots (5)$$

When the solution is saturate with respect to $Ag_2(CN)_2$, (5) passes into:

$$c_2 c_1 = L \quad \dots \dots \dots (5a)$$

where L is the product of solubility of silvercyanide.

Now a precipitate will be formed on the anode, as soon as $c_{2a} c_{1a}$ has become L , and the electrolysis will have to be conducted so that $c_{2a} c_{1a}$ remains $< L$. c_{1a} , c_{2a} etc. denotes the concentration close to the anode, C_1 , C_2 etc. denoting the concentration at the boundary plane of the diffusion layer with the rest of the liquid.

According to § 2 of the preceding paper, the quantity of cyanogen ions diffusing per second towards the anode, is equal to:

$$\frac{D_3}{86400} \frac{C_3 - c_{3a}}{\delta}$$

So long as no $Ag_2(CN)_2$ is precipitated, these will form ions $Ag(\overline{CN})_2$ which move away from the anode through diffusion. The quantity of this is given by:

$$\frac{D_1}{86400} \frac{c_{1a} - C_1}{\delta}$$

From which follows that:

$$2 D_1 (c_{1a} - C_1) = D_3 (C_3 - c_{3a}) \quad \dots \dots \dots (6)$$

The current density is:

$$d = 1.117 D_1 \frac{c_{1a} - C_1}{\delta} \quad \dots \dots \dots (7)$$

This current density is therefore maintained through the cyanogen ions diffusing to the anode, and ions of $Ag(\overline{CN})_2$ being formed there, which diffuse away from the anode. If the current density is increased, it will attain a value at which not enough \overline{CN} diffuses to the anode for $Ag(\overline{CN})_2$ to be exclusively formed; also $Ag_2(CN)_2$ will then have to be formed at the anode. When the current density is regulated so that the solution at the anode is just saturate with $Ag_2(CN)_2$, but no appreciable quantity of $Ag_2(CN)_2$ is deposited, the equations (6) and (7) hold, and at the same time:

$$c_{2a} c_{1a} = L \quad \dots \dots \dots (5a)$$

and

$$c_{2a} c_{3a}^2 = K c_{1a} \quad \dots \dots \dots (4)$$

From (4), (5a), and (6) follows:

$$c_{1a} = \frac{2D_1C_1 + D_3C_3}{2D_1 + D_3 \sqrt{\frac{K}{L}}} \dots \dots \dots (8)$$

and from (7)

$$d = \frac{1.117}{\delta} D_1 \frac{D_3C_3 - D_3C_1 \sqrt{\frac{K}{L}}}{2D_1 + D_3 \sqrt{\frac{K}{L}}} \dots \dots \dots (9)$$

$\sqrt{\frac{K}{L}}$ is very small for silver cyanide, about 10^{-3} , and when C_1 is not very large with respect to C_3 we may write:

$$d = \frac{1.117}{2\delta} D_3 C_3 \dots \dots \dots (10)$$

This equation gives, therefore, the current density below which no deposition of a precipitate on the anode takes place.

It appears from it that this current density is the greater as the concentration of the complex former is greater, the diffusion coefficient greater, and δ smaller. By means of vigorous stirring and increase of temperature we can work with a greater current density.

For the rest the current density, at which the anode is covered with a precipitate, is about the same for all complex salts (for a same value of C_3), the coefficient of diffusion differing little. Of

course this holds only when $\sqrt{\frac{K}{L}}$ is small. The values of K

and L have, therefore, no influence. When now $\sqrt{\frac{K}{L}}$ is not very small, or C_1 great with respect to C_3 , equation (9) must be used instead of (10). The current density is now smaller, the numerator being smaller and the denominator greater than in (10).

The potential, at which the deposition of $Ag_2(CN)_2$ begins, is found by substitution of (9) in equation (16) of the preceding paper:

$$E = \varepsilon + 0.058 \log K + 0.058 \log \frac{2D_1C_3 - 2D_1C_1 \sqrt{\frac{K}{L}}}{2D_1 + D_3 \sqrt{\frac{K}{L}}} - 0.116 \log \frac{D_3C_3 \sqrt{\frac{K}{L}} + 2D_1C_1 \sqrt{\frac{K}{L}}}{2D_1 + D_3 \sqrt{\frac{K}{L}}} \dots \dots \dots (11)$$

If, therefore, a current density prevails given by equation (9), the liquid just at the anode is saturate with $\text{Ag}_2(\text{CN})_2$, but not in more distant parts of the diffusion layer, as here the concentration of $\overline{\text{CN}}$ is greater, and the silver cyanide dissolves under formation of $\text{Ag}(\overline{\text{CN}})_2$. Hence the layer of silver cyanide will not become thicker for constant current density.

If the current density is increased, not enough $\overline{\text{CN}}$ -ions will diffuse to the anode to form again complex ions with the $\text{Ag}_2(\text{CN})_2$ formed by the $\text{Ag} + \text{Ag}(\overline{\text{CN}})_2$. Part of the cyanogen ions will now yield $\text{Ag}_2(\text{CN})_2$ with the silver of the anode. This part will be the greater as the current density is greater. For a given value of the latter practically all the $\text{Ag}(\overline{\text{CN}})_2$ and $\overline{\text{CN}}$ will be consumed to yield $\text{Ag}_2(\text{CN})_2$ at the anode. For a still greater value of d the silver will then go into solution as Ag^+ .

So long as the $\text{Ag}_2(\text{CN})_2$ is deposited only on the anode and not in the liquid, the following equation holds with close approximation:

$$d = \frac{1.117}{\sigma} [D_1 (C_1 - c_{1a}) + D_3 (C_3 - c_{3a})] \quad \dots \quad (13)$$

or in connection with (4) and (5a):

$$d = \frac{1.117}{\sigma} \left[D_1 \left(C_1 - \frac{L}{c_{2a}} \right) + D_3 \left(C_3 - \frac{\sqrt{KL}}{c_{2a}} \right) \right] \quad \dots \quad (14)$$

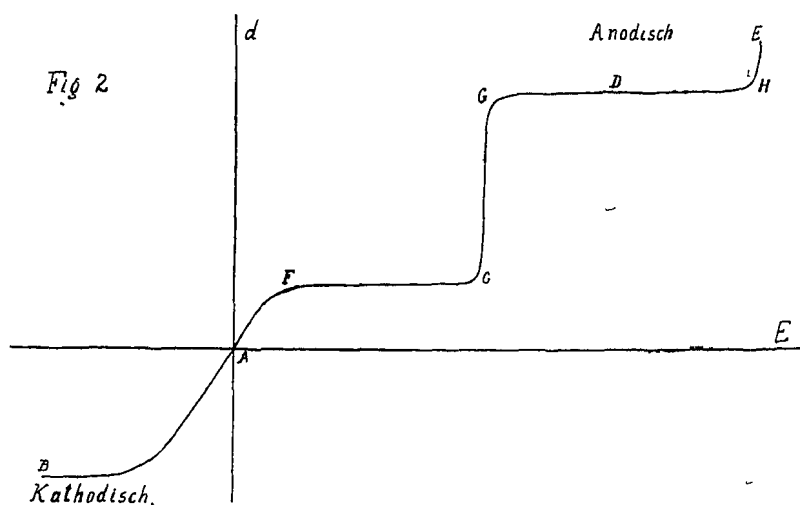
This equation combined with:

$$E = \varepsilon + 0.058 \log c_{2a}$$

yields the current potential line.

When at last the current density becomes so great that the quantity of $\text{Ag}(\overline{\text{CN}})_2$ and $\overline{\text{CN}}$ diffusing to the anode, is not great enough to maintain this current density, silver ions will also go into solution, which precipitate at some distance from the anode as $\text{Ag}_2(\text{CN})_2$. This corresponds then with the precipitation of AgCl in the liquid, as has been treated in § 4. These two cases are, however, not properly comparable, as at the precipitation of AgCl the liquid is everywhere saturate with AgCl , whereas in the case of $\text{Ag}_2(\text{CN})_2$ the liquid in the diffusion layer is saturate with silver cyanide up to a certain distance from the anode, but not the whole liquid. Consequently an equation of the current potential line will hold here which agrees with that for AgCl in its main points, but not entirely.

Fig. 2 gives the current tension line of a solution which is $0.1n$ with respect to $\text{Ag}(\overline{\text{CN}})_2$ and $0.1n$ with respect to $\overline{\text{CN}}$. The portion BA holds for cathodic polarisation, AE for anodic polarisation.



From *A* to *C* exclusively $\text{Ag}(\overline{\text{CN}})_2$ is formed. At *C* the deposition of $\text{Ag}_2(\text{CN})_2$ on the anode begins, from *C* to *G* it becomes greater and greater, at *G* besides the deposition of cyanogensilver on the anode, this compound also begins to precipitate in the liquid; at *D* the quantities of $\text{Ag}_2(\text{CN})_2$ being deposited on the anode and in the liquid are equal, and finally from *H* to *E* the cyanogen silver precipitates practically exclusively in the liquid.

It is clear that in practice a current density will be worked with which is smaller than *F*. It is, indeed, possible to make the current density somewhat greater than *F* without $\text{Ag}_2(\text{CN})_2$ being deposited on the anode, but this slight increase of the current density gives a very great increase of polarisation-tension, which can amount to about 0.4 or 0.5 V. A too great current density at the anode, therefore, gives rise here to an appreciable loss of energy.

Chemical Laboratory of the University.

Amsterdam, October 1916.

Physiology. "An exact method for the determination of the position of the eyes at disturbances of motion." By Dr. C. OTTO ROELOFS. (Communicated by Prof G. VAN RIJNBERK).

(Communicated in the meeting of October 28, 1916).

In a communication to the Meeting of the 26nd of January 1916 I indicated, in what way it is possible to calculate the position of the axis round which the eye has, as it were, turned, when we know the abduction, deorsumduction and inward rotation, caused