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Chemistry. — “Some Particular Cases of Current potential Lines” I.

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

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1. *Introduction.* When a metal is immersed in a solution that contains the ions of this metal, there arises between the metal and the solution a potential difference, which when equilibrium has set in, is given by the formula

$$E = V_{met} - V_{sol} = \epsilon + \frac{0.058}{n} \log c. \quad (1)$$

for a temperature of 18°, in which formula c is the concentration, n the valency of the ion, and ϵ the value that the potential difference has when the ion concentration is 1.

If the metal is made cathode, the potential difference changes, and the change is the greater as the current density is greater. The line indicating the potential difference at the cathode (or anode) as function of the current density is the current potential line or more strictly speaking the current density potential line. The course of this line has been theoretically examined for some cases. For a theoretical treatment it is required in the first place that also for the electrolysis permanent equilibrium between the metal and the solution is assumed to exist, so that the above given equation is always valid.

The change of E when the current circulates is then the consequence of a change of c , or ϵ , or of both. As ϵ is a constant for a given metal and solvent and at constant temperature and pressure, ϵ can only change when the metal that deposits electrolytically, has other properties than the metal of the cathode. This is e.g. the case when the metal separates in another modification which is not in equilibrium with the first form of the metal, or when the inner composition of the metal is another.¹⁾

In the following considerations we shall leave out of account this possibility, hence we shall assume that ϵ is constant, and examine in what way c depends on the current density, which then at the same time enables us to know the dependence of E on the current density.

The simplest case is here that the dissolved electrolyte is entirely

¹⁾ SMITS and ATEN, These Proc. XVI, p. 699; XVII, p. 37 and 680; XVIII, p. 1485.

ionized into simple, anhydrous ions. NERNST¹⁾ and his pupils have derived an equation of the current potential line for this in the following way.

On deposition of a metal the solution gets poorer in metal ions in the neighbourhood of the cathode; the concentration of the metal ions at the cathode would very soon have become 0, and then the deposition of metal would stop, when not continually metal ions were added to the cathode. This supply takes place in two ways. First in this way that metal ions migrate with the current to the cathode, secondly in this way that the ions go to the cathode by diffusion.

The migration of the metal ions with the current can be practically excluded by addition of an excess of a second electrolyte. In this case the transmission of the current takes chiefly place through the ions of the added electrolyte, and only the diffusion of the ion that is discharged, is to be taken into account. If the added electrolyte is chosen so that it has the same anion as the original one, the diffusion coefficient of the metal ion is proportional with its mobility, viz. for a binary electrolyte at 18° $0,0224 u$, in which u is the electrolytic mobility, expressed in rec. ohms.

If the solution is strongly stirred, it may be assumed that the liquid has the same concentration throughout, except in a very thin layer on the electrode, which is not set in motion by the stirring. In this layer, the thickness of which is dependent on the velocity of the stirring, the movement of the ion only takes place by diffusion. When we electrolyze with a constant current density, and all circumstances remain the same for the rest, a stationary state will arise in this diffusion layer. An equal number of ions then pass per second through every section of the diffusion layer, and all the ions arriving per second at the cathode, are discharged per second there. This latter condition gives a connection between the current density and the diffusion velocity.

If the concentration of the ions in the solution outside the diffusion layer is C and at the cathode c , and the thickness of the diffusion layer δ , the gradient of concentration in the diffusion layer is $\frac{C-c}{\delta}$, and the quantity of ions passing per second through a section of 1 cm². is $\frac{D}{86400} \frac{C-c}{\delta}$, if D is the coefficient of diffusion per day.

¹⁾ Cf. NERNST, Ber. **30** (1897) 1553. SALOMON, Z. phys. Chemie **24** (1897) 54, **25** (1898) 365, COTTRELL *ibid* **42** (1903) 385, GRASSI, *ibid* **44** (1903) 460 BRUNNER, *ibid* **47** (1904) 56, NERNST and MERRIAM, *ibid*. **53** (1905) 235.

The same quantity of ions must be discharged per second at 1 cm². of area of the cathode. The charge of this quantity of ions is therefore equal to the current density d

$$d = \frac{96500}{86400} D \frac{C-c}{\delta},$$

$$d = 1.117 D \frac{C-c}{\delta} \dots \dots \dots (2)$$

and by combination of (1) and (2) we get :

$$E = \epsilon + \frac{0.058}{n} \log \left(C - \frac{d\delta}{1.117 D} \right) \dots \dots \dots (3)$$

A similar equation holds for the anodic polarisation.

Here $d = 1.117 D \frac{c_a - C}{\delta}$, where c_a represents the concentration of the metal ions at the anode.

The anodic and the cathodic polarisation may also be represented by the same equation, when the current density at one of the electrodes, e.g. the cathode, is taken negative.

Then we get :

$$d = 1.117 D \frac{c-C}{\delta} \dots \dots \dots (4)$$

and

$$E = \epsilon + \frac{0.058}{n} \log \left(C + \frac{d\delta}{1.117 D} \right) \dots \dots \dots (5)$$

In figure 1 the general course of this line is represented by a . Positive current densities here refer to the anode, negative ones to the cathode. It is seen from the course of the line that with decreasing values of the potential the current density at the cathode approaches to a limiting value. This current density, which cannot be exceeded, bears the name of limiting current. The value of this current density follows from (4).

The smallest value that c can have, is 0 ; hence the greatest value for the cathodic current density :

$$d_{K \text{ limit}} = - 1.117 D \frac{C}{\delta} \dots \dots \dots (6)$$

This cathodic limiting current is, therefore, proportional to the concentration of the ions in the electrolyte, and to the diffusion coefficient, and in inverse ratio to the thickness of the diffusion layer.

There does not exist a limiting current in the same sense at the anode. When, however, anode and cathode have the same area, the current density is the same for them. Hence :

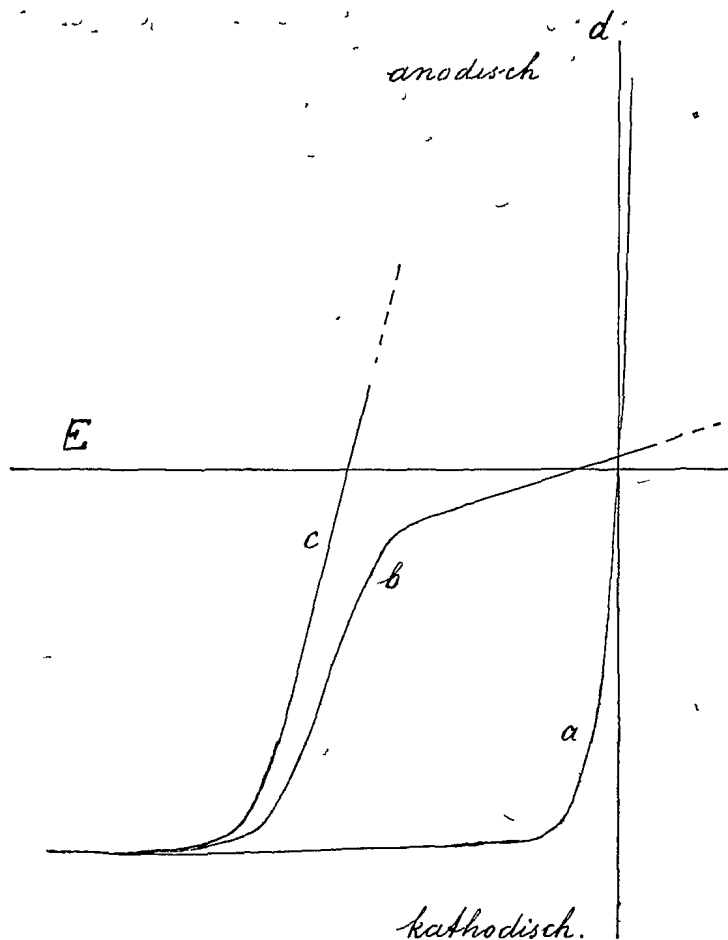


Fig. 1.

anodisch = anodic ; kathodisch = cathodic

$$d_a = 1.117 D \frac{C}{\delta} \dots \dots \dots (7)$$

for the cathodic limiting current, and :

$$E_a = \varepsilon + \frac{0.058}{n} \log 2C.$$

$$E_a = \varepsilon + \frac{0.058}{n} \log C + \frac{0.058}{n} \log 2 \dots \dots \dots (8)$$

From which follows that the polarisation voltage at the anode is equal to $\frac{0.017}{n}$, when the current density is equal to the cathodic limiting current. This value is, therefore, a constant, which is independent of the nature of the electrolyte, of the concentration, and

of the velocity of stirring, when the stirring is equally vigorous at the cathode and at the anode.

It is, indeed, also possible to speak of an anodic limiting current, in so far as at a certain current density the concentration of the ions at the anode can become greater than that in a saturate solution of the electrolyte. In this case the electrolyte will crystallize out on the anode, on account of which the current will be broken, or at least weakened.

As $c_a = 2C$ for the cathodic limiting current, this crystallizing cannot take place when the original concentration of the ions in the solution is half that of the saturate solution.

For small current densities :

$$\frac{\Delta E}{\Delta d} = \frac{0.025}{n} \frac{d}{1.117 DC} \dots \dots \dots (9)$$

So that for small current densities the current density for a given polarisation tension ΔE is proportional to the concentration.

On comparison of the course of this theoretical line with the experimentally determined lines it appears that in some cases (nitrates and chlorates of different heavy metals) the course of the two lines agrees. In a great many cases the course of the real lines is, however, different, namely so, that in many cases they are much flatter, especially in the beginning, about as the line *b* in figure 1. This is the case for solutions in which complex ions occur, also in case of hydrogen generation, and for metals that can show passivity. In the two last cases the divergent course does not lie in the value of c , but of ϵ , so that they are left out of consideration. For the complex ion the current opinion is ¹⁾ that the deviations are caused by a slow formation of elementary ions from complex or hydrated ions.

This view rests chiefly on observations by HABER and RUSS ²⁾ on reduction of organic compounds, and of LE BLANC and SCHICK ³⁾ on the results of alternate current electrolysis in solutions of complex ions.

EUCKEN ⁴⁾, however, has shown that though the complex ions rapidly split up into simple ones, the current potential line belongs to the type *b* and not to the type *a* of figure 1.

The derivation which EUCKEN gives, is pretty intricate, as he bases it on the supposition that the simple ions are formed with a

¹⁾ Cf. e.g. FOERSTER, Elektrochemie wassriger Lösungen. Leipzig 1915, p. 252 et seq.

²⁾ Z. phys. Chemie 47 (1904) 257.

³⁾ Z. phys. Chemie 46 (1903) 213, Z Elektrochemie 9 (1903) 636

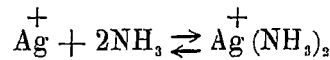
⁴⁾ Z phys. Chemie 64 (1908) 562.

limited velocity, draws up a general equation for this, and derives from this the equation in case of rapid establishment of the equilibrium by assuming the velocity constant to be infinitely great.

2. *Complex Ions.*

In the following way we arrive, however, easily at the equation of the current potential line in a solution of complex ions.

Let us take as an example a solution of a silver salt in ammonia, in which the complex ions $\text{Ag}^+(\text{NH}_3)_2$ occur, which are in equilibrium with free ions Ag^+ and molecules NH_3 .



then, as

$$K \cdot C_{\text{Ag}^+} \cdot C_{\text{NH}_3}^2 = C_{\text{Ag}^+(\text{NH}_3)_2}^+$$

and

$$E = \varepsilon + 0.058 \cdot {}^{10}\log C_{\text{Ag}^+}$$

$$E = \varepsilon - 0.058 \cdot {}^{10}\log K + 0.058 \cdot {}^{10}\log C_{\text{Ag}^+(\text{NH}_3)_2}^+ - 0.116 \cdot {}^{10}\log C_{\text{NH}_3}$$

When in general an n -valent ion A combines with p -molecules or ions B , then

$$E = \varepsilon - \frac{0.058}{n} \cdot {}^{10}\log K + \frac{0.058}{n} \cdot {}^{10}\log C_{AB_p} - \frac{0.058}{n} \cdot p \cdot {}^{10}\log C_B \quad (10)$$

By electrolysis the ions AB_p are now discharged on the cathode, the metal A is deposited on the cathode, B remaining in solution. At the cathode there arises, therefore, a deficit of the ions AB_p , and an excess of B . The latter moves away from the cathode through diffusion, the former towards the cathode.

When a stationary state has set in, the following equation will hold for the ions AB_p :

$$d = 1.117 D_1 \frac{eK_1 - C_1}{\delta}, \dots \dots \dots (11)$$

This equation holds for the anodic polarisation, when the current density at the anode is taken positive. The index 1 refers to complex ions.

With regard to the particles B we may state that at the cathode an equal number must disappear through diffusion as are liberated through discharge of the complex ions, hence p times the number of complex ions diffusing towards the cathode.

This last quantity is

$$\frac{pD_1}{86400} \frac{C_1 - eK_1}{\delta}, \dots \dots \dots (12)$$

whereas there vanish by diffusion :

$$\frac{D_2}{86400} \cdot \frac{c_{K_2} - C_2}{d}, \dots \dots \dots (13)$$

when the index 2 refers to the particles of the complex former.

From this follows :

$$p D_1 (C_1 - c_{K_1}) = D_2 (c_{K_2} - C_2) \dots \dots \dots (14)$$

This combined with (11), yields :

$$c_{K_2} = C_2 - \frac{pd\delta}{1.117D_2} \dots \dots \dots (15)$$

On substitution of these values in (10) the equation of the current potential line becomes :

$$E = \varepsilon - \frac{0.058}{n} {}^{10}\log K + \frac{0.058}{n} {}^{10}\log \left(C_1 + \frac{d\delta}{1.117D_1} \right) \left\{ \begin{array}{l} \\ - 0.058 \frac{p}{n} {}^{10}\log \left(C_2 - \frac{pd\delta}{1.117D_2} \right) \end{array} \right. \dots \dots \dots (16)$$

The course of this line depends in the same way on the concentration of the complex ions, as for simple salts on the concentration of the elementary ions. The term $-\frac{0.058 {}^{10}\log K}{n}$ causes the potentials to be more negative than for simple salts, K always having a very great value for the complex ions considered here. The above considerations do not apply to ions of slight complexity, as for this we should not only have to take the diffusion of the complex ions into account, but also the diffusion of the elementary ions present.

Accordingly the value of K has only influence on the situation of the line, not on the form.

The last term of (16) has the greatest influence on the form of the line. It causes the line to run very flat in the beginning. The slope of the current potential line for small current densities is given by :

$$\left(\frac{\Delta E}{\Delta d} \right)_{d=0} = \frac{0.025}{n} \frac{\delta}{1.117D_1 C_1} + \frac{0.025}{n} \frac{p^2 \delta}{1.117D_2 C_2}, \dots \dots \dots (17)$$

Hence the value of $\frac{\Delta E}{\Delta d}$ will be much greater than for simple salts, especially for small value of C_2 . The factor $0.025 \frac{p^2}{n}$ causes the line to run the flatter as the number of molecules bound by the ion, is greater. In general the line will, therefore, run flatter for bivalent ions than for univalent ones, because $\frac{p}{n}$, hence the number of mole-

cules bound by an equivalent of an ion, is in many cases constant for the same complex former.

If C_2 , the concentration of the complex forming molecules, is great, the term $\frac{0.025 p^2}{n} \cdot \frac{\delta}{1.117 D_2 C_2}$ has less influence, and therefore the current tension line has a more normal course.

Because the complexity constant in equation (16) only occurs in the term $0.058^{10} \log K$, it seems that the complexity of the ion has no influence on the form of the line. This is only true for equal values of C_2 . For ions of different complexity C_2 will in general be different, and that greatest for the least complex ions. In consequence of this a current potential line of a less complex ion has a more normal course than that of an ion of greater complexity.

The expression for the cathodic limiting current is the same as in the case of simple ions, namely :

$$d_{limit} = - \frac{1.117 D_1 C_1}{\delta} \dots \dots \dots (17a)$$

An anodic limiting current exists here no more than in the case of simple salts. According to equation (16) the greatest current density possible at the anode would be that for which :

$$C_2 = \frac{pd\delta}{1.117 D_2},$$

as for a greater value of d the last term of (16) would become the logarithm of a negative value. For this current density equation (16), however, no longer holds. This case will be more fully discussed in a later chapter.

In Fig. 1 the line b is drawn for an electrolyte as $\text{Ag}(\text{NH}_3)_2^+$, which is $0.1 n$ for the complex ions, and $0.001 n$ for NH_3 , c holding for the same electrolyte, but with $0.1 n \text{ NH}_3$. This last line agrees pretty well in form with that for simple ions, a .

3. *Hydrated Ions.* The above derivations are, however, not quite complete, in so far as the hydration of the ions is not taken into account.

That the ions in aqueous solutions are hydrated, may be assumed to be an established fact. Whether the water is chemically bound, or is carried along to join the movement of the ions in another way is an open question, which, however, is immaterial for this purpose. Nor is the number of molecules, carried along by the different ions, accurately known.¹⁾

¹⁾ For a summary of the present state of the problem of hydration see NILRATAN DHAR. Z. f. Elektrochemie 20 (1914) 57.

Further it is not known whether complex ions as $\text{Ag}^+(\text{NH}_3)_2$ are hydrated too, or whether the molecules NH_3 have replaced the water molecules of the hydrated ion.

That the water carried along by the ions must be of influence on the course of the current tension line easily appears in the following way: The hydrated metal ions which are discharged at the cathode, leave their water behind. Hence there takes place an accumulation of water at the cathode. The solution at the cathode will, therefore, be more dilute than in the case of anhydrous ions, as in the latter case only the ions disappear from the solution, but besides water is still added here. Consequently for a given current density a greater polarisation voltage will belong to hydrated ions than to anhydrous ions.

The way in which the water liberated at the cathode disappears, is different from the way in which the ammonia of the complex ion $\text{Ag}^+(\text{NH}_3)_2$ moves away from the cathode. The released water can namely not move away by diffusion, because for the water there exists practically no difference of concentration. There will, however, take place a movement of the water from the cathode, because always a new quantity of water is liberated at the cathode, and this supplants the already present water. Hence the consequence will be that the liquid as a whole gets a movement away from the cathode.

On the ground of these considerations we arrive at an equation of the current potential line. When a gramme equivalent of the metal ion carries along with it a molecules of water, then when a current density d prevails, $\frac{d}{96500}$ gramme equivalents will be discharged per second; hence $\frac{d}{96500} a$ mol. of water will be liberated, occupying a volume of $18a \frac{d}{96500}$ cm³.

The liquid moves, therefore, with a velocity of $18a \frac{d}{96500}$ cm. per sec. from the cathode. Let a concentration difference $\frac{dc}{dx}$ exist in the diffusion layer at a distance x from the cathode, when a stationary state has set in. Then the quantity of ions, diffusing per second to the cathode is $\frac{D}{86400} \frac{dc}{dx}$.

As the liquid moves away from the cathode with a velocity

$18a \frac{d}{96500}$ cm./sec., the quantity of ions that reaches the cathode per second must be diminished by $18a \frac{d}{96500}$, so that the quantity of ions arriving at the cathode in a second, is given by:

$$\frac{D}{86400} \frac{dc}{dx} - 18a \frac{d}{96500} c. \dots \dots \dots (18)$$

which expression must, therefore, be equal to $\frac{d}{96500}$.

From this follows:

$$d \cdot (1 + 18ac) = 1.117 D \frac{dc}{dx} \dots \dots \dots (19)$$

or

$$\frac{d}{1.117 D} dx = \frac{dc}{1 + 18ac}$$

By integration:

$$\frac{d}{1.117 D} x = \frac{1}{18a} \ln(1 + 18ac) + K \dots \dots \dots (20)$$

in which for $x = 0$ $c = c$, and for $x = \delta$ $c = C$, hence

$$\frac{d}{1.117 D} \delta = \frac{1}{18a} \ln \left(\frac{1 + 18aC}{1 + 18ac} \right)$$

If the cathodic current density is taken negative, the anodic positive, the following equation holds:

$$\frac{d\delta}{1.117 D} = \frac{1}{18a} \ln \left(\frac{1 + 18ac}{1 + 18aC} \right) \dots \dots \dots (21)$$

both for cathodic and for anodic polarisation.

By combining (21) with the equation for the potential difference

$$E = \varepsilon + \frac{0.058}{n} \log c$$

we can indicate E as function of d .

The cathodic limiting current is here:

$$d_{K \text{ limit}} = - 1.117 \frac{D}{18a\delta} \ln(1 + 18aC) \dots \dots \dots (22)$$

while

$$\left(\frac{\Delta E}{\Delta d} \right)_{d=0} = \frac{0.025 \delta (1 + 18aC)}{1.117 DCn} \dots \dots \dots (23)$$

It appears from these equations as was indeed to be expected, that the influence of hydration on the course of the current potential line is slight. When the solution contains 1 gram-ion per liter, when

$c = 0.001$ and a is 6, the limiting current is $0.95 \times$ the limiting current for the same anhydrous ions, and $\left(\frac{\Delta E}{\Delta d}\right)_{d=0}$ is $1.1 \times$ this value without hydration.

Though the determination of the current potential line supplies us with a means for the determination of the hydration of the ions, this means will only be serviceable when we succeed in carrying out the determination of the current potential line very accurately. Theoretically this method may be put on a line with the method followed by BUCHBOCK¹⁾, WASHBURN²⁾ and others, where the degree of hydration is derived from an indirect determination of the quantity of water liberated at the cathode. According to equation (21) we find here the hydration of the cation alone, whereas BUCHBOCK and WASHBURN's method furnishes the difference of the products of hydration and mobility of cation and anion.

When we polarize anodically with a current density equal to the cathodic limiting current, we get:

$$l(1 + 18 ac_a) = 2l(1 + 18 aC) \dots \dots (24)$$

Hence we have

$$c_a = 2.1 C$$

for the value of hydration and concentration assumed above, whereas we have $c_a = 2C$ without hydration.

Hence the influence of the hydration appears to be slight also at the anode.

Some special cases present themselves with the anodic polarisation when the metal ion can form a sparingly soluble compound with one of the present anions as for solutions of the most complex salts, for electrolysis of solutions of halogenides with a silver anode etc. In some cases it is desirable to prevent the formation of the sparingly soluble solution, as in the electrolysis of solutions of complex cyanides, in other cases it is desired that the compound is deposited on the anode, e.g. in the electrolytical determination of the halogens, and sometimes too it is desirable that the compound separates in the liquid, namely in the method of LÜCKOW³⁾ for the electrolytical formation of metal compounds.

In virtue of the above considerations it is now possible to give the conditions on which the process will take place in one way or another.

¹⁾ Z. f. physik. Chemie 55 (1906) 563.

²⁾ Jahr. d. Radioaktivität 5 (1908) 493, 6 (1909) 69.

³⁾ Z. f. Elektrochemie 3 (1897) 482.

4. Anodic formation of silverhaloids.

Let us suppose the case that a silver anode is placed in a solution of sodium chloride with an excess of sodium nitrate, so that only the diffusion of the chlorine ion is to be taken into account, not its migration. On anodic polarisation the chlorine ions will be discharged at the silver, and then give AgCl. When, however, the current density is so great that fewer chlorine ions diffuse towards the anode than corresponds to this current density, also silver ions will go into solution. Strictly speaking the latter always takes place, because silver chloride is not absolutely insoluble, and therefore not all the AgCl formed will remain on the anode, but will go into solution for a small part.

In the following way we now arrive at an equation of the current potential line for anodic polarisation of silver in NaCl.

For a given current density there prevails at the anode a certain chlorine ion-concentration c_{1a} , and a certain silver ion-concentration c_{2a} . The product of these values is equal to the solubility product of silver chloride

$$c_{1a} c_{2a} = L.$$

Not only at the anode, but also in the diffusion layer and in the whole liquid the solution is saturate with AgCl, hence

$$C_1 C_2 = L$$

holds everywhere.

In the diffusion layer c_1 and c_2 have values which are a function of the distance x to the anode, in the rest of the liquid they have a constant value, which we denote by C_1 and C_2 .

Now per unit of time a certain quantity of chlorine ions arrive through diffusion at the anode, there disappear per unit of time a certain quantity of silver ions; the sum of these two quantities, multiplied by the charge per gramme ion, gives the current density.

Here the quantity of ions passing through a section of the diffusion layer, is not the same for every section as it is in the preceding cases, for here also silver chloride must deposit, which causes chlorine ions and silver ions to disappear in equivalent quantities.

If we now consider a volume of the diffusion layer between a section at a distance x from the anode, and another at a distance $x + dx$, the quantity of silver ions or chlorine ions passing through the first section will in general not be equal to that passing through the second.

Through the section x a quantity of chlorine ions $-\frac{D_1 dc_1}{dx}$ will

diffuse, through the section $x + dx$ a quantity $- D_1 \left(\frac{dc_1}{dx} + \frac{d^2c_1}{dx^2} dx \right)$ in the direction of increasing x . The quantity of chlorine ions, which is deposited as AgCl is, therefore, the difference between the two quantities $D_1 \frac{d^2c_1}{dx^2} dx$.

In the same way a quantity of silver ions is deposited equal to $D_2 \frac{d^2c_2}{dx^2} dx$; these two are equal, hence:

$$D_1 \frac{d^2c_1}{dx^2} = D_2 \frac{d^2c_2}{dx^2}, \quad \dots \dots \dots (25)$$

$$\frac{d^2c_2}{dx^2} = \frac{D_1}{D_2} \frac{d^2c_1}{dx^2}.$$

$$\frac{dc_2}{dx} = \frac{D_1}{D_2} \frac{dc_1}{dx} + A \quad \dots \dots \dots (26)$$

$$c_2 = \frac{D_1}{D_2} c_1 + Ax + B, \text{ in which } c_2 = \frac{L}{c_1} \quad \dots \dots (27)$$

The values of A and B are found in the following way:

For $x = 0$ $c_1 = c_{1a}$ and $c_2 = c_{2a}$, the concentration of \overline{Cl} , resp. \overline{Ag} at the anode,

$$\text{hence} \quad c_{2a} = \frac{D_1}{D_2} c_{1a} + B, \quad B = c_{2a} - \frac{D_1}{D_2} c_{1a},$$

for $x = \delta$ $c_1 = C_1$ and $c_2 = C_2$, the concentration of \overline{Cl} , resp. \overline{Ag} in the solution.

$$C_2 = \frac{D_1}{D_2} C_1 + A\delta + c_{2a} - \frac{D_1}{D_2} c_{1a},$$

$$A = \frac{C_2 - \frac{D_1}{D_2} C_1 - \left(c_{2a} - \frac{D_1}{D_2} c_{1a} \right)}{\delta} \quad \dots \dots \dots (28)$$

If we now call the current density maintained by the diffusion of the chlorine ions d_1 and that maintained by the diffusion of the silver ions d_2 , then:

$$d_1 = 1.117 D_1 \left(\frac{dc_1}{dx} \right)_{x=0} \quad \dots \dots \dots (29)$$

$$d_2 = -1.117 D_2 \left(\frac{dc_2}{dx} \right)_{x=0} \quad \dots \dots \dots (30)$$

and the total current density

$$d = d_1 + d_2 = 1.117 D_1 \left(\frac{dc_1}{dx} \right)_{x=0} - 1.117 D_2 \left(\frac{dc_2}{dx} \right)_{x=0} \quad (31)$$

As further $c_1 c_2 = L$:

$$c_1 \frac{dc_2}{dx} + c_2 \frac{dc_1}{dx} = 0$$

This equation combined with (26) yields:

$$\left(\frac{dc_1}{dx} \right)_{x=0} = - \frac{Ac_{1a}}{\frac{D_1}{D_2} c_{1a} + c_{2a}} \quad (32)$$

$$\left(\frac{dc_2}{dx} \right)_{x=0} = \frac{Ac_{2a}}{\frac{D_1}{D_2} c_{1a} + c_{2a}} \quad (33)$$

Now d_1 becomes:

$$d_1 = -1.117 D_1 \frac{Ac_{1a}}{\frac{D_1}{D_2} c_{1a} + c_{2a}} \quad (34)$$

and d_2 becomes:

$$d_2 = -1.117 D_2 \frac{Ac_{2a}}{\frac{D_1}{D_2} c_{1a} + c_{2a}} \quad (35)$$

If in these equations the value of A from (28) is introduced, we get:

$$d_1 = -1.117 D_1 \frac{c_{1a} \left[C_2 - \frac{D_1}{D_2} C_1 - \left(c_{2a} - \frac{D_1}{D_2} c_{1a} \right) \right]}{\frac{D_1}{D_2} c_{1a} + c_{2a}}$$

or

$$d_1 = \frac{1.117 D_1 c_{1a} D_2 (c_{2a} - C_2) + D_1 (C_1 - c_{1a})}{\delta D_1 c_{1a} + D_2 c_{2a}} \quad (36)$$

and

$$d_2 = \frac{1.117 D_2 c_{2a} D_2 (c_{2a} - C_2) + D_1 (C_1 - c_{1a})}{\delta D_1 c_{1a} + D_2 c_{2a}} \quad (37)$$

in which $c_{1a} c_{2a} = C_1 C_2 = L$.

The total current density is now given by:

$$d = 1.117 \frac{D_2 (c_{2a} - C_2) + D_1 (C_1 - c_{1a})}{\delta} \quad (38)$$

This equation combined with:

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

yields the course of the current tension line.

Figure 2 gives a number of current potential lines for a silver anode in solutions for a chloride from $C_1=10^{-2}$ to $C_1=10^{-7}$.

On the axis of abscissae the $^{10}\log C \text{ Ag}^+$ has been drawn which is proportional to the potential, on the ordinate axis the current density d . In this $D_1 = D_2$ has been put and $L = 10^{-10}$.

With a comparatively great chlorine ion concentration, 10^{-2} , the

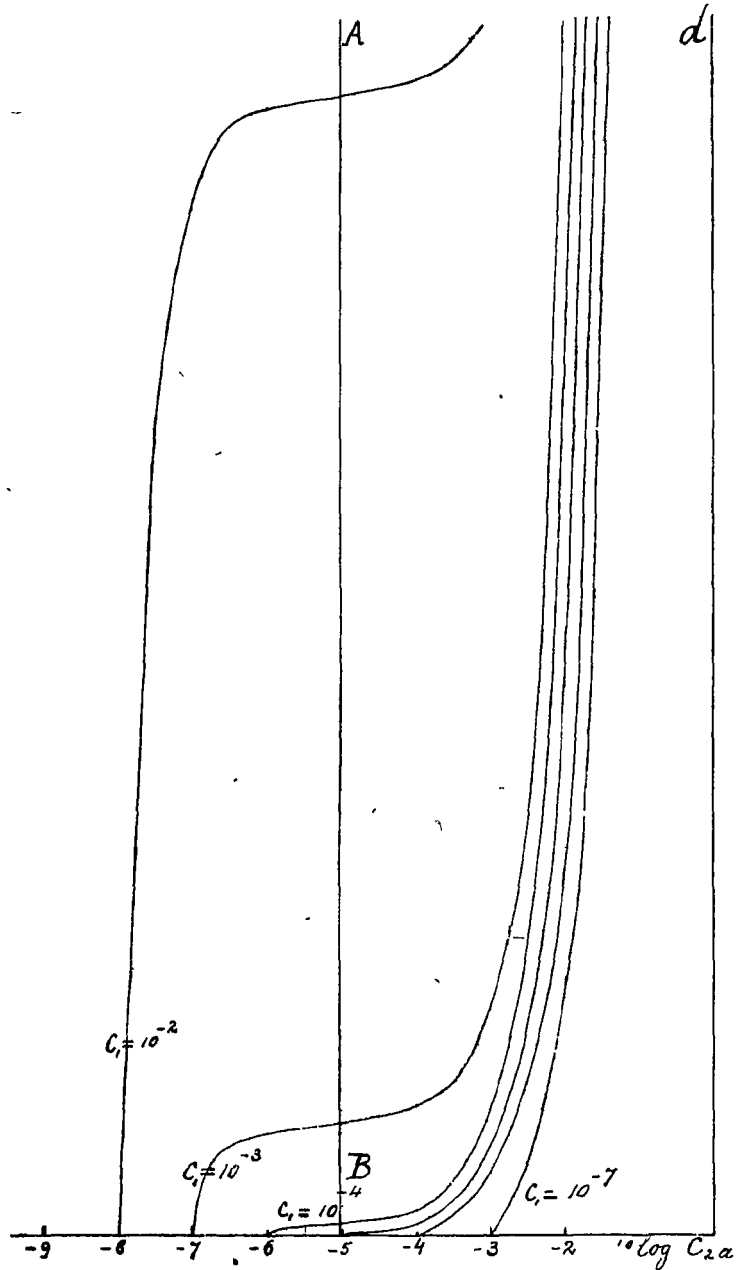


Fig. 2.

potential of the silver is least positive for $d=0$; with increasing intensity of the current the metal becomes at first only little more positive, till at a given current density the line suddenly bends, so that the potential becomes much more positive, and eventually on further increase of the current density it rises again more slowly. The same phenomenon is presented by the line for $C_1=10^{-3}$, but for smaller current density and also the line for $C_1=10^{-4}$ faintly shows this course. With smaller chlorine ion concentration the course of the current potential line approaches the normal course more. If the current potential line lies on the left side of the vertical line AB , for which $C_{2a}=10^{-5}=\sqrt{L}$, the current is chiefly used for deposition of AgCl on the anode, the part lying on the righthand side of the line AB denotes current densities, at which the silver chloride is deposited in the liquid.

This appears in the following way:

Equations (36) and (37) give the current density for deposition of AgCl on the anode and in the liquid.

$$\text{The proportion } \frac{\text{AgCl on the anode}}{\text{AgCl in the liquid}} = \frac{d_1}{d_2} = \frac{D_1 c_{1a}}{D_2 c_{2a}}$$

If we call β the fraction of the total current density used for silver chloride formation on the anode, then

$$d_1 = d\beta \quad \text{en} \quad d_2 = d(1 - \beta) \quad \dots \dots \dots (39)$$

and

$$\frac{\beta}{1-\beta} = \frac{D_1 c_{1a}}{D_2 c_{2a}}, \text{ or, as } c_{1a} c_{2a} = L.$$

$$c_{2a} = \sqrt{\frac{LD_1(1-\beta)}{D_2\beta}} \dots \dots \dots (40)$$

and

$$c_{1a} = \sqrt{\frac{LD_2\beta}{D_1(1-\beta)}} \dots \dots \dots (41)$$

By substitution of these values of c_{1a} and c_{2a} in (38), we get

$$d = \frac{1.117}{\delta} \left[D_1 C_1 - D_2 C_2 + \sqrt{LD_1 D_2 \frac{1-\beta}{\beta}} - \sqrt{LD_1 D_2 \frac{\beta}{1-\beta}} \right] \dots (42)$$

where $C_1 C_2 = L$.

In figure 3 β has been drawn as function of the current density. From this appears that for small current densities β is almost constant. Here practically all the AgCl is deposited on the anode. If the current density is increased, there comes a value of the current density where β decreases rapidly, and for still greater current

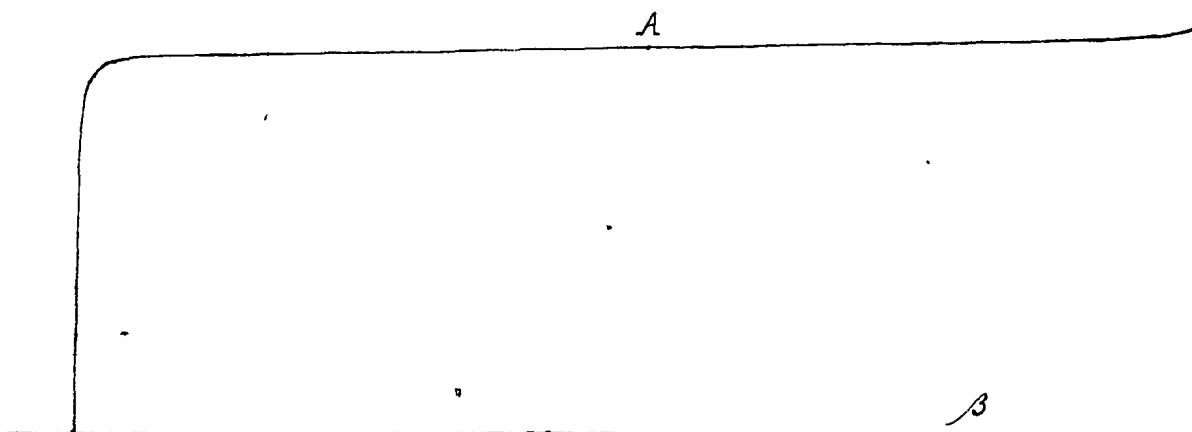


Fig. 3.

density β becomes almost 0, i. e. practically all the silver chloride is deposited in the liquid.

The point of inflection A in the line gives the limit between current densities, at which the AgCl is mostly deposited on the anode, and those at which the AgCl for the greater part deposits in the liquid. The density of the current in A may be called the *critical current density*, the value of β is here $1/2$. Hence we find from (42) for the critical current density:

$$d_{K_c} = \frac{1.117}{\delta} [D_1 C_1 - D_2 C_2] \quad (43)$$

If this equation is written in the form:

$$d_{K_c} = \frac{1.117}{\delta} \left[D_1 C_1 - D_2 \frac{L}{C} \right] \quad (44)$$

we may write, when C_1 is great compared with \sqrt{L} :

$$d_{K_c} = \frac{1.117}{\delta} D_1 C_1$$

In this case the critical current density is therefore proportional to the concentration of the chlorine ions, and it is given by the same equation as the cathodic limiting current for simple salts.

For great values of C_1 the critical current density is therefore, independent of the value of the solubility product, i. e. the value is the same for all halogens, as D_1 is here about equal.

It is different when C_1 has a small value, one that is comparable with \sqrt{L} .

The critical current density is $= 0$, when $D_1 C_1 = D_2 \frac{L}{C_1}$ or, D_1 and D_2 differing little, when $C_1 = \sqrt{L}$. For silver chloride, for which $L = 10^{-10}$, the critical density will therefore be $= 0$ for $C_1 = 10^{-5}$. Already at the smallest possible current density more AgCl will here be deposited in the liquid than on the anode. If on the other hand we work with an iodide, practically all the silver iodide will be deposited on the anode for $C_1 = 10^{-5}$ as $L_{AgI} = 10^{-16}$ and the critical current density is not $= 0$ until $C_1 = 10^{-8}$.

By the aid of the above considerations it is now possible to indicate in what way the electro-analytic determination of the halogens can take place most rationally, as will be set forth in the following paper.

Chemical Laboratory of the University.

Amsterdam, June 1916.

Mathematics. — “*Skew Frequency Curves.*” By M. J. VAN UVEN.
(Communicated by Prof. J. C. KAPTEYN).

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

The skewness of a frequency-curve appertaining to some observed quantity x may be explained, as Prof. J. C. KAPTEYN¹⁾ has shown, without dropping the normal Gaussian law of error, namely by supposing that, instead of the observed quantity x , a certain function of x : $Z = F(x)$, is spread according to the normal law.

Denoting the mean value of Z by M and the modulus of precision by h , the quantity

$$z = h(Z - M) = h\{F(x) - M\} = f(x)$$

will be distributed round the mean value zero with the modulus of precision unity, so that the probability that z is found between z_1 and z_2 is represented by

$$W_{z_1}^{z_2} = \frac{1}{\sqrt{\pi}} \int_{z_1}^{z_2} e^{-z^2} dz.$$

¹⁾ J. C. KAPTEYN: *Skew Frequency Curves in Biology and Statistics*; Groningen, 1903, Noordhoff.