THE DIFFUSION
OF
ELECTROLYTES

J. J. HERMANS

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OF
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CONTENTS.

Page

THE DIFFUSION OF A MIXTURE OF ELECTROLYTES.

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INTRODUCTION.

Electrochemistry deals with two kinds of problems: thermodynamic and kinetic. As far as the thermodynamical properties of electrolytic solutions are concerned (e.m.f.'s of cells, osmotic pressure, boiling-point, etc.) one has to restrict oneself to equilibria.

Introducing the "Lösungstension" Nernst succeeded in giving a theory of galvanic cells in the case of ideal solutions. This theory has afterwards been extended to non-ideal solutions, but it never went beyond the case of equilibrium. The number of cells of this kind is rather limited. Almost all measurements of p_H, oxidation- and reductionpotentials, etc., make use of cells which are essentially irreversible because they contain liquid-liquid-junctions, so that diffusion takes place and therefore a diffusionpotential can occur. A thermodynamical treatment of these systems is *in principle wrong*. We wish to emphasize this point in spite of the fact that the contrary is repeatedly affirmed. We shall return to this point on page 7.

These systems must therefore be treated by kinetic methods. One can only expect to obtain an exact theory of cells with liquid-liquid-junctions by studying the irreversible process of diffusion.

Nernst was the first to attack the problem of the diffusion of electrolytes. As well known his theory restricts itself to the case of ideal solutions. As in all practical measurements we have to deal with solutions which are too concentrated to be treated as ideal, the original theory will have to be corrected. There are two kinds of corrections to be made. In the first place one must take into account that the concentrations must be replaced by the activities. These activities cannot be calculated for all concentrations, but as long as the concentrations are small, the theory of Debije and Hückel yields a good approximation.

It appears however, that a second correction must be introduced at the same time. The diffusion is also changed by a hydrodynamical interaction of the ions. The motion of an ion is transferred to other ions by the surrounding liquid. This has been called electrophoretic effect *).

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*) P. Debije and E. Hückel, Physik. Z. **25**, 49 (1924).

This dissertation is divided in two parts. In the first part the diffusion of a single electrolyte will be studied, particularly with respect to the behaviour in non-ideal solutions. Both the activity and the electrophoretic effect will be taken into account, but only for concentrations where all effects are linear in $\sqrt{c}$, and higher powers of $\sqrt{c}$ can be neglected. The results of this theory will be compared with experiments, some of which are already mentioned in the literature, while others have been carried out by the author. In one case the influence of the solvent has been studied; this influence is predicted in first approximation by the theory. It may at once be stated that the theory appears to be confirmed up to concentrations varying from 0.01 to 0.03 N.

In the second part the diffusion of a mixture of electrolytes will be discussed. Here we shall restrict ourselves to the case of ideal solutions.

I. The diffusion of a single electrolyte.

1. The theory of diffusion of an electrolyte, as given by Nernst[1]) leads to the following results. 1. The electrolyte diffuses with a mobility which lies between those of both ions. 2. During diffusion there exists a potentialdifference between every two points of different concentrations c_1 and c_2. This potentialdifference (the "diffusionpotential") is proportional to $\log c_1/c_2$, and independent of the manner in which the concentration varies between both points.

Nernst's treatment is essentially a kinetic one. Attempts have been made to calculate the diffusionpotential by a quasi thermodynamical reasoning. This thermodynamical treatment leads to the same result as the kinetic theory in the case of ideal solutions. This has probably furthered the opinion that a similar thermodynamical reasoning could also be applied to real electrolytic solutions[2]). We shall show that this opinion is wrong; and it is very important to insist on this point, because this wrong opinion has penetrated in several books on thermodynamics and electrochemistry[3]), and has led to the very far-reaching conclusion that cells with diffusion only yield information about mean activities, and not about the activities of the separate ions.

Suppose we wish to measure a diffusionpotential. We then place

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[1]) W. Nernst, Z. physik. Chem. 4, 129 (1889).

[2]) P. B. Taylor, J. Phys. Chem. 31, 1478 (1927).

[3]) E. A. Guggenheim, Modern Thermodynamics, London 1933, page 148; G. N. Lewis and M. Randall, Thermodynamik, Wien 1927, page 289; M. Le Blanc, Lehrb. d. Elektrochemie, Leipzig 1925, page 239; C. Drucker, Handb. d. Exp. Physik 1933 XII 2, page 21.

an electrode which is reversible with regard to one of the ions, in a solution of concentration c_1, another in a solution of concentration c_2, and join both solutions, taking care that the distance between the electrodes and the diffusion layer is so large that the concentrations in the neighbourhood of the electrodes remains practically constant for a long time. We have thus got a concentration-cell with diffusion.

Now the usual thermodynamical treatment of this cell leads to the result that the e.m.f. is a function of the transportnumber of the electrolyte and of the mean activity, while the activities of the respective ions do not occur in it.

2. In order to understand what this means, we first shall consider more closely the concept of activity. We shall take as an example a non-ideal gas. The energy of a molecule in this gas is altered by the v. d. Waals forces. The thermodynamic properties, which can be studied by experiments, differ from those of an ideal gas.

An assembly of a number, say n, of molecules in a given volume, shows the thermodynamic properties of an assembly of m molecules ideal gas in this volume, and one can describe these properties as if the gas were ideal, provided the concentration n is replaced by the "activity" m. The ratio $m/n = f$ is called activity-coefficient. It is a function of the concentration, while we have $f = 1$ in the ideal case. Now in a mixture of two gases the activity-coefficients of both components need not be equal. For definiteness consider a mixture of helium and chlorine. The activity of the chlorine is determined by forces between helium and chlorine and by forces between chlorine and chlorine. In the activity of helium, however, only the forces between helium and chlorine enter, the forces between helium and helium being comparatively small. The activity-coefficient of helium in this mixture will therefore differ much less from unity than that of chlorine.

In an electrolytic solution the activity of the anion can also differ from that of the cation. Even if we only take into account the Coloumb forces, the activity in any case depends on the radius of the ion. Ions of opposite charge can approach much more closely when the radius is small; the distribution of charge round a small ion is therefore different from that round a large ion: so the activity is smaller.

The above considerations are only qualitative. An exact definition of activity must make use of the expression for the thermodynamic potential of the mixture concerned. If one neglects the contribution of phase-boundaries to the value of this potential, it can be written: $Z = \sum_i n_i \cdot \partial Z / \partial n_i$, where

> $$\frac{\partial Z}{\partial n_i} = \mu_i$$
>
> is a homogeneous function of degree zero of the numbers n_i, i.e. depends only on the concentrations.
>
> Now in the ideal case:
>
> $$\mu_i = \varphi_i(pT) + kT \log c_i$$
>
> c_i being the molar concentration $n_i/\sum_i n$.
>
> In the non ideal case this equation does not hold and must be replaced by another expression. Formally we can always write
>
> $$\mu_i = \varphi_i(pT) + kT \log f_i c_i$$
>
> where f_i is a function of p, T, n_1, $n_2 \ldots$ The introduction of these coefficients f_i has proved to be advantageous for the classification of many experimental results.

While it seems to be agreed that the activity-coefficients f and f' of both ionspecies are in general different, it is not so with the question whether these quantities are accessible to experiment. It can be shown[4]) that all measurements which are based on thermodynamical equations (e.m.f. of cells in equilibrium, vapour-pressure, freezing point etc.) can only yield information about the mean activity γ, which is defined by the equation[5]):

$$\gamma = \sqrt{ff'}$$

This is connected with the fact that a potential-term which accounts for the electric energy, must be added to the partal Gibbs potential $\mu = \mu_0 + kT \log (fc)$ of an ion in a certain phase. For, if two phases are in equilibrium with each other, their electric potentials will in general be different. As all thermodynamical methods make use of the equilibrium between two or more phases, we have always to do with partial thermodynamic potentials of the ions, in which the electric energies are inserted. If ψ is the electric potential of the phase and e the charge of the positive ion, its thermodynamic potential becomes $\mu + e\psi$; and for the negative ion: $\mu' - e\psi$. Is we wish to find the partial thermodynamic potential of the electrolyte, the unknown potential ψ must be eliminated, and thus we only find the sum:

$$\mu + \mu' = \mu_0 + \mu'_0 + kT \log (fcf'c) = \mu_0 + \mu'_0 + 2\,kT \log \gamma c,$$

which apparently means that no ionactivities can be obtained.

3. If now, according to the thermodynamical treatment of cells with diffusion, their e.m.f. were determined by the mean activity, obviously we could never obtain information about the ionactivities

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[4]) E. A. Guggenheim, J. Phys. Chem. **33**, 842 (1929); **34**, 1540, 1758 (1930).

[5]) For convenience sake we restrict ourselves to the case of a binary electrolyte.

from these e.m.f.'s. It has already been noted that the so-called thermodynamical treatment of diffusionpotentials yields the same result as the kinetic theory in the case of ideal solutions. The kinetic theory for non-ideal solutions, which shall be considered in this dissertation, however yields another result than the usual thermodynamical reasoning. A closer examination by Oosterhoff and the present author [6]) showed that this thermodynamical treatment is not permissible. This is connected with the fact that there exists no equilibrium in a cell with diffusion.

Consider a cell:

(A) . . . $H_2/HCl\ c_1/AgCl,\ Ag,\ AgCl/HCl\ c_2/H_2$.

To calculate the e.m.f. of this cell we can apply thermodynamics as long as there exists equilibrium. When we join the H_2-electrodes by a conductor, in other words: when the cell is short-circuited, this condition is no longer fulfilled, and the thermodynamical calculation of the potentialdifference between the H_2-electrodes will have to be reconsidered very carefully.

Now a concentration-cell with diffusion is nothing but an internally short-circuited cell of the type (A). The positive ions which move from the concentrated solution into the dilute one, represent a current *i*. The negative ions which move in the same direction, represent a current —*i*. So the diffusion can be regarded as a closed current, and a cell with diffusion as:

(B) . . . . $H_2/HCl\ c_1/HCl\ c_2/H_2$

can therefore be compared with a cell of the type (A) in which the H_2-electrodes are short-circuited. With the use of this parallel it could be made clear in the cited article that the usual thermodynamical treatment of the cell (B) is not permissible. It could also be seen why the thermodynamical and the kinetic theory lead to the same result in the special case of ideal solutions.

4. From the fact that the diffusion is a kinetic phenomenon, which does not suffer a thermodynamical treatment, it becomes clear that the statement, mentioned above, that no ionactivities can be determined with the aid of diffusionpotentials, is not conclusive. Whether such a determination will be possible in practice, depends on our knowledge about diffusionpotentials, (cf. also page 25). So it becomes clear that an exact theory of electrolytic diffusion in non-ideal solutions, will become important in electrochemistry. In order to test the theory experimentally we have restricted ourselves to cases where the

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[6]) L. J. Oosterhoff and J. J. Hermans, Phil. Mag. 23 (1937).

assumption $f = f'$ has a sense, but this treatment has to be considered as a first step. One can only extend the theory to higher concentrations with some confidence, if the first approximation is verified by both theory and experiment. This extension to higher concentrations has not been tried in this thesis because of the very uncertain speculations which would have to be applied at present. The expression for the diffusionpotential which will be derived in this dissertation, has already been published[7]. Starting from it, Szabó[8] proposed an extension to higher concentrations in a way which is very similar to that of Hückel's[9] extension of the $\sqrt{c}$-law for the activity-coefficient. In the case of HCl the result was satisfactory, but until now Szabó's method could not be applied to other electrolytes.

5. An extension of the theory of diffusion to real solutions should take into account the interionic forces, the forces between ions and solvent, and even the variation of the interaction between molecules of the solvent, due to the presence of ions[*]. As to the interaction of ions we shall take the point of view of Debije and Hückel. The results of this theory are only reliable in the case of dilute solutions, and consist of the introduction of a $\sqrt{c}$-term.

We know much less about the interaction of ions and solvent. The results of the theories concerning the Born-effect[10] and the solvatation are rather uncertain, but there are reasons to believe that the dependence on concentration of these effects is only felt in higher powers of $\sqrt{c}$. The way in which solvatation depends on concentration seems never to have been studied; that of the Born-effect could, however, be calculated[11]. The influence appeared to be of the same order of magnitude as that part of the Debije-Hückel-effect which is described by higher powers of $\sqrt{c}$ than the first.

Finally the interaction of solvent-molecules can be altered by the presence of ions. In some respect the theory of Hückel[12] who took into consideration the alteration of the dielectric constant with the concentration of the electrolyte, can be regarded as an attempt to calculate this effect. Here also, there resulted an influence perceptible in higher powers of $\sqrt{c}$ only. Thus only the $\sqrt{c}$-effect of

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[7] J. J. Hermans, Z. physik. Chem. (A) **176**, 55 (1936).

[8] Z. Szabó, Naturwiss. **24**, 539 (1936).

[9] E. Hückel, Physik. Z. **26**, 93 (1925).

[*] An excellent summary has been given by G. Kortüm, Das opt. Verhalten gelöster Elektr., Stuttgart 1936.

[10] c.f. page 19.

[11] J. J. Hermans, Z. Physik. **97**, 681 (1935).

[12] E. Hückel, Physik. Z. **26**, 93 (1925).

the Coloumb forces between the ions have been considered in our analysis. In such cases where the theory can be applied (the concentrations being small enough) the results in the quantities to be measured may amount to several percent.

The results of the theory are compared with experiments mentioned in the literature. Some experiments concerning diffusionpotentials of NaCl and $BaCl_2$ in water and HCl in a mixture of alcohol and water, have been carried out by the present author. The results are very satisfactory and make it probable that the assumption $f = f'$ holds good up to concentrations 0.02 N or 0.03 N.

II. The diffusion of a mixture of electrolytes.

1. The mixtures are treated in a separate section. There exists an important difference from the diffusion of a single electrolyte, which is caused by the fact that the equations of motion, even in the case of ideal solutions, cannot be integrated unless one makes a special supposition about the structure of the diffusion layer. In fact we shall have to make use of some very radical approximations. So a correction for the interaction of the ions seems rather premature for the present.

2. The diffusion of a mixture of electrolytes is a very important problem. Duclaux[13]) recently indicated the important part which it plays in biological processes. Further the potentialdifferences which occur during electrolytic diffusion, make themselves felt in a large number of measurements, e.g. in the determination of p_H from the e.m.f. of cells. The knowledge of these p_H plays in its turn an important part in biology and soil science. Finally unknown diffusionpotentials practically always occur in the measurements of Quintin[14]), concerning ionactivities of several electrolytes. On grounds which are more or less plausible, these diffusionpotentials are estimated or neglected.

3. Some very remarkable phenomena result from the diffusion of a mixture of electrolytes. They can play an important or even determining part in many processes.

Arrhenius[15]) already deduced from Nernst's theory, that the diffusion of HCl must be accelerated considerably by the presence of KCl and found it confirmed by experiment. Thovert[16])

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[13]) J. Duclaux, Diffusion dans les liquides, Paris 1936.

[14]) M. Quintin, J. chim. phys. **33**, 433 (1936); C. R. **202**, 123 (1936).

[15]) S. Arrhenius, Z. physik. Chem. **10**, 51 (1892).

[16]) J. Thovert, Ann. Physique **26**, 366 (1902).

observed that in this case the potassiumchloride, though originally having the same concentration everywhere, takes part in the diffusion in a direction opposite to that of the HCl. Measurements of this nature seem, however, never to have been done afterwards. In this dissertation we partly returned to them, and examined some general results of the theory, comparing them with experiment.

The most important results in this respect are: 1. The diffusion-potential between two mixtures remains approximately constant. 2. During diffusion extrema in the concentrations can occur. This latter result seems never to have been studied by direct experiments. The character of Thover's observation, mentioned above, makes it very probable that extrema of this kind played a part in it, but he did not mention it explicitely.

In this thesis the existing theories have been submitted to a critical examination. A theory for small gradient of potential has been added. Some measurements of cells with diffusing mixtures have been carried out. Moreover a direct experimental proof of the extrema, mentioned above, could been given.

THE DIFFUSION OF AN ELECTROLYTE.

I. Theoretical part.

Introductory Remarks.

Suppose that a solution of an electrolyte is brought into contact with a solution of this electrolyte in the same solvent, the concentration being, however, different. At large distances from the plane of contact the concentrations remain unaltered, and their gradients are zero. Between both spaces a diffusion layer is formed, in which both ions diffuse from the concentrated solution into the dilute one. On account of their different mobilities they will try to do this with different velocities. As soon, however, as the ions with the largest mobility "overtake" the slower ions, we get a space charge and therefore a gradient of potential: grad φ, which slows down the rapid ions and accelerates the slower ones, so that both ions move with the same average velocity. In order to calculate this common velocity and to find the potential difference between both spaces, one must know the equations of motion for the ions.

Considering more closely an ion in the diffusion layer, it is now clear that it is subjected to a gradient of both concentration and potential. From the latter we immediately deduce an electric force, and it will therefore be appropriate to describe the influence of the concentration-gradient too, by a force of some nature if we wish the gradient of both concentration and potential to be involved in the calculation at the same time.

This has already been done by Nernst¹), who found the expression

$$-kT\ grad\ (ln\ n)$$

for this "force" in the case of ideal solutions²). We shall derive this expression in a way which differs from Nernst's treatment in so far as we need not suppose with Nernst that the osmotic pressure *as such* is the force which acts on the dissolved particles.

The total force on an ion of charge e becomes:

$$-kT\ grad\ (ln\ n) - e\ grad\ \varphi.$$

On the other hand one can deduce the friction ϱ on an ion, in the case it moves with unit velocity, from its mobility. The velocity of the ion under the influence of the force $-kT\ grad\ (ln\ n) - e\ grad\ \varphi$ simply becomes equal to this force divided by ϱ.

The equations of motion thus arrived at are only valid in the case of ideal solutions. Our purpose will be to correct them for the case of real solutions, making use of the theory of Debije and Hückel. We then have to make two different corrections. If we consider a given ion, calling it "central ion" and placing it in the origin, we know that it is surrounded by an ion-sphere which has an excess of ions of opposite charge. Thus the potential energy of an ion decreases when the concentration of the electrolyte increases. Besides the pseudo force $-kT\ grad\ (ln\ n)$ a real electric force due to this potential energy, acts on the ion, so that the "force" which drives the ion to points of lower concentration, is smaller. Our first task will be to derive a general expression for this total force.

Moreover the ion-sphere has still another, more direct, influence on the velocity of the central ion. For the forces which act on the ion-sphere have the result that the fluid at the origin gets a certain motion (electrophoretic effect). The central ion therefore does not move in a medium at rest, but in a medium which has itself a certain velocity. In the theory of conductivity Debije and Hückel³) calculated this electrophoretic effect by introducing the electric forces on the surrounding volume-elements in the hydrodynamic equations of Stokes. Here we shall follow a shorter way by directly applying

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¹) W. Nernst, Z. physik. Chem. **4**, 129 (1889).

²) The reader who is not familiar with the notation grad, can replace it by $\partial/\partial x$. In that case one must restrict oneself to the diffusion in one single direction: the axis x.

³) P. Debije and E. Hückel, Physik. Z. **25**, 49 (1924).

some results of hydrodynamics. It will appear that this method is a very general one and can also be applied to other cases.

There exists a simplification of Debije and Hückel's calculation by Onsager[4]). This author divided the space round the origin into spherical shells. These shells contain a space-charge and therefore undergo an electric force, say *Kdr*. For the contribution of such a shell at distance *r* from the central ion, to the velocity at the origin, Onsager simply writes: $Kdr/6\pi\eta r$. The total influence of the ionsphere is found by integration over all *r*.

It is, however, difficult to see why this method is permissible, for the shells considered are not rigid at all. From the general hydrodynamical equations, to be given here, it will become clear why Onsager's calculation leads to the right result.

Our analysis will consist of five parts:

1. The calculation of the "Penetrationsdruck" in ideal solutions.
2. The calculation of the "Penetrationsdruck" in non-ideal solutions.
3. The application of hydrodynamics to the problem of the mutual influence of motions.
4. The application of the results obtained to the diffusion of an electrolyte.
5. Some considerations about ion activities in so far as these are important for the theory concerned.

Finally the results will be compared with some experiments mentioned in the literature.

"Penetrationsdruck" in ideal solutions.

When there exists a concentration-gradient of a dissolved substance, its particles are impelled to move towards points of lower concentration. Following Nernst's initiative one can *describe* this tendency by a force, identified by Nernst with the osmotic pressure, and called "Penetrationsdruck" by Brusž[5]). This description becomes particularly clear by means of the following artifice[6]).

Imagine the concentration-gradient maintained by means of an external field. If *U* is the potential energy of a particle in this field, the distribution is determined by the expression of Maxwell—Boltzmann:

$$n = A\, exp(-U/kT)$$

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[4]) L. Onsager, Physik. Z. **27,** 388 (1926).

[5]) B. Brusž, Z. physik. Chem. A **162,** 31 (1932).

[6]) A. Einstein, Ann. Physik (4) **17,** 549 (1905).

where A is a constant, and n the number of particles in unit volume. The presence of this field means a force —grad U for each particle. This very force is balanced by the "force" that drives the particles towards points of lower concentration. Therefore this latter force is

$$+grad\ U = -kT\ grad(ln\ n).$$

Applied to the problem of diffusion one must make the hypothesis, that this force *remains* $-kT\ grad(ln\ n)$, when there is no external field, i.e. no equilibrium, so that the particles diffuse. Accelerations can be left out of consideration, as the friction is so large that, under the influence of a given force, each particle gets practically instantaneously the maximum velocity which it can obtain from that force. Finally the friction is proportional to the velocity, a point that has been minutely investigated (cf. e. g. Ulich[7]).

Thus the equation of diffusion becomes:

$$(1) \quad . \ . \ . \ . \ . \ . \ . \quad \rho\vec{v} = -kT\ grad\ (ln\ n).$$

in which ρ is a frictional factor. We thus have derived Fick's law:

$$n\vec{v} = -kT/\rho \cdot grad\ n = -\mathfrak{D}\ grad\ n.$$

The hypothesis that the "driving force" during diffusion has the same value as when exactly balanced by an external field, can hardly be maintained otherwise than by assuming that the deviation from thermodynamic equilibrium, though existing, is small. Considering an element of volume in the solution, one must suppose the state of this element close to equilibrium; in other words: the gradient of concentration must be small. Thus the expression $-kT\ grad(ln\ n)$ will be all the more valid the smaller the concentration-gradient. A deviation from this law also means a deviation from Fick's law. In experiments concerning diffusion, a possible influence of the slope of the concentration-gradient has, so far as we know, never been taken into account.

"Penetrationsdruck" in non-ideal solutions.

As has been said, the tendency of the ions to move towards points of lower concentration is diminished by the interionic forces.

For the "force" which describes this tendency, Onsager[8] used the expression:

$$(2) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad -grad\ \mu,$$

μ being the partial Gibbs potential of the dissolved substance. It can easily be seen that this expression becomes identical with the expression $-kT\ grad\ (ln\ n)$ if applied to the case of ideal solutions. A real demonstration of formula (2), however, seems never to have

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[7] H. Ulich, Hand- und Jahrb. der Chem. Physik **6**, II (1933).

[8] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

been given. It can be proved by generalising the foregoing considerations. If we have a mixture of substances, all of them being in some concentration-gradient or other, we can again suppose these gradients maintained by external fields, which exert on each of the components the necessary forces, leaving it out of consideration whether such fields can be practically realised or not.

On account of these fields a particle of the i'th component may have a potential energy U. If n_i is the number of particles of this component in unit volume and F the free energy in unit volume of mixture, one can find the condition for equilibrium as follows.

Divide the space occupied by the mixture into elements $d\tau$. If we assume the free energy of the mixture to be independent of the concentration gradients, this free energy can be written:

$$\int (F + \Sigma_i n_i U_i) d\tau$$

and the total amount of the component i: $\int n_i d\tau$. Varying the numbers n_i at constant temperature, leaving these amounts and also the total volume unaltered, we must have $\delta F = 0$.

Thus: $$\int \Sigma_i \left(\frac{\partial F}{\partial n_i} + U_i \right) \delta n_i \, . \, d\tau = 0; \int \delta n_i \, . \, d\tau = 0$$

which leads to: $$\frac{\partial F}{\partial n_i} + U_i = C_i = \text{const.}$$

The force which drives the i'th component towards points of lower concentration, becomes: $+grad\ U_i = -grad\ (\partial F / \partial n_i)$.

We have, however [9]), $\left(\frac{\partial F}{\partial n_i} \right)_{vT} = \left(\frac{\partial Z}{\partial n_i} \right)_{pT} = \mu_i$.

Z being the Gibbs potential; and thus the expression (2) has been arrived at.

Of course here too the problem remains that we are not quite sure whether it is possible unambiguously to define a "driving force" in the case of real diffusion and if it has the same value $-grad\ \mu$. Finally it may be noticed that solvent and dissolved substance have been treated as completely equivalent, as, of course, they should be.

Mutual influence of motions.

In general the motion of a dissolved particle will be influenced by that of others. A general theory of this phenomenon seems never to have been developed, and indeed such a theory would require a complete knowledge of the way in which the movement of a body in

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[9]) H. A. Lorentz, Thermodynamica, Leiden 1929, page 107.

a viscous fluid is transmitted to another. This phenomenon can only be described if we introduce some simplifying suppositions.

In the following calculation we shall make use of a result, obtained by Oseen[10]). The form in which these equations are applied here, originates with Burgers[11]). Oseen studied the motion of a viscous fluid due to certain forces. For our purpose we can restrict ourselves to the case that a force F with components XYZ acts at the origin, the original motion of the fluid being a motion with uniform velocity V in the direction of the x-axis. In that case there is added to the original motion a velocity:

$$(3) \quad \ldots\ldots \left\{ \begin{aligned} u &= \frac{1}{8\pi\eta}\left\{ X\triangle\psi - X\frac{\partial^2\psi}{\partial^2 x} - Y\frac{\partial^2\psi}{\partial x\partial y} - Z\frac{\partial^2\psi}{\partial x\,\partial z} \right\} \\ v &= \frac{1}{8\pi\eta}\left\{ Y\triangle\psi - X\frac{\partial^2\psi}{\partial x\partial y} - Y\frac{\partial^2\psi}{\partial y^2} - Z\frac{\partial^2\psi}{\partial y\,\partial z} \right\} \\ w &= \frac{1}{8\pi\eta}\left\{ Z\triangle\psi - X\frac{\partial^2\psi}{\partial x\partial z} - Y\frac{\partial^2\psi}{\partial y\,\partial z} - Z\frac{\partial^2\psi}{\partial z^2} \right\} \end{aligned} \right.$$

Here ψ is a function of the coordinates xyz, the density σ, the velocity V, and the coefficient of internal friction η:

$$\psi = \frac{2\eta}{\sigma V}\int_0^{\frac{\sigma V(r-x)}{2\eta}} \mathrm{d}\omega \, \frac{1-e^{-\omega}}{\omega}, \text{ where } r^2 = x^2 + y^2 + z^2.$$

$\triangle\psi$ stands for $\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2$.

As an approximation for small values of $\sigma Vr/\eta$ (the so-called Reynold's number), ψ becomes: $\psi = r - x$. In fact, we have for small values of $\sigma V(r-x)/2\eta$:

$$\psi = \psi\left[\frac{\sigma V(r-x)}{2\eta}\right] = \psi(0) + \frac{\sigma V(r-x)}{2\eta}\psi'(0).$$

But $\psi(0) = 0$ and $\psi'(0) = 2\eta/\sigma V \,.\, \lim\limits_{s\to 0}(1-e^{-s})/s = 2\eta/\sigma V$.

Thus $\quad \psi = \dfrac{\sigma V(r-x)}{2\eta}\dfrac{2\eta}{V} = r - x.$

In this approximation the density σ does not occur in the formulae, which means that inertia-effects are neglected. The results to be obtained might therefore also be calculated from Stokes' hydrodynamical formulae, in which inertia-terms have also been neglected.

With the so simplified expression for ψ, the equations (3) can be written:

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[10]) C. W. Oseen, Hydrodynamik, Leipzig 1927, page 28.

[11]) J. M. Burgers (Delft), private communication.

$$(4) \quad . \quad . \quad . \quad . \quad \begin{cases} u = \dfrac{1}{8\pi\eta}\left(\dfrac{X}{r} + \dfrac{Px}{r^3}\right) \\ v = \dfrac{1}{8\pi\eta}\left(\dfrac{Y}{r} + \dfrac{Py}{r^3}\right), \text{ where } P = xX + yY + zZ. \\ w = \dfrac{1}{8\pi\eta}\left(\dfrac{Z}{r} + \dfrac{Pz}{r^3}\right) \end{cases}$$

This result does not contain the original velocity V and is therefore also valid if $V = 0$. Further it can be proved that these considerations hold good when the force F depends on the time, provided the alteration with time is sufficiently slow.

The problem, important for the diffusion, can now be formulated as follows. Suppose the fluid divided into elements of volume $d\tau$, and let certain forces act on these elements. We ask what movement is caused by these forces at a given point. If we choose this point as origin, a force $F(XYZ)d\tau$ that acts on an element $d\tau$ with coordinates xyz, brings about a movement at 0 of the form (4), provided we replace xyz in (4) by $-x$, $-y$, $-z$. That is:

$$(5) \quad . \quad . \quad . \quad . \quad \begin{cases} u = \dfrac{d\tau}{8\pi\eta}\left(\dfrac{X}{r} + \dfrac{Px}{r^3}\right) \\ v = \dfrac{d\tau}{8\pi\eta}\left(\dfrac{Y}{r} + \dfrac{Py}{r^3}\right) \\ w = \dfrac{d\tau}{8\pi\eta}\left(\dfrac{Z}{r} + \dfrac{Pz}{r^3}\right) \end{cases}$$

The total velocity, generated at 0 by the forces $Fd\tau$ on the surrounding elements, becomes:

$$(6) \quad . \quad . \quad . \quad . \quad \begin{cases} u = \dfrac{1}{8\pi\eta}\displaystyle\int\left(\dfrac{X}{r} + \dfrac{Px}{r^3}\right) d\tau \\ v = \dfrac{1}{8\pi\eta}\displaystyle\int\left(\dfrac{Y}{r} + \dfrac{Py}{r^3}\right) d\tau \\ w = \dfrac{1}{8\pi\eta}\displaystyle\int\left(\dfrac{Z}{r} + \dfrac{Pz}{r^3}\right) d\tau \end{cases}$$

where the integration must be extended over the space round the origin.

This result can be applied to the problem of diffusion, when we take it for granted, that the forces, acting on the diffusing particles and transferred by these particles to the element of liquid, in which they are situated, can really be treated as volume-forces.

This holds good for particles which are at a comparatively large distance from the origin (that means: at a distance which is large compared with molecular dimensions). For particles in the immediate neighbourhood of 0 it can only be an approximation.

If we wish to examine closely the influence of such a particle on the motion of the fluid at 0, we should have to pay close attention to its movement and shape. Consequently we must restrict ourselves to small concentrations, where the dissolved particles seldom meet at small distance, so that the influence which they exert in that case on each others' motion, may be neglected.

A particle at 0 now does not move in a medium at rest, but in a liquid moving in consequence of the forces around 0: the velocity (6) is simply added to the velocity of the particle.

We shall return to equation (6) when calculating the electrophoretic effect. Here we only mention the important fact that this equation yields a velocity zero in the case of random distribution. For, if $n_i d\tau$ stands for the number of particles of the i'th component in the element of volume $d\tau$, e_i for the charge of such a particle, the force acting on this element becomes:

$$\vec{F}\, d\tau = -\Sigma_i (n_i \, grad \, \mu_i + n_i e_i \, grad \, \varphi) \, . \, d\tau$$

φ being the electric potential. In the case of random distribution we have: $\Sigma_i n_i e_i = 0$, because there exists no space charge. Moreover $\Sigma_i n_i \, grad \, \mu_i = 0$, on account of the theorem of Gibbs-Duhem. In fact, this theorem expresses that, whenever the numbers n_i are altered at constant p and T, maintaining the state of equilibrium, the alteration of the partial Gibbs potentials must satisfy the condition: $\Sigma_i n_i \, grad \, \mu_i = 0$. So it supposes the existence of thermodynamical equilibrium, but it has already been stated that the deviation from equilibrium must be supposed small. Thus we have $F = 0$, and therefore in (6): $u = v = w = 0$.

This result means that the dissolved particles do not disturb each others movement when they have no influence on each others distribution in space, that means: when there is distribution at random. In that case the velocities need not be the same, of course, as in the pure solvent, but can only be altered in so far as the internal friction is changed by the dissolved substances.

Now imagine a charged particle at the origin 0. The distribution round about 0 is no longer at random, and the forces on the surrounding particles are therefore different from zero. As, however, the deviation from random distribution rapidly decreases with increasing distance r, we can restrict ourselves in the integrals (6) to a volume which is small from a macroscopic point of view. In this volume the force F can be regarded as constant, which is the more so as this force is due to the gradients of n and φ which — as we know — must be considered as small.

Onsager's method, mentioned in the introduction, can, of course, only be applied to the case of spherical symmetry. His expression $Kdr/6\pi\eta r$ for the contribution of a spherical shell at distance r to the velocity at 0, can immediately be derived from (5).

For, if we choose the axis x in the direction of K, (5) becomes:

$$u = \frac{K}{8\pi\eta}\left(\frac{1}{r}+\frac{x^2}{r^3}\right)4\pi r^2 dr \qquad v = \frac{K}{8\pi\eta}\cdot\frac{xy}{r^3}4\pi r^2 dr \quad w = \frac{K}{8\pi\eta}\cdot\frac{xz}{r^3}4\pi r^2 dr$$

Integration over the whole spherical shell yields: $v = w = 0$, and: $u = Kdr/6\pi\eta r$, q. e. d.

Application to the diffusion of an electrolyte.

Onsager and Fuoss[12]) have already taken up the calculation of electrolytic diffusion, but have not applied it to the diffusion-potential itself. Their purpose having been, to calculate the velocity of diffusion without restricting themselves to the first power of the square root of the concentration, it is necessary to make some remarks.

First we do not think it logically consistent to keep a quadratic term in the expansion of $exp(\varepsilon\psi/kT)$, while using at the same time for ψ the expression: $\psi = e/Dr \,.\, exp(-\varkappa r)$. For this ψ is the solution of Debije-Hückel's differential equation $\triangle\psi - \varkappa^2\psi = 0$, which arises from the equation $\triangle\psi = -4\pi/D\left[e_1 n_1\, exp\left(\frac{e_1\psi}{kT}\right) + e_2 n_2\, exp\left(\frac{e_2\psi}{kT}\right)\right]$ when omitting powers of ψ higher than the first.

In calculating the electrophoretic force the authors do not take into consideration the motion of the solvent, which also diffuses. Its contribution to the expression (6) can only be neglected so long as the restriction to the first power of $\sqrt{c}$ is made.

Finally the ion activities are simply equalized; no distinction is made, not even by a single word, between these and the average activity, this perhaps under the influence of the Taylor-Guggenheim opinion (compare page 25), that such a distinction is purely conventional. Therefore it seems to us that the terms, which are not linear in $\sqrt{c}$, cannot be regarded as exact.

Besides these considerations there may be mentioned another influence, which for the present makes an accurate theory of electrolytic diffusion impossible: the Born-effect of ion-mobility[13]). This is caused by the fact that the dipoles of the solvent get a rotatory motion in consequence of the moving electric field of the ions.

They are hindered in this rotation by the internal friction of the solvent, and conversely this means a restraining influence on the ion. As the electric potential in the neighbourhood of an ion changes with the concentration of the electrolyte, the Born-effect must depend on this concentration[14]). Fortunately this dependence does not make itself felt in the first power of $\sqrt{c}$[15]), but it appears in the higher terms and thus renders these terms rather

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[12]) L. Onsager and R. Fuoss, J. Phys. Chem. **36**, 2689 (1932).

[13]) M. Born, Z. Physik **1**, 211 (1920).

[14]) K. Sitte, Z. Physik **79**, 330 (1932).

[15]) J. J. Hermans, Z. Physik **97**, 681 (1935); **104**, 100 (1936).

uncertain. For the theory of the Born-effect must make use of some very radical approximations and its numerical results must needs be accepted with great reserve.

Summarizing, we can say that, for the time being, the diffusion of an electrolyte is hardly or not at all accessible to theory, unless we restrict ourselves to concentrations which are so small that higher powers of $\sqrt{c}$ can be neglected.

When the diffusing substance is an electrolyte, each separate ion is submitted to a "Penetrationsdruck". The ions however cannot diffuse independent of each other, for as soon as the more rapid ions overtake the slower ones, there originates an electric charge density, and as a result a potential-gradient $-grad\ \varphi$, which slows down the rapid ions and accelerates the slower ones, the result being that both ions move with the same average velocity v.

If $e_1 = z_1 \varepsilon$ is the charge of the first ion and $e_2 = z_2 \varepsilon$ the charge of the other, the existence of a potential-gradient means forces $-e_1\ grad\ \varphi$ and $-e_2\ grad\ \varphi$ respectively; and these forces have opposite sign because e_1 and e_2 have opposite sign. They must be added to the respective "Penetrationsdrucke", so that the entire forces acting on the ions, become respectively:

$$-grad\ \mu_1 - e_1\ grad\ \varphi \text{ and } -grad\ \mu_2 - e_2\ grad\ \varphi.$$

One can also add the electric energies $e_1\varphi$ and $e_2\varphi$ of the ions, to the partial thermodynamic potentials μ_1 and μ_2 (Guggenheim[16]) and so arrive at potenials $\mu'_i = \mu_i + e_i\varphi$. The force acting on the i'th ion, becomes —grad μ_i. Formally this is perhaps more precise: the splitting up into two terms fits in, however, more closely with the visualisation of the way in which the diffusion-potential is brought about.

The velocities of the ions with respect to their immediate neighbourhood is now determined by the equations:

$$(7) \quad . \quad . \quad . \quad . \quad \left\{ \begin{aligned} \varrho_1 \vec{v}_1 &= -grad\ \mu_1 - e_1\ grad\ \varphi. \\ \varrho_2 \vec{v}_2 &= -grad\ \mu_2 - e_2\ grad\ \varphi. \end{aligned} \right.$$

ϱ is a frictional factor, being inversely proportional to the mobility l of the ion concerned. One has:

$$(8) \quad . \quad . \quad . \quad . \quad \varrho = 15.3 \,.\, 10^{-8} \,.\, \frac{w}{l}$$

where $w = |z| =$ the valency of the ion and l its mobility.

In fact l is defined in the following way. If the solution contains 1 gram-equivalent of the electrolyte between two parallel planes which are 1 cm

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[16]) E. A. Guggenheim, J. Phys. Chem. **33**, 842(1929); **34**, 1540, 1758(1930).

apart, and we apply a potential difference of 1 Volt between these planes, the electric conductivity of the ion i is l_i reciprocal Ohms. As each gram-equivalent transports 96500 Coulombs, the velocity of the ion is $l_i/96500$.

On the other hand the force, acting on the ion, is $1/300 \,.\, w \,.\, 4,78.10^{-10}$ dynes, because 1 Volt $=$ 1/300 e.s.u. and the charge of the ion is $w \,.\, 4,78.10^{-10}$ e.s.u. Thus:

$$\varrho = \frac{w}{300} 4.78.10^{-10} \frac{96500}{l} = 15.3.10.^{-8} \frac{w}{l}$$

Of course the potential φ is connected with the concentrations n_1 and n_2 by the equation of Poisson:

(9) . . . . $\Delta \varphi = -4\pi/D.(e_1 n_1 + e_2 n_2)$

If n_1 were exactly to n_2 as $-e_2$ is to e_1, there would be no space charge at all, and a potential difference φ can therefore only exist if the ratio n_1/n_2 deviates from $-e_2/e_1$. But, as an extremely small deviation from this ratio is enough to yield a large space charge, (9) can be replaced by:

(10) . . . . $e_1 n_1 + e_2 n_2 = 0.$

At first sight this may seem paradoxical, as the potential φ owes its very existence to the presence of a space charge. And indeed one cannot conclude from (9), on account of (10), that $\Delta \varphi$ would be zero. One simply has to cancel equation (9) and to replace it by (10). For (10) does not mean that $\Delta \varphi$ is small or even zero, but only means that the expression $e_1 n_1 + e_2 n_2$ can be neglected compared with $e_1 n_1$ and $e_2 n_2$. This point has been discussed already by Planck[17]) and has once more been maintained in a later discussion with Sitte[18]). An accurate analysis has been given by the author[19]).

Now the velocities $\vec{v}_1$ and $\vec{v}_2$ are not velocities with respect to an observer, because the solution in the immediate neighbourhood of an ion gets a velocity in consequence of the electrophoretic effect. Calling this additional velocity $-\delta\vec{v}_1$ for the first ion, it is found by substituting for the volume-forces $\vec{F}d\tau$ in (6), the expression:

$$-[n_1 \,grad\, \mu_1 + n_2 \,grad\, \mu_2 + (n_1 e_1 + n_2 e_2) \,grad\, \varphi]\, d\tau$$

It has already been mentioned that this force is zero when there is a random distribution. A result differing from zero, can therefore only be obtained in so far as the distribution around the ion considered deviates from the random distribution. Now the number of ions of

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[17]) M. Planck, Ann. Physik (Wied.) **40,** 561 (1890); Z. Physik **93,** 696 (1935); **94,** 469 (1935).

[18]) K. Sitte, Z. Physik **93,** 698 (1935).

[19]) J. J. Hermans, Z. physik. Chem. (A) **176,** 55 (1936).

a given species i in unit volume is given in first approximation by Debije-Hückel's expression:

$$n_i = \overline{n_i}\left(1 - \frac{e_i\, e_l}{DkT}\,\frac{e^{-\varkappa r}}{r}\right)$$

$\overline{n_i}$ being the average concentration of the ions i, e_1 the charge of the central ion, r the distance from this ion, $\varkappa$ is the reciprocal characteristic length in Debije-Hückel's theory:

$$\varkappa^2 = \frac{4\pi}{DkT}\left(e_1^2\overline{n}_1 + e_2^2\overline{n}_2\right)$$

Therefore the deviation from the uniform distribution is:

$$-\,\overline{n}_i\,\frac{e_i\, e_l}{DkT}\,\frac{e^{-\varkappa r}}{r}\ ,$$

and F becomes:

$$\vec{F} = \frac{e_l}{DkT}\,\frac{e^{-\varkappa r}}{r}\left[e_1\,\overline{n}_1\, grad\,\mu_1 + e_2\overline{n}_2\, grad\,\mu_2 + \left(e_1^2\,\overline{n}_1 + e_2^2\,\overline{n}_2\right) grad\,\varphi\right]$$

If we abbreviate now:

(11) . . . . . $e_1{}^2\overline{n}_1 + e_2{}^2\overline{n}_2 = \varepsilon^2 n$

we have, on account of: $e_1\overline{n}_1 + e_2\overline{n}_2 = 0$, the following formulae for $\overline{n}_1$ and $\overline{n}_2$:

(12) . . . . $\overline{n}_1 = \dfrac{\varepsilon^2\, n}{e_1(e_1 - e_2)}\,;\ \overline{n}_2 = \dfrac{-\,\varepsilon^2\, n}{e_2(e_1 - e_2)}$

As we restrict ourselves to the first power of $\sqrt{c}$, we write:

$$\mu_i = \mu_i{}^0 + kT\, ln\, c_i - \frac{e_i{}^2\varkappa}{2\,D}$$

The molar concenrtation c_i can be replaced by the volume concentration, the difference being linear in c and thus may be neglected. Making use of (12) we then have:

(13) . . . $grad\ \mu_i := kT\ .\ grad\,(ln\ n) - \dfrac{e_i{}^2}{2\,D}\, grad\ \varkappa$

(14) . . . . . . $\vec{F} = \dfrac{-\,e_1\varepsilon^2\, e^{-\varkappa r}}{DkT\quad r}\left[\dfrac{e_1 + e_2}{2\,D}\, n\ grad\ \varkappa - n\ grad\ \varphi\right]$

In the case of binary electrolytes the first term of the right hand side is zero, because in that case $e_1 + e_2 = 0$. But for non-binary electrolytes too this first term can be neglected with regard to the second. For we have:

$$\varkappa^2 = \frac{4\,\pi\,\varepsilon^2 n}{DkT}\ ;\ grad\ \varkappa = \frac{\varkappa}{2\,n}\, grad\ n.$$

And thus the expression in parentheses in (14) can be written:

$$(15) \quad . \; . \; . \; . \; . \; . \; . \; \frac{e_1 + e_2}{4\,D} \varkappa \; grad \; n - n \; grad \; \varphi.$$

Now from the equation (7) it can be concluded that $grad\,\mu$ and $e\; grad\,\varphi$ have the same order of magnitude. But $grad\,\mu \simeq kT\; grad\,(ln\,n) = kT/n \,.\, grad\,n$. Thus $n\; grad\,\varphi$ has the order of magnitude $kT/\varepsilon \,.\, grad\,n$. The first term in (15) is therefore to the second as $\varepsilon^2\varkappa/DkT$ is to unity. This latter proportion is small as long as the concentration is small. In (14) there only remains: $\vec{F} = \frac{e_1\varepsilon^2}{DkT} \frac{e^{-\varkappa r}}{r} n\; grad\,\varphi$. If now we choose the x-axis in the direction of $grad\,\varphi$, we have in equation (6):

$$v = w = 0;\; u(= -\delta v_1) = \frac{1}{8\,\pi\eta} \frac{e_1\varepsilon^2 n\; grad\,\varphi}{DkT} \int \frac{e^{-\varkappa r}}{r} \left(\frac{1}{r} + \frac{x^2}{r^3}\right) d\tau.$$

If we write Θ for the angle between r and the x-axis, this becomes:

$$u = \frac{e_1\varepsilon^2 n\; grad\,\varphi}{4\,\eta\, DkT} \int_0^\infty e^{-\varkappa r}\, dr \int_0^\pi (1 + \cos^2\Theta) \sin\Theta \; d\Theta.$$

$$Or:\; u = \frac{2\,e_1\varepsilon^2 n\; grad\,\varphi}{3\,\eta\, DkT\,\varkappa} = \frac{e_1\varkappa}{6\,\pi\eta}\, grad\; \varphi.$$

$$(16) \quad . \; . \; . \; . \; . \; . \; . \; \delta\vec{v}_1 = \frac{-e_1\varkappa}{6\,\pi\eta}\, grad\; \varphi.$$

The equations of motion can finally be written:

$$(17) \quad . \; . \; \begin{cases} \varrho_1 (\vec{v} - \frac{e_1\varkappa}{6\,\pi\eta}\, grad\,\varphi) = -\,grad\,\mu_1 - e_1\; grad\,\varphi \\ \varrho_2 (\vec{v} - \frac{e_2\varkappa}{6\,\pi\eta}\, grad\,\varphi) = -\,grad\,\mu_2 - e_2\; grad\,\varphi \end{cases}$$

The detailed calculation, given here for the electrophoretic effect, is advantageous, in so far as it is quite general. It can also be applied in cases, where the distribution of electric charge round about the central ion has not sperical symmetry; and is even useful when the hydrodynamical equations do not hold in the approximation here used, i. e. when the Reynols' number is too large. In that case one need only replace the function ψ in the equation (3) by a more exact expression [20]).

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[20]) Prof. H. A. Kramers (Leiden) to whom the author is indebted for many criticisms, pointed out that the ions which contribute to the volume-force F, make up part of the ion sphere round the origin. Here we meet with the difficulty whether the partial thermodynamic potential μ_i of such an ion has a well-defined physical meaning or not. Possibly one had to make a correction of some kind for the presence of space charge. As, however, this space charge is in first approximation proportional to $\sqrt{c}$, we probably only neglect terms of higher order. Further the diffusion potential φ and the Debije-Hückel-potential ψ are assumed to be merely superposed. This assumption can, however, be supported by a closer examination.

Before integrating the equations (17) we must investigate the problem of ion-activities. In calculating the electrophoretic force we restricted ourselves already to the first approximation ($\sqrt{c}$-law). Moreover we stated on page 19, why an exact theory of electrolytic diffusion must for the present be regarded as impossible, unless one restricts oneself to this $\sqrt{c}$-law. Now we shall consider another factor still, which stands in the way of the theoretical as well as the experimental determination of diffusion potentials.

Ion-activities.

To determine the diffusion-potential between two differently concentrated solutions of an electrolyte, one measures the electromotive force of a concentration-cell with diffusion. In diagram:

$$\begin{array}{c} \text{electrode } A/\text{solution } (c_1)/\text{solution } (c_2)/\text{electrode } A. \\ E_1 \qquad\qquad L \qquad\qquad E_2 \end{array}$$

Suppose the electrolyte to be a mono-mono-valent substance. Then we have:

$$E_1 = \text{const.} + kT/\varepsilon \, . \, ln\, f_1 c_1$$

$$E_2 = -\text{const.} - kT/\varepsilon \, . \, ln\, f_2 c_2$$

Here f_1 is the activity-coefficient of that ion, with regard to which the electrodes A are supposed to be reversible, taken at the concentration c_1; f_2 is the same coefficient at the concentration c_2. The e.m.f. of the element is:

(18) . . . . $E = L + kT/\varepsilon \, . \, ln\, f_1 c_1 / f_2 c_2$

The activities $f_1 c_1$ and $f_2 c_2$ are ion-activities, as distinct from the average activities $\gamma_1 c_1$ and $\gamma_2 c_2$ which can be determined by experiments. These are defined by the formula:

(19) . . . . $2\, ln\, \gamma = ln\, f + ln\, f'$,

f' being the activity-coefficiene of the other ion.

The determination of γ has been realised with great accuracy for many substances[21]. Starting from the $\sqrt{c}$-law of Debije and Hückel semi-theoretical formulae[22] have been proposed, which reproduce $ln \gamma$ within the attainable accuracy of measurements. And it is also by pure theoretical extension of the original theory that one has succeeded in conquering a larger concentration-domain[23]. But

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[21] G. Akerlöf, J. Am. Chem. Soc. **54**, 4125 (1932); E. Güntelberg, Z. physik. Chem. **123**, 199 (1926); U. B. Bray, J. Am. Chem. Soc. **49**, 2372 (1927).

[22] E. Hückel, Physik. Z. **26**, 93 (1925).

[23] N. Bjerrum, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. **7**, Nr. 9 (1926); H. Müller, Physik. Z. **28**, 324 (1927); T. H. Grondwall, V. K. La Mer and K. Sandved, Physik. Z. **29**, 358 (1928).

from all this nothing can be deduced about the ion activities themselves. The best thing to do is to suppose

(20) . . . . $f = f' = \gamma$

for small concentrations of the electrolyte. But one cannot say, up to what concentration this equation holds. The measured value E in (18) yields a different diffusion potential L for each special division of $\ln f$ and $\ln f'$ over $2 \ln \gamma$ in (19). In the theoretical calculation of L, however, one must already choose such a division. And thus one is well on the way in a vicious circle. It is true that this circle is not entirely closed, for in principle one could try any choice of $\ln f$ in the theoretical formula for L and in the experimental value (18) at the same time. But this would mean that one had to accept the exactness of the theoretical expression for L beforehand. And this very expression is far from sure if one wishes more than the $\sqrt{c}$-law. Therefore we shall only examine this $\sqrt{c}$-law, using the assumption (20) for the ion-activities. A result is, that we must renounce trying to trace up to what concentration the $\sqrt{c}$-law is valid, because we never know if differences between theory and experiment must be imputed to errors in the expression for L or to an inaccuracy in the assumption (20).

It will be proved that in this way the experiments in solutions with water as a solvent can be reproduced up to concentrations of about 0.02 N. or even 0.03 N. With regard to the Debije-Hückel-theory of electrolytes this is a rather considerable concentration: generally the limit of usefulness of this theory for electrode-potentials lies beneath 0.01 N. One must, however, bear in mind that diffusion-potentials are relatively small compared with electrode potentials: the same relative error sooner falls under the possible errors of experiment.

The search for ion-activities is one of the most interesting tasks of electrochemistry, and has been taken up more than once in recent years[24]). Some authors go so far as to express the opinion, that the determination of ion-activity must be regarded as impossible and that the very concept has no physical meaning at all[25]). According to Guggenheim its determination can only be based on mere convention.

This opinion is partly due to a wrong formula for the diffusion potential[26]). Further it is evident from the above treatment, that an independent determination of diffusion potentials can be used as a determination of ion-activities; and such an independent determination of diffusion potenitals can certainly not be

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[24]) Z. Szabó, Z. physik. Chem. A **176**, 131 (1936); M. Quintin, J. chim. phys. **33**, 433 (1936); Compt. rend. **202**, 123 (1936).

[25]) E. A. Guggenheim, J. Phys. Chem. **33**, 842 (1929); **36**, 1758 (1930); Phil. Mag. **22**, 983 (1936); P. B. Taylor, J. Phys. Chem. **31**, 1478 (1927).

[26]) c.f. L. J. Oosterhoff and J. J. Hermans, Phil. Mag. **23** (1937).

regarded as impossible in principe[27]). And indeed, others have not denied the possibility of determining ion-activities, and have even tried to derive them from experiments[28]). The problem is, however, still far from being solved. Both practice and theory of the diffusion potentials will probably play an important part in this respect, and therefore it seemed desirable to examine more closely the limiting law for infinite dilution, because the extension to higher concentrations will very likely have to originate with this limiting law. An attempt in this direction has already been made by Szabó[29]).

Finally some words may be added about non-binary electrolytes. For we must extend the equation (20) to this case.

If a molecule of the dissolved substance is ionised into ν_1 ions of charge $z_1\varepsilon, \nu_2$ ions of charge $z_2\varepsilon$, one has: $\nu_1 z_1 + \nu_2 z_2 = 0$, while the average activity-coefficient is defined by:

$$\ln\gamma = \frac{\nu_1 \ln f_1 + \nu_2 \ln f_2}{\nu_1 + \nu_2}$$

In Debije-Hückel's first approximation $\ln f_i$ is proportional to z^2_i, say.

$$\ln f_i = z_i^2 . \ln f.$$

Thus:

$$\ln\gamma = \frac{\nu_1 z_1^2 + \nu_2 z^2_2}{\nu_1 + \nu_2} . \ln f$$

And therefore finally:

$$(21) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \ln f_i = \frac{z_i^2(\nu_1 + \nu_2)}{\nu_1 z_1^2 + \nu_2 z_2^2} . \ln\gamma$$

The equally was introduced by Guggenheim[30]) as a convention. Here we shall use it as a hypothesis. For instance in the case of $BaCl_2$:

$$(22) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \ln f_{Cl} = {}^1/_2 \ln\gamma ; \; \ln f_{Ba} = 2 \ln\gamma .$$

$\sqrt{c}$-law for the diffusion-coefficient.

If one substitutes the expression (13) for μ in the equations of motion (17), then eliminating φ, one finds:

$$\overrightarrow{nv} = (-\mathrm{grad}\, n) . kT \frac{e_2 - e_1}{e_2\varrho_1 - e_1\varrho_2} \left[1 + \frac{e_1 e_2 \varkappa}{4DkT} - \frac{e_1 e_2}{e_2 - e_1} \frac{(\varrho_1 - \varrho_2)^2}{e_2\varrho_1 - e_1\varrho_2} \frac{\varkappa}{6\pi\eta} \right]$$

Here all powers of $\varkappa$, higher than the first, have been neglected.

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[27]) J. J. Hermans, Z. physik. Chem. A **176,** 131 (1936).

[28]) M. Quintin (l.c.).

[29]) Z. Szabó, Naturwissenschaften **24,** 539 (1936).

[30]) E. A. Guggenheim, J. Phys. Chem. **33,** 842 (1929); **34,** 1540, 1758 (1930).

Remembering the equations (8) for ϱ, and substituting the valencies w of the ions, this becomes:

$$n\vec{v} = (-\mathrm{grad}\,n)\,.\,kT\,\frac{10^8}{15.3}\cdot\frac{w_1+w_2}{w_1w_2}\,\frac{l_1l_2}{l_1+l_2}\left[1-\frac{w_1w_2\,\varepsilon^2\varkappa}{4\,DkT}-\frac{w_1w_2}{w_1+w_2}\,\frac{(\varrho_1-\varrho_2)^2}{w_1\varrho_2+w_2\varrho_1}\,\frac{\varkappa}{6\,\pi\,\eta}\right]$$

Considering first the case of ideal solutions ($\varkappa = 0$), this result expresses that the electrolyte as a whole diffuses with the diffusion-coefficient:

$$(23)\quad \ldots\ldots\quad \mathfrak{D}_o = \frac{10^8}{15.3}\,kT\,\frac{w_1+w_2}{w_1\,w_2}\,\frac{l_1\,l_2}{l_1+l_2}$$

The diffusion coefficient $\mathfrak{D}$ for non-ideal solutions can to a first approximation be expressed by the ratio:

$$\frac{\mathfrak{D}}{\mathfrak{D}_o} = 1-\frac{w_1\,w_2\,\varepsilon^2\varkappa}{4\,DkT}-\frac{w_1\,w_2}{w_1+w_2}\cdot\frac{(\varrho_1-\varrho_2)^2}{w_1\,\varrho_2+w_2\,\varrho_1}\,\frac{\varkappa}{6\pi\,\eta}$$

The last summand is rather small in all cases that occur in water. For instance it has a value of about $0.18.10^{-8}\varkappa$ for HCl in water at room-temperature, in opposition to a last-but-one term of about $1.8.10^{-8}\varkappa$. For most other electrolytes in water the electrophoretic term is still smaller, being almost zero for KCl, ϱ_1 and ϱ_2 differing very little in that case.

There do not exist many reliable data about the dependence of $\mathfrak{D}$ on c, as most experiments have been carried out at too large concentrations. The measurements of Sitte[31]) indicate indeed a linear relation between $\mathfrak{D}$ and $\sqrt{c}$, but the factor of $\sqrt{c}$ would be almost twice the theoretical one.

$\sqrt{c}$-law for the diffusionpotential.

If we eliminate the velocity $\vec{v}$ in (17), always omitting higher than first powers of $\varkappa$, we find:

$$\mathrm{grad}\,\varphi = \frac{-1}{\frac{e_1}{\varrho_1}-\frac{e_2}{\varrho_2}}\left(1+\frac{e_1-e_2}{\frac{e_1}{\varrho_1}-\frac{e_2}{\varrho_2}}\,\frac{\varkappa}{6\,\pi\,\eta}\right)\left(\frac{\mathrm{grad}\,\mu_1}{\varrho_1}-\frac{\mathrm{grad}\,\mu_2}{\varrho_2}\right)$$

Using (13) for grad μ and integrating:

$$(24)\quad \varphi = \mathrm{const.}-\frac{kT}{\varepsilon}\,\frac{\frac{l_1}{w_1}-\frac{l_2}{w_2}}{l_1+l_2}\left\{\ln c-\frac{l_1w_1-l_2w_2}{\frac{l_1}{w_1}-\frac{l_2}{w_2}}\,\frac{\varepsilon^2\varkappa}{2\,DkT}+\frac{w_1+w_2}{l_1+l_2}\,\frac{15.3.10^{-8}\varkappa}{3\,\pi\,\eta}\right\}$$

Here we have also used the equation (8) for ϱ.

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[31]) K. Sitte, Z. Physik **91**, 622 (1934).

The electrophoretic effect, which finds expression in the last term, obviously always means an enlargement of the absolute value of the diffusion potential; the last but one term can be positive as well as negative. It is, of course, negative in the case of binary electrolytes ($w_1 = w_2$), but it can become positive for other substances, e.g. Na_2SO_4 and $BaCl_2$ in water.

In (24) we have:

$$\varkappa = \sqrt{\frac{4\,\pi\varepsilon^2\,n}{DkT}}$$

and thus $\varkappa$ is proportional to $\sqrt{c}$. If we take together both terms in (24) which contain $\varkappa$, in the form $A\sqrt{c}$, the diffusion potential between two solutions of concentrations c_1 and c_2 takes the form:

$$(25)\quad .\quad \varphi_1 - \varphi_2 = L = -\,\mathrm{k}T/\varepsilon\,.\,\frac{\dfrac{l_1}{w_1} - \dfrac{l_2}{w_2}}{l_1 + l_2}\left\{ ln\,\frac{C_1}{C_2} + A\,(\sqrt{c_1} - \sqrt{c_2}) \right\}$$

A being negative, when the electrophoretic term does not cancel the other (electrostatic) term, e.g. HCl in water, but being positive (and rather large) when both terms are positive, e.g. $BaCl_2$. And finally, when both terms have the same order of magnitude but opposite sign, the electrolyte shows a diffusion potential practically given by the classic formula of Nernst[32]), for instance NaCl and LiCl.

Comparison with experiment.

As for measurements, mentioned in the literature, only HCl, NaCl, LiCl and $BaCl_2$ receive consideration. The rare statements concerning other electrolytes have this fault that the examined concentrations are too large.

We shall always suppose, that (21) holds. To calculate $ln\gamma$ we shall make use of empirical formulae; the electrode potential, indicated as E_e, can be calculated from such γ with an accuracy of about 0.1 mV. The total e.m.f. of the element shall be denoted by E, the difference $E—E_e$ is the empirical diffusion potential. It will always be compared with the theoretical value $L(th)$, calculated from (24), and often with $L(N)$, this latter being the diffusion potential as given by Nernst's classical formula.

All potentials are expressed in millivolts, all concentrations in grammolecule per *l*.

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[32]) W. Nernst, Z. physik. Chem. **4**, 129 (1889).

HCl in water 18°. H. Jahn 33).

$$Ag/AgCl/HCl\ c_1/HCl\ c_2/AgCl/Ag.$$

$$^{10}log\ \gamma = \frac{-0.352\sqrt{2c}}{1+0.782\sqrt{2c}} + 0.080 \,.\, 2c$$ 34)

$l_H = 315.1$ 35) $l_{Cl} = 65.5$ 36) $\eta_{81} = 0.01056$ 37

$$L = 37.85 \left\{ {}^{10}log\ c_1/c_2 - 0.344 (\sqrt{c_1} - \sqrt{c_2}) \right\}$$

Table I.

HCl in water 18°.

c_1	c_2	E	E_e	$E - E_e$	L (th)	L (N)
0.003329	0.01665	64.28	38.79	25.49	25.50	26.43
0.001665	0.03342	119.55	72.24	47.31	47.40	49.25
0.001665	0.01665	92.35	55.74	36.61	36.66	37.81
0.001665	0.01113	76.64	46.13	30.51	30.36	31.20
0.001665	0.008315	64.87	39.12	25.75	25.75	26.41
0.001665	0.006686	56.14	33.87	22.27	22.29	22.83
0.001665	0.005561	48.84	29.40	19.44	19.36	19.88
0.003329	0.03330	91.62	55.18	**36.44**	**36.00**	37.82
0.003329	0.01113	48.17	29.16	19.01	19.20	19.82
0.003329	0.008308	36.59	22.14	14.45	14.58	15.02
0.003329	0.006661	27.78	16.82	10.96	11.08	11.39
				$\overline{\Delta}$	0.038	0.83
				$\overline{\Delta^2}$	0.0107	

All experiments agree completely with theory, accept one at the concentration 0.0333, which is perhaps too large for application of the formula.

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33) H. Jahn, Z. physik. Chem. **33**, 554 (1900); **41**, 288 (1902); cf. also J. J. Hermans, Z. physik. Chem (A) **176**, 55 (1936). For the case: HCl in water at 25°, Szabó extended the theoretical formula (25) to higher concentrations: Z. Szabó, Naturwissenschaften **24**, 539 (1936).

34) E. Hückel, Physik. Z. **26**, 93 (1925).

35) F. Kohlrausch and H. Holborn, Leitv. Elektr., Leipzig 1916, p. 214, mention a value $l = 315$; A. A. Noyes and K. G. Falk, J. Am. Chem. Soc. **34**, 479 (1912): $l = 314.5$; Ch. A. Kraus and W. Parker, J. Am. Chem. Soc. **44**, 2449 (1922): $l = 315.6$. Taking this average value $l = 315.1$ we obtain a transport number 0.172 which is in excellent agreement with the value mentioned by C. Drucker, Z. physik. Chem. **62**, 742 (1908) and by H. Riesenfeld, Z. physik. Chem. **68**, 455 (1910).

36) F. Kohlrausch and H. Holborn, Leitv. Elektr., Leipzig 1916; Z. Elektrochem. **13**, 333 (1907).

37) H. Ulich, Hand- und Jahrb. d. chem. Physik **6**, II (1933).

NaCl in water 18°. H. Jahn[38]).

Ag/AgCl/NaCl c_1/NaCl c_2/AgCl/Ag.

$$^{10}log\ \gamma = \frac{-0.500\sqrt{c}}{1 + 0.810\sqrt{2c}} + 0.0308 \, . \, 2c\ ^{39)}$$

Transport number $t_{Na} = 0.397$[40]).

Sum of the ion mobilities $\lambda_0 = 108.8$. $\eta_{18} = 0.01056$[41]).

$$L = 12.00 \left\{ {}^{10}log\ c_1/c_2 - 0.100\,(\sqrt{c_1} - \sqrt{c_2}) \right\}$$

The largest concentration, up to which the limiting law is valid, probably lies beneath $c = 0.03$. For this concentration the difference between $L(th)$ and $L(N)$ *is* $12.0{,}1 \, . \sqrt{0.03} = 0.21$ *mV*. In general these differences lie therefore within the limits of experimental errors: the diffusion potential practically follows Nernst's formula.

Table II.

NaCl in water 18°.

c_1	c_2	E	E_e	$E_e - E$	L (th)	L (N)
0.001674	0.006686	26.52	33.69	7.17	7.17	7.22
0.001674	0.008364	30.73	39.08	8.35	8.32	8.38
0.001674	0.01117	36.08	46.00	9.92	9.82	9.90
0.001674	0.01673	43.60	55.62	12.02	11.90	12.00
0.001674	0.03344	56.14	71.92	15.78	15.44	15.61
0.01000	0.02000	12.93	16.48	3.55	3.56	3.61
0.01000	0.03003	20.56	26.04	5.48	5.64	5.73
0.02000	0.05007	16.70	21.48	4.78	4.68	4.78

The differences between $E_e - E$ and $L(th)$ are never more than 0.12 mV., except at the concentrations 0.03344 and 0.03003, which are perhaps somewhat too large.

NaCl in water 25°. Mc. Innes and Brown[42]).

Ag/AgCl/NaCl 0.1 /NaCl c/AgCl/Ag.

$$^{10}log\ \gamma = \frac{-0.5067\sqrt{c}}{1 + 0.837\sqrt{2c}} + 0.0316 \, . \, 2c\ ^{43)}$$

One of the concentrations was always 0.09956, thus being too large

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[38]) H. Jahn, Z. physik. Chem. **33**, 554 (1900); **41**, 288 (1902).

[39]) H. S. Harned and L. F. Nims, J. Am. Chem. Soc. **54**, 423 (1932).

[40]) D. A. Mc. Innes, J. Am. Chem. Soc. **37**, 2301 (1915).

[41]) Vide No. 37.

[42]) D. A. Mc. Innes and A. S. Brown, J. Am. Chem. Soc. **57**, 1356 (1935).

[43]) Vide No. 39.

to apply the limiting law. Taking $l_{Na} = 50.10$ 44), $l_{Cl} = 76.32$ 44), $\eta_{25} = 0.008937$ 45), this limiting law would run:

$$L = 12.26 \left\{ {}^{10}\log 0.1/c - 0.096 (\sqrt{0.1} - \sqrt{c}) \right\}$$

As could be expected, this expression yields values for L, which are smaller than those actually found. A complete agreement can be reached with the expression:

$$L = K - 12.26 \left({}^{10}\log \; c/0.1 - 0.096\sqrt{c} \right).$$

In table III we have chosen the value —0.09 mV. for K.

Table III.

NaCl in water 25° $c_1 = 0.09956$; $c_2 = c$.

c_1	c_2	E	E_e	$E_e - E$	L (th)	△
0.09956	0.004983	56.46	72.46	16.00	15.94	+ 0.06
„	0.006978	49.91	64.15	14.24	14.18	+ 0.06
„	0.009966	43.03	55.37	12.34	12.38	— 0.04
„	0.01994	29.80	38.45	8.65	8.65	+ 0.00
„	0.02988	22.19	28.65	6.46	6.51	— 0.05
„	0.03988	16.81	21.77	4.96	5.02	— 0.06
„	0.04983	12.69	16.43	3.74	3.86	— 0.12
„	0.05977	9.31	12.09	2.78	2.92	— 0.14
„	0.07967	4.06	5.26	1.20	1.43	— 0.23
„	0.09956	0.00	0.00	0.00	0.28	— 0.28

It is seen, that systematic errors begin to occur at $c = 0.04$. Of course L could also have been reproduced by a formula of Nernst: $L = L_0 - 12.26 \,.\, {}^{10}\log c/0.1$. This has not been carried out in the table.

LiCl in water 25°. Mc. Innes and Beattie 46).

I: Ag/AgCl/LiCl c_1/LiCl c_2/AgCl/Ag

II: Ag/AgCl/LiClc_1/Liamlg/LiCl c_2/AgCl/Ag.

Supposing $f = f' = \gamma$, we have for the electromotive forces:

$$E_I = kT/\varepsilon \,.\, \ln \gamma_1 c_1/\gamma_2 c_1 - L$$

$$E_{II} = 2kT/\varepsilon \,.\, \ln \gamma_1 c_1/\gamma_2 c_2$$

Obviously: $L = \frac{1}{2} E_2 - E_1$.

The ratio c_1/c_2 was always the same, namely 10. Although the number of measurements at sufficiently low concentrations is too small to draw reliable conclusions, it is striking, that L increases with c:

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44) D. A. Mc. Innes, Shedlovsky and Longsworth, J. Am. Chem. Soc. **57**, 1356 (1935).

45) Vide No. 37.

46) D. A. Mc. Innes and J. A. Beattie, J. Am. Chem. Soc. **42**, 1117 (1920).

c_1 =	0.01	0.03	0.1	0.3
c_2 =	0.001	0.003	0.01	0.03
E_I =	39.06	37.60	35.89	35.21
E_{II} =	113.90	112.75	110.55	111.17
L =	17.89	18.78	19.39	20.38

This behaviour does not agree with the theoretical law (25), taking here the form:

$$L = 19.34 \left\{ {}^{10}log\ c_1/c_2 - 0.056 (\sqrt{c_1} - \sqrt{c_2}) \right\}$$

The correction is however very small, so that perhaps terms, which are not linear in $\sqrt{c}$, soon play a part, and these of course can have another sign. Moreover measurements with amalgam-electrodes are usually badly reproduceable when the electrolyte-concentration is small, and finally LiCl does not occupy a very favourable place among electrolytes, in so far as it shows hydrolysis at high dilutions [47].

$BaCl_2$ in water, 25°, Jones and Dole [48].

$$Ag/AgCl/BaCl_2\ c/BaCl_2\ 0.05/AgCl/Ag.$$

$$^{10}log\ \gamma = \frac{-1.734 \sqrt{c}}{1 + 2.331 \sqrt{c}} + 0.132 \,.\, c\ ^{49)}$$

In (25) the absolute values of the ion mobilities are only important for the $\sqrt{c}$-correction. Far more important for the diffusion-potential is the ratio between these mobilities. Accurate measurements of the transport number have been carried out by Jones and Dole [50]) from $c = 0.01$ to $c = 1$. These authors found the empirical formula:

$$(26) \quad \ldots\ldots \quad t_{Ba} = \frac{1.4476}{1 + 0.07010 \sqrt{c}} - 1$$

Thus at infinite dilution: $t_0 = 0.4476$. With a mobility 76.32 [51]) for the chloride-ion, which certainly does not differ more than 0.2 from the real value, one would find for the mobility of Ba the small value 61.84, which is rather unlikely. For this would mean $\lambda_0 = 138.16$, while on the other hand Jones and Dole [52]) reproduce the conductivity of $BaCl_2$ by the formula:

$$\lambda = 141.06 - \frac{318.1 \sqrt{c}}{1 + 4.628 \sqrt{c}} - 15.56 \,.\, c\ ^{52)}$$

valid from $c = 0.001$ to $c = 1.0$. Moreover these measurements of

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[47]) Gmelin's Handb. Anorg. Chem., Berlin 1927, 20, 143.

[48]) G. Jones and M. Dole, J. Am. Chem. Soc. **51**, 1081 (1929).

[49]) S. A. Tippets and R. F. Newton, J. Am. Chem. Soc. **56**, 1675 (1934).

[50]) G. Jones and M. Dole, J. Am. Chem. Soc. **51**, 1081 (1929).

[51]) Vide No. 44.

[52]) G. Jones and M. Dole, J. Am. Chem. Soc. **52**, 2248 (1930).

conductivity agree well with those of Kohlrausch and Grüneisen[53]) and those of Remy and Reisener[54]). The formula (26) has apparently been adapted too much to higher concentrations. Neither does it yield the theoretical slope for $c = 0$.[55]). We therefore use for the mobility of Ba the value: $141.06 - 76.32 = 64.74$. Thus we find:

(27) . . . $L = 18.42 \left\{ {}^{10}\log c_1/c_2 + 2.00 (\sqrt{c_1} - \sqrt{c_2}) \right\}$

As the concentration 0.05 g/mol. per l is too large, we must use the expression:

$$L = K + 18.42 ({}^{10}\log 0.05/c - 2.00 \sqrt{c}) = K + \chi(c)$$

Table IV.

$BaCl_2$ in water 25°.

c	E	E_e	$E_e - E$	$\chi(c)$	K
0.001	58.4	94.5	36.1	30.1	6.0
0.005	33.3	54.8	21.5	15.8	5.7
0.01	22.8	38.1	15.3	9.2	6.1
0.025	9.4	16.2	6.8	− 0.3	7.1

Choosing $K = 5.9$ mV. the first three measurements can obviously be satisfactorily reproduced. The electrode-potential E_e was calculated by using formula (22), page 26 Of course the choice of the constant K has altogether been adapted to the experiments. One can however convince oneself, that the formulae are rather "sensitive". For it is not possible to reproduce the first three experiments with the aid of a Nernst-formula: $L = L_o + 18.42 \log 0.05/c$. To that end L_o would have to be taken successively as 4.8, 3.1 and 2.4 mV.

There exist some experiments of Drucker[56]) concerning $BaCl_2$ in water. We tried to reproduce them with formula (27). It appeared however, that large experimental errors must have crept into his measurements, for his values are scattered very irregularly round about the theoretical ones. If these deviations had to be imputed to the formulae, they would of course have shown a regular nature.

Recapitulating it can be said, that the theory is confirmed up to a concentration 0.03 g/mol. per l in the case of HCl and NaCl, and 0.01 g/mol. per l in the case of $BaCl_2$. Other experiments will be mentioned in the next part.

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[53]) F. Kohlrausch and E. Grüneisen, Ber. Berl. Akad. 1216 (1904).

[54]) H. Remy and H. Reisener, Z. physik. Chem. **124**, 43 (1926).

[55]) L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).

[56]) C. Drucker, Z. Elektrochem. **19**, 803 (1913).

THE DIFFUSION OF AN ELECTROLYTE.

II. Experimental Part.

The experiments will be discussed in two parts:

A. NaCl and $BaCl_2$ in water.
B. HCl in a mixture of alcohol and water.

As has been noticed before, the electrolytes HCl, $BaCl_2$ and NaCl represent three particular cases with respect to the theoretical limiting law. According to (24) page 27 the diffusion potential of HCl is smaller than Nernst predicted, that of $BaCl_2$ is larger and that of NaCl is nearly equal to it, because the electrophoretic term is nearly cancelled by the electrostatic one.

A. NaCl and $BaCl_2$ in water.

Only the cells with AgCl-electrodes were studied, according to the scheme:

$$Ag/AgCl/\text{electrolyte } c_1/\text{electrolyte } c_2/AgCl/Ag.$$

The electromotive force was determined with the aid of the usual compensation-method (Student's potentiometer), with a cadmium-normal element as a standard cell and a ballistic galvanometer of Kipp (Delft).

For the preparation of the AgCl-electrodes a prescription of Elema[1]) was followed. For 24 hours a platinum electrode is silvered in a solution of potassium silver cyanide by a current of 0.1 milliampere; the other electrode is of silver. After careful washing, the electrode is left in distilled water for one night. It is then chlorinated for 5 hours with a current of 0.2 milliampere in 0.1 N. HCl; an electrode of platinized platinum serves as cathode. During this process, and also after it, the electrodes are not exposed to the light.

Such electrodes very often show a potential difference when placed opposite one another in a solution, a potential difference which can even amount to more than 0.5 mV. It disappears, however, after the electrodes have been left short-circuited in the solutions. In the rare cases that this difference maintained itself, the electrode concerned was again silvered and chlorinated. Each electrode was always kept short-circuited with others in the solution, in which it had to serve afterwards, for several hours or if possible for one night. As Elema states, the colour of such AgCl-electrodes is light brown, slightly reddish.

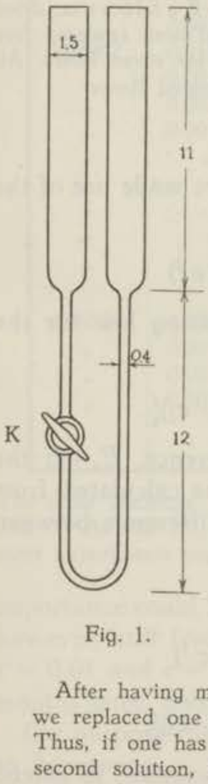

Fig. 1.

The measuring tube. Because of the comparatively small sensitiveness of the galvanometer we chose a tube of the simplest type, so as to give the electrolyte the smallest conceivable resistance.

The tube in question is represented in fig. 1. The cock *K* has the same width as the U-shaped tube itself, viz. 4 mm diameter. This diameter of 4 mm is purposely taken so large, so as not to increase the resistance unneccessarily. We always filled the right hand tube with that solution, which had the greatest density. In that case it remains beneath the specific lighter fluid during the diffusion, so that disturbing currents are avoided.

Procedure in the measurements. After having placed the AgCl-electrodes with fitting corks at both ends, we fastened the filled-up tube in a thermostat. After some time, when the electrolyte could reasonably be supposed to have reached the temperature required, the tap *K* was opened. Diffusion sets in and after some minutes the potential difference between both electrodes reaches a constant value.

After having measured this value several times, with intervals of 10 minutes, we replaced one of the electrodes by another and repeated the measurement. Thus, if one has prepared *p* electrodes for the first and *q* electrodes for the second solution, these can be combined to *pq* pairs. The differences in the measured potential difference never amounted to more than 0.2 mV.

Example:	1. NaCl 18°,	$c_1 = 0.009987$		$c_2 = 0.02997$		
	$E =$ 26.8	26.6	26.7	26.7	26.7	
	26.6	26.8	26.9	26.6		average: 26.7
	2. NaCl 18°,	$c_1 = 0.001248$		$c_2 = 0.01997$		
	$E =$ 68.6	68.7	68.9	68.8	68.7	
	68.7	68.6	68.7			average: 68.7

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[1]) B. Elema, Dissert. Utrecht, 1930.

When an e.m.f. deviated more than 0.2 mV from the average, it was not taken into account. If the electrode concerned showed the same deviating behaviour after having been short-circuited once more with another, we silvered it over again.

The method described here has the advantage, that an electrode, made unfit by some cause or other, can immediately be detected. The simultaneous use of more, mutually short-circuited electrodes in the measuring tube lacks this advantage. A disadvantage is, of course, that the solution is momentarily exposed to the air during the changing of electrodes.

Henceforth only the average potential differences will be recorded. The number of observations, from which such an average was determined, varied from eight to twelve.

The solutions. Weighed quantities NaCl resp. $BaCl_2$ Kahlbaum, dried by glowing, were dissolved in distilled water, which had been rendered free from carbonic acid by leading CO_2-free air through it for seven hours. All other solutions were prepared by careful dilution in calibrated flasks.

NaCl in water, 18° ± 0.05.

For the calculation of the electrode potential E_e we made use of the formula:

$$^{10}\log \gamma = \frac{-0.500\sqrt{c}}{1+0.810\sqrt{2c}} + 0.0308\,.\,2c$$ [2]

assuming that the ion activities are equal. The limiting law for the diffusion potential reads:

$$(28) \quad . \quad . \quad L = 12.00 \left\{ ^{10}\log \frac{c_1}{c_2} - 0.100\,(\sqrt{c_1} - \sqrt{c_2}) \right\}$$

(compare page 30). E is the total potential difference, $E_e - E$ the experimental L, and $L(th)$ the diffusion potential as calculated from (28). Within the limits of accuracy there is no difference between $L(th)$ and the Nernst-formula $L(N)$: Table V.

$BaCl_2$ in water, 25° ± 0.02.

$$^{10}\log \gamma = \frac{-1.734\sqrt{c}}{1+2.331\sqrt{c}} + 0.132\,.\,c$$ [3]

$$L = 18.42 \left\{ ^{10}\log \frac{c_1}{c_2} + 2.00\,(\sqrt{c_1} - \sqrt{c_2}) \right\}$$

For this limiting law compare page 33. It seemed desirable, to extend the measurements of Jones and Dole with $BaCl_2$ (compare page 32) to smaller concentrations, and to examine at the same time more closely, at what concentrations the limit of usefulness for the formula lies. The lowest concentration at which observations of some

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[2] H. S. Harned and L. F. Nims, J. Am. Chem. Soc. **54**, 423 (1932).

[3] E. A. Tippets and R. F. Newton, J. Am. Chem. Soc. **56**, 1675 (1934).

Table V.

NaCl in water 18°.

c_1	c_2	E_e	E	$E_e - E$	L (N)	L (th)
0.009987	0.05004	−38.1	−29.6	−8.5	−8.4	−8.2
„	0.02997	−26.7	−20.9	−5.8	−5.7	−5.6
„	0.002497	34.4	(22.8)	(11.6)	7.2	7.2
„	„	„	27.4	7.0	„	„
„	„	„	27.3	7.1	„	„
„	0.001248	51.8	41.2	10.6	10.8	10.7
0.01997	0.002497	51.3	40.9	10.4	10.8	10.7
„	„	51.3	40.7	10.6	„	„
„	0.001248	68.7	54.1	14.6	14.5	14.4
0.02997	0.01997	9.8	8.0	1.8	2.1	2.1
„	0.005002	43.8	34.3	9.5	9.3	9.3
„	0.002497	61.1	48.3	12.8	13.0	12.9
„	0.001248	78.5	(55.3)	(23.2)	16.6	16.5
„	„	„	(57.8)	(20.7)	„	„
„	„	„	62.1	16.4	„	„
„	„	„	62.0	16.5	„	„
„	„	„	62.1	16.4	„	„
				$\overline{\Delta^2} =$	0.034	0,035
0.05004	0.02997	12.3	9.3	3.0	2.7	2.6
„	0.005002	56.0	43.7	12.3	12.0	11.8
„	0.002497	73.3	57.1	16.2	15.6	15.4
„	0.002497	73.3	57.0	16.3	15.6	15.4
				$\overline{\Delta^2} =$	0.26	0.44

The table confirms, that the limiting law can be used up to a concentration of 0.03 N. At 0.05 N. distinct deviations begin to occur. For some unknown reason some experiments proved to be failures. These are mentioned within parentheses.

importance could be carried out, was 0.000823. As irregular deviations, however, still frequently occur here, we repeated the observations at $c = 0.01$ and $c = 0.001$. These measurements were carried out several months later, and are reproduced in table VII (c in mol/l).

On purpose the table VI has been written in four parts, according to decreasing c_1. If we take into consideration the possible errors in E_e, the agreement with the theoretical limiting law can be regarded as complete in part 3 and 4. Above $c = 0.01$ systematic deviations begin to occur, amounting to several millivolts at $c = 0.03$.

B. HCl in a mixture of 40 mol. % C_2H_5OH and 60 mol. % H_2O, 25°.

Whereas the diluted solutions of numerous electrolytes in water show an electrochemical behaviour, which is in good agreement with

Table VI.

$BaCl_2$ in water at 25°.

c_1	c_2	E_e	E	$E_e - E$	L (th)	L (N)
0.03310	0.01004	28.4	16.8	11.6	12.6	9.6
0.03310	0.002498	62.2	39.2	23.0	25.6	20.7
0.03310	0.001316	78.0	48.0	32.3	35.1	29.5
0.03297	0.000824	89.8	57.5	30.0	31.2	25.8
				$\overline{\Delta}$	1.9	— 2.8
0.01648	0.001316	61.6	38.4	23.2	23.6	20.2
0.01648	0.001316	61.6	38.6	23.0	23.6	20.2
0.01648	0.001645	56.1	35.0	21.1	21.6	18.4
				$\overline{\Delta}$	0.5	— 3.0
0.009988	0.00200	39.3	24.7	14.6	14.9	12.9
0.009988	0.001007	56.5	35.8	20.7	20.9	18.4
0.009988	0.000823	61.3	(41.2)	(20.1)	22.6	20.0
0.009988	0.000823	61.3	(36.2)	(25.1)	22.6	20.0
0.009988	0.000823	61.3	38.6	22.7	22.6	20.0
0.009988	0.000823	61.3	39.1	22.2	22.6	20.0
				$\overline{\Delta}$	0.2	— 2.2
0.005012	0.002002	22.5	14.5	8.0	8.3	7.3
0.005012	0.001011	39.7	25.4	14.3	14.3	12.9
0.005012	0.000824	44.6	28.9	15.7	15.9	14.4
				$\overline{\Delta}$	0.2	— 1.0

Table VII.

$BaCl_2$ in water at 25°.

c_1	c_2	E_e	E	$E_e - E$	L (th)	L (N)
0.01000	0.001006	56.5	35.6	20.9	20.9	18.4
0.01000	0.001006	56.5	35.4	21.1	20.9	18.4
0.01000	0.001006	56.5	(42.5)	(14.0)	20.9	18.4
0.01000	0.001006	56.5	35.8	20.7	20.9	18.4
0.01000	0.001006	56.5	(29.8)	(26.7)	20.9	18.4
0.01000	0.001006	56.5	35.7	20.8	20.9	18.4
0.01000	0.001006	56.5	35.6	20.9	20.9	18.4
				$\overline{\Delta}$	0.02	— 2.4

the electrostatic theory — with regard to both the thermodynamic properties and the electric conductivity (see for example H. Falkenhagen[4])) — the results in other solvents can as yet by no means be regarded as a general confirmation of that theory. First of all this applies to the slope $d\lambda/d\sqrt{c}$ (λ being the conductivity and c the concentration). It often shows large deviations (100 % or more) from its theoretical value. In many cases the thermodynamical behaviour could not be explained either. In connection with our work, only some observations in alcohols and in mixtures of alcohol and water may be mentioned, out of the vast material that has been compiled in this domain.

Nonhebel and Hartley[5]) hold that the thermodynamic behaviour of HCl in CH_3OH is in better agreement with the theory of Milner[6]) than with that of Debije and Hückel. La Mer and Carpenter[7]), Brönsted, Delbanco and Volquartz[8]) and also Hansen and Williams[9]) examined several inorganic salts, in CH_3OH and in C_2H_5OH with respect to the thermodynamic properties. The limiting law of Debije-Hückel is regarded by them as invalid for these solvents. Hawkins and Partington[10]) go even further; according to these authors the thermodynamic behaviour of some salts in C_2H_5OH do not in the least agree with Debije-Hückel's theory.

As to the conductivity, according to H. Desai, Naik and B. Desai[11]) the formula of Onsager cannot be applied to various salts in CH_3OH, C_2H_5OH and C_3H_7OH. Thus Murray-Rust and Hartley[12]) state, that $-d\lambda/d\sqrt{c}$ for HCl in C_2H_5OH is nearly twice as large as theory predicts. On the other hand Copley, Murray-Rust and Hartley[13]) mention for a series of inorganic salts in C_2H_5OH a slope of the conductivity, which deviates a good deal less from the theoretical value, than is the case in the experiments of H. Desai, Naik and B. Desai. According to Thomas and Marum[14]) the conductivity of NaCl, NaBr and NaJ in CH_3OH and C_2H_5OH is in agreement with theory; and Connell, Hamilton and

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[4]) H. Falkenhagen, Electrolytes, Paris, 1934.

[5]) G. Nonhebel and H. Hartley, Phil. Mag. (6) **50**, 729 (1925).

[6]) S. R. Milner, Phil. Mag. (6) **23**, 551 (1912); **25**, 743 (1913).

[7]) V. K. La Mer and E. L. Carpenter, J. Phys. Chem. **40**, 287 (1936).

[8]) J. N. Brönsted, A. Delbanquo and K. Volquartz, Z. physik. Chem. A **162**, 128 (1932).

[9]) L. A. Hansen and J. W. Williams, J. Am. Chem. Soc. **52**, 2759 (1930).

[10]) F. S. Hawkins and J. R. Partington, Trans. Faraday Soc. **24**, 518 (1927).

[11]) H. Desai, F. Naik and B. Desai, Chem. Zentr. 1934, II, 1901.

[12]) D. M. Murray Rust and H. Hartley, Proc. Roy. Soc. London (A) **126**, 84 (1929).

[13]) E. D. Copley, D. M. Murray Rust and H. Hartley, J. Chem. Soc. London 1930, 2492.

[14]) L. Thomas and E. Marum, Z. physik. Chem. A **143**, 191 (1929).

Butler[15]) mention for LiCl in water-alcohol-mixtures an alteration of conductivity with concentration, which agrees within attainable accuracy of measurements with the formula of Onsager. The conductivity of $AgNO_3$ in some organic solvents (including C_2H_5OH) confirms the theory too. (Müller, Griengel and Mollang[16])).

But the thermodynamical properties too are considered by more than one experimentor to be in accordance with Debije-Hückel's theory. Lucasse[17]), and Scatchard[18]) too, reproduce the activity of HCl in water-alcohol-mixtures by the half empirical, half theoretical formula of Hückel:

$$-\log \gamma = \frac{u\sqrt{c}}{1+A\sqrt{c}} - B.c$$

in which u is calculated from the theoretical limiting law. The same course was adopted by Mc. Innes[19]) for HCl in CH_3OH. Other experiments with electrolytes in alcohols or alcohol-water-mixtures are mentioned by Harned and Fleischer[20]), Noyes and Baxter[21]), Barak and Hartley[22]), Woolcock, Hartley and Hughes[23]), Drucker and Schingnitz[24]), Woolcock and Hartley[25]), Prsheborowski[26]), Illasko, Cadenac and Salit[27]), Clark, Gatty, Hughes and Hartley[28]), Kreider and Jones[29]).

Sometimes diffusion potentials were studied. It is, however, impossible to test the theoretical limiting law (page 27), the examined concentrations being too large, and the transport number being moreover not known accurately enough. We may mention: 1. Harned and Fleischer[20]), HCl in C_2H_5OH and in alcohol-water-mixture. Only two concentrations below 0.01 N. 2. Erdey-Gruz[30]), HCl in water-alcohol-mixtures. Concentrations too large. 3. Woolcock, Hartley and Hughes[23]), HCl in C_2H_5OH. Concentrations too large. 4. Drucker and Schingnitz[24]), NaBr and LiCl in C_2H_5OH. Some of these measurements have been carried out at sufficiently low concentrations, to make a comparison with theory possible. The transport number of

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[15]) L. C. Connell, Hamilton and Butler, Proc. Roy. Soc. London (A) **147**, 418 (1934).

[16]) R. Müller, F. Griengl and J. Mollang, Monatsh. **47**, 83 (1926).

[17]) W. W. Lucasse, Z. physik. Chem. **121**, 254 (1926).

[18]) G. Scatchard, J. Am. Chem. Soc. **47**, 2098 (1925).

[19]) D. A. Mc. Innes, Chem. Rev. **18**, 335 (1936).

[20]) H. S. Harned and M. H. Fleyscher, J. Am. Chem. Soc. **47**, 82, 92 (1925).

[21]) A. A. Noyes and W. P. Baxter, J. Am. Chem. Soc. **47**, 2122 (1925).

[22]) M. Barak and H. Hartley, Z. physik. Chem. A **165** 272 (1933).

[23]) J. W. Woolcock, H. Hartley and B. Hughes, Phil. Mag. (7) **11**, 222 (1931).

[24]) C. Drucker and R. Schingnitz, Z. physik. Chem. **122**, 149 (1926).

[25]) J. W. Woolcock and H. Hartley, Phil. Mag. (7) **5**, 1133 (1928).

[26]) J. S. Prsheborowski, J. Russ. Phys. Chem. Soc. **62**, 313 (1930).

[27]) M. Illasko, Cadenac and Salit, Chem. Zentr. 1930, I, 2851.

[28]) D. N. Clark, Gatty, Hughes and Hartley, J. Chem. Soc. London 1933, 658.

[29]) H. R. Kreider and H. C. Jones, Am. Chem. J. **45**, 282 (1911).

[30]) T. Erdey-Gruz, Z. physik. Chem. **131**, 81 (1928).

these salts in C_2H_5OH is also known with an accuracy of 1 to 2% by the experiments of Barak and Hartley[22]) and Woolcock, Hartley and Hughes[23]). As, however, Drucker and Schingnitz measured only with AgCl-electrodes, the diffusion potentials cannot be calculated with sufficient accuracy from their experiments, as long as no activities are known.

We have examined the electrolyte HCl in a mixture of 40 mol. % alcohol and 60 mol. % water at a temperature of 25°. The dielectric constant of this solvent amounts to $D = 41.0$ [31]). The coefficient of internal friction is $\eta = 0.0221$ [32]).

To apply the limiting law (24 page 27) we must know the transport number at infinite dilution and the sum of the ion mobilities at infinite dilution, that is, λ_0. It is clear that the first of these quantities is the most important, as λ_0 only occurs in he correction-term. A correction of Nernst's formula has only sense, if the proportion $(l_1 - l_2) : (l_1 + l_2)$ is known with an accuracy of at least 1 %.

The solutions. Weighed quantities of absolute alcohol, distilled from quick lime were mixed with weighed quantities of distilled water. The specific conductivity of the alcohol amounted to $0{,}6 \cdot 10^{-6}$; the specific conductivity of the water was $2{,}7 \cdot 10^{-6}$, that of the mixture $1{,}7 \cdot 10^{-6}$. Diluting on the other hand a solution of HCl in water with absolute alcohol, we obtained a solution of HCl in the mixture in question, the concentration of which was determined by titration.

This titration was carried out with NaOH and methyl orange as an indicator. To the liquid, which was used to compare when titrating, we always added as much alcohol as the examined mixture contained, for the colour of methyl orange depends in some degree on the percentage of alcohol. All other solutions of HCl were obtained by accurate dilution with the alcohol-water-mixture in question.

Determination of λ_0 (25° ± 0.02). Measurements of conductivity

Table VIII.

Equiv. conductivity of HCl in alcohol-water, 25°.

$\varkappa_0 = 1.7 . 10^{-6}$ λ = eq. conductivity. c = conc. in grmol/l

c = 0.0335	0.0201	0.0151	0.0134	0.0100	0.0067
$\sqrt{c}$ = 0.1830	0.1418	0.1158	0.1230	0.1000	0.0819
λ = 83.10	86.41	87.98	88.65	90.07	91.70
c = 0.00335	0.00165	0.00100	0.000670	0.000335	0.000165
$\sqrt{c}$ = 0.0597	0.0406	0.0316	0.0259	0.0183	0.0128
γ = 94.05	95.55	96.48	96.77	97.0	96.8

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[31]) G. Akerlöf, J. Am. Chem. Soc. **54**, 4125 (1932).

[32]) Landolt-Bornstein, Physik. Chem. Tab., Hauptwerk I, 140.

were carried out in a bulb with capacity 0.0651. The apparatus used by us will be described by Schrijver[33]).

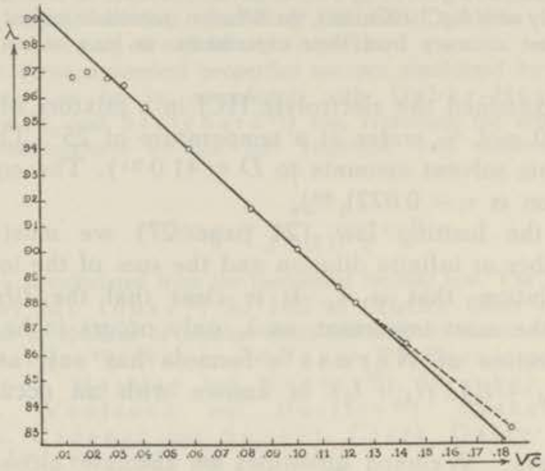

Fig. 2.

In fig. 2 the equivalent conductivity λ of table VIII has been compared with $\sqrt{c}$. A straight line is found with slope

$$\frac{d\lambda}{d\sqrt{c}} = -\,92.9 \text{ while } \lambda_0 = 99.4.^{*})$$

This slope is in excellent agreement with Onsager's formula:

$$\lambda = \lambda_0 - x\sqrt{c}, \text{ with } x = \frac{0.818 \,.\, 10^6}{(DT)^{3/2}}\,\lambda_0 + \frac{82.0}{\eta\sqrt{DT}}$$

We find namely with $\lambda_0 = 99.4$ $D = 41.0$ $T = 298$ $\eta = 0.0221 : x = 93.7$. At concentrations below 0.001 λ deviates from the straight line. The cause of this deviation could not be traced.

Determination of the transport number t_{Cl} *(25° ± 0.1).* The transport number was determined analytically by measuring the alteration of concentration, caused by an electric current. The vessel used for it is represented by fig. 3. At both ends an electrode of platinized platinum is placed. For some hours a current goes through the apparatus. The electrodes are then removed, and the cock K is closed after having taken care that the liquid in the right tube rises as high as line a, which has been indicated on the outside beforehand.

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[33]) L. A. Schrijver, Rec. trav. chim. Soon to be published.

*) Calculated by the method of least squares, leaving $c < 0.00067$ and $c > 0.015$ out of account.

The volume V from K to a had been determined by weighing the equal volume of water:

$$V = 34.94 \text{ cm}^3.$$

Now the contents of this right hand tube are titrated with NaOH or $Ba(OH)_2$ and methyl orange as an indicator; again we add to the liquid, with which to compare (during titration), the same amount of alcohol as is present in the titrated mixture itself (compare page 31). The solutions, which contained 0.15 tot 0.03 g/mol. per *l*. were thus titrated with $Ba(OH)_2$ 0.1 N., free from carbonic acid. The solutions with concentrations below 0.03 N. were titrated with NaOH 0.02 N. If the original concentration is c g/mol. per *l*, the strength of the current $i \cdot 10^{-3}$ Ampere, the time τ seconds, and the number of g/mol. HCl, found in th volume $V : s \cdot 10^{-3}$, the transport-number is:

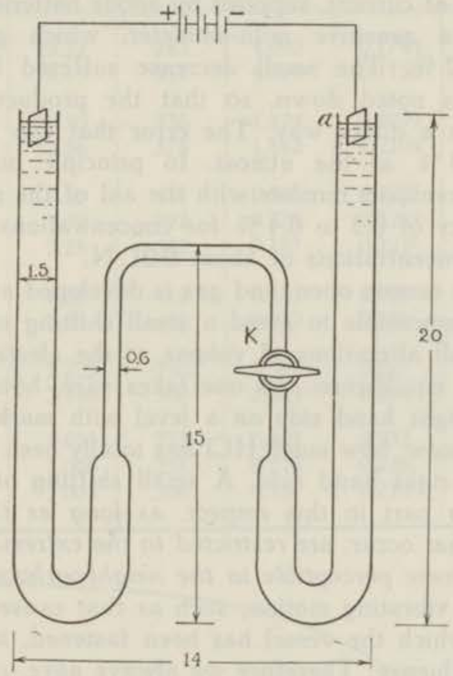

Fig. 3.

$$(29) \quad \ldots\ldots \quad t_{Cl} = \frac{F}{i\tau}(34.94 \cdot c - s)$$

where F (= 1 Faraday) = 96493. For there disappeared at the right hand side $t_{Cl} i \cdot 10^{-3} \cdot \tau \cdot F^{-1}$ g/mol. There was originally $34.94 \cdot c \cdot 10^{-3}$ g/mol., and $s \cdot 10^{-3}$ is left. This immediately leads to (29).

Now, in our case, the accuracy of a titration can be estimated at about 0,002 . 10^{-3} g/mol., which means that the number of g/mol. HCl in the volume V can be determined with an accuracy of 0,002 . 10^{-3} g/mol. In fact this is equivalent to one drop of 0.05 N. solution, which generally causes a change of colour which is just perceptible. As s lies in the neighbourhood of $30c$, an error of 0,002 . 10^{-3} g/mol. means a relative error in s of $0{,}002/30c$. That is 0.1 % for c about 0.1 and a little more than 1 % for $c = 0.01$.

The strength of current, supplied by anode batteries, was measured by means of a sensitive milli-ammeter, which gave i with an accuracy of 0.2 %. The small decrease suffered by i during the experiment, was noted down, so that the product $i\tau = \Sigma i(\tau) \,.\, \Delta\tau$ was obtained in a direct way. The error that can now occur in $i\tau$, amounts to 0.3 % at the utmost. In principle one can therefore determine the transport number with the aid of the method described with an accuracy of 0.3 to 0.4 % for concentrations of about 0.1 N. and 1 % for concentrations of about 0.01 N.

As both ends remain open, and gas is developed at both electrodes, it is probably impossible to avoid a small shifting of the liquid as a whole. For small alterations of volume at the electrodes can disturb the hydrostatic equilibrium. As one takes care, however, to get the liquid on the right hand side on a level with mark a, it is only of importance to know, how much HCl has totally been transported from the left to the right hand side. A small shifting of the liquid as a whole plays no part in this respect, *as long as the alterations of concentration that occur, are restricted to the extremities of the vessel and do not become perceptible in the neighbourhood of the cock K.*

An irregular vibrating motion, such as that caused by stirring the thermostat in which the vessel has been fastened, appeared to exert considerable influence. Therefore we always gave up stirring, nevertheless easily maintaining the temperature at 25° ± 0.1. Changing the current i and the time τ, t_{Cl} was not altered, as can be seen in table IX. Moreover, we determined in exactly the same manner the transport number of HCl in water at 25° at a concentration $c = 0.01112$. Taking $i = 6.86$, $\tau = 193$ min, we found $s = 0.248$. Thus $t = 0.171$. Kohlrausch[34]) mentions a value 0.169 at $c = 0.01$, Longsworth[35]): 0.175.

The values t of table IX are plotted against c and $\sqrt{c}$ in fig. 4.

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[34]) F. Kohlrausch and H. Holborn, Das Leitverm. d. Elektr., Leipzig, 1916, p. 213.

[35]) L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).

At infinite dilution $t_0 = 0.231 \pm 0.001$. Therefore the ion mobilities are: $l_H = 76.4$ and $l_{Cl} = 23.0$. $(l_1 - l_2) : (l_1 + l_2) = 0.358 \pm 0.002$.

Table IX.

Transport number t of HCl in alc.-water, 25°.
$i \,.\, 10^{-3}$ = average strength of current.
c = original concentration in g/mol. per l.
$s \,.\, 10^{-3}$ = number of g/mol. HCl, found in volume V.

c	i	τ in min.	s	t	average
0.1427	29.22	283	4.090	0.1744	
0.1427	18.15	412	4.174	0.1750	0.1747
0.0714	15.30	336	1.824	0.2099	
0.0714	12.26	375	1.892	0.2109	0.2104
0.0335	7.25	432	0.736	0.222^5	
0.0335	7.32	392	0.771	0.224^0	
0.0335	7.28	380	0.787	0.223^1	0.223^2
0.02856	7.20	412	0.585	0.224	
0.02856	5.96	440	0.629	0.226	0.225
0.01430	2.225	350	0.389	0.227	
0.01430	2.250	360	0.384	0.228	0.227^5
0.00715	1.605	272	0.187	0.232	
0.00715	1.006	238	0.216	0.228	
0.00715	2.005	396	0.137	0.229	0.229

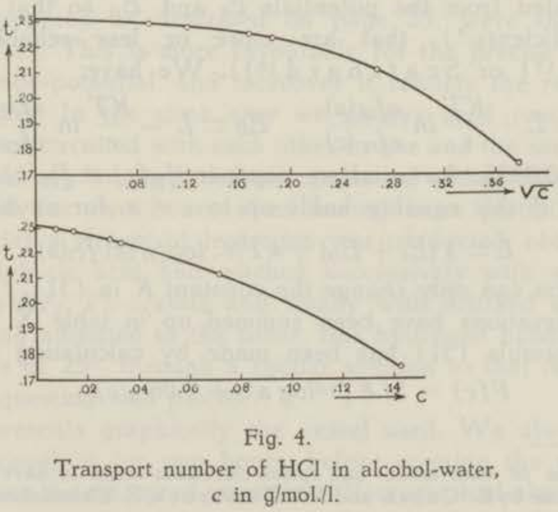

Fig. 4.

Transport number of HCl in alcohol-water,
c in g/mol./l.

The theoretical limiting law, as derived by Longsworth[35]) from the theory of Debije-Hückel does not hold for this transport number. This limiting law prescribes, that the slope at infinite dilution must satisfy the equation:

$$\left(dt/d\sqrt{c}\right)_{c=0} = \frac{2\,t_0 - 1}{\lambda_0}\,\frac{82.0}{\eta\sqrt{DT}}$$

This would be —0.182, while the absolute value of the experimental slope is at most 0.05.

The diffusion potentials of HCl in alcohol-water, 25° ± 0.05.

With the values $t_0 = 0.231$ and $\lambda_0 = 99.4$ the limiting law for the diffusion potential becomes:

$$(30) \quad . \; . \; . \quad L = 31.8 \left\{ {}^{10}log \frac{c_1}{c_2} - 1.06\,(\sqrt{c_1} - \sqrt{c_2}) \right\}$$

We measured the cells with both anion- and cation-electrodes, while one of the concentrations was chosen constant: 0.0335. Thus:

$Pt/H_2/HCl\ 0.0335/HCl\ c/H_2/Pt$ . . . . E_I

$Ag/AgCl/HCl\ 0.0335/HCl\ c/AgCl/Ag$ . . . . . . E_{II}

c varied from 0.00134 to 0.01675 g/mol. per l. It was impossible to choose the other concentration so low, that a direct comparison with the formula (30) could be carried out, as the resistance of the solutions would become too large, to allow a reliable measurement. Instead of (30) we must therefore examine a formula:

$$(31) \quad . \; . \; . \quad L = 31.8 \left\{ {}^{10}log \frac{0.0335}{c} + 1.06\sqrt{c} \right\} - K$$

L is calculated from the potentials E_I and E_{II} so that we need no activitycoefficients *), that are more or less reliable (compare Lucasse[17]) or Scatchard[18])). We have:

$$E_I = L + \frac{KT}{\varepsilon}\,ln\,\frac{af_H(a)}{cf_H(c)} \qquad E_{II} = L - \frac{KT}{\varepsilon}\,ln\,\frac{af_{Cl}(a)}{cf_{Cl}(c)}$$

where $a = 0.0335$. As usual we suppose: $f_H(c) = f_{Cl}(c)$. It is of no importance, if this equality holds up to $c = a$, for anyhow we find:

$$L = \tfrac{1}{2}\,(E_I + E_{II}) + kT/\varepsilon\,.\,log f_H(a)/f_{Cl}(a).$$

The last term can only change the constant K in (31).

The observations have been summed up in table X. Comparison with the formula (31) has been made by calculating the function

$$F(c) = 31.8\,({}^{10}log\, a/c + 1.06\,\sqrt{c})$$

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*) The use of both anion- and cation-electrodes seems to have been proposed for the first time by E. Cohen and W. Tombrock, Z. Elektrochem. **13**, 612 (1907).

and the difference: $K = F(c) - L$. In the same way we have compared the results with the formula of Nernst, which would run here:

$$L = F_N(c) - K_N, \text{ with } F_N(c) = 31.8 \, . \, {}^{10}\log a/c.$$

Table X.

Diffusion potential of HCl in alcohol-water, 25°. $c_1 = a = 0.0335$; $c_2 = c$. For convenience we have always written the absolute values of the potential differences, so that L is found as $\frac{1}{2}(E_I - E_{II})$ instead of $\frac{1}{2}(E^I + E_{II})$.

c	F (c)	F_N (c)	E_I	E_{II}	L	K	K_N
0.00134	45.7	44.5	116.2—116.6	33.0—33.3	41.4—41.8	3.9—4.3	2.7—3.1
0.001675	42.8	41.4	108.0—108.3	30.6	38.7—38.9	3.9—4.1	2.5—2.7
0.00210	39.8	38.3	99.6	28.2	35.7	4.1	2.6
0.00335	33.8	31.8	82.6	22.8	29.9	3.9	1.9
0.00672	25.0	22.2	57.3	15.3	21.0	4.0	1.2
0.00837	22.2	19.2	49.2	13.2	18.0	4.2	1.2
0.01675	13.9	9.6	24.3	6.5	8.9	5.0	0.7

From the values K and K_N it can be seen, that the formula (31) can reproduce the observations up to a concentration of about 0.009 N., while the formula of Nernst obviously would not hold beyond 0.0025 N.

Technique of the measurements. As we used hydrogen-electrodes it was necessary, to wait till the electrode potentials had adjusted themselves. It was therefore easier, not to exchange the AgCl-electrodes during the measurements, and therefore three AgCl-electrodes, prepared as described on page 35, were shortcircuited with each other. This is more favourable for the precise adjustment of the electrode-potential, and moreover it renders the resistance of the cell smaller. In the same way we always used two hydrogen-electrodes, shortcircuited with each other in one and the same solution. They consisted of platinized platinum, polarised cathodically in diluted sulphuric acid for two hours after having been platinized. Along these electrodes a stream of hydrogen was conducted, obtained from zinc and sulphuric acid and washed successively with solutions of $KMnO_4$, $AgNO_3$, Pb-acetate and finally with distilled water.

Before being admitted to the tubes, this hydrogen bubbled first, at a temperature of 25°, through a similar solution to that in which the electrode in question was placed.

Fig. 5 represents graphically the vessel used. We always passed hydrogen through it for two hours, before opening the cock. After these two hours the measured potential differences had always reached their constant values. They were measured eight times at intervals of

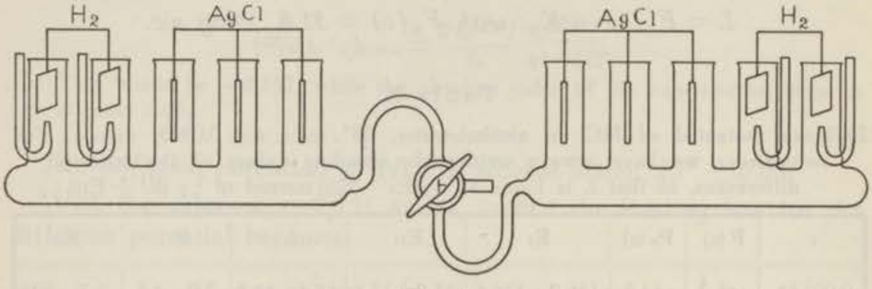

Fig. 5.

about 15 minutes, and they never showed greater fluctuations than 0.2 mV. In table X we only mentioned the average value.

The experiments with HCl in a mixture of 40 mol. % alcohol and 60 mol. % water at 25°, have been carried out in order to study a solvent with a smaller dielectric constant than that of water. From $c = 0.0008$ to $c = 0.008$, the equivalent conductivity agrees with Onsager's formula. The transport number does not agree with the formula of Shedlovsky, cf. page 46.

The diffusion potential can be calculated from the theoretical limiting law up to a concentration 0.009, while this law could be applied to the diffusion potential of HCl in water up to a concentration of about 0.03. This difference in behaviour is probably due to the small dielectric constant (41 in the mixture concerned instead of 78 in water).

DIFFUSION OF A MIXTURE OF ELECTROLYTES.

I. Theoretical part.

A. A SUMMARY OF THE EXISTING THEORIES.

Introduction.

If there are more than two ionspecies, we have for each ion an equation of motion like (7) page 20. We restrict ourselves to the case of infinite dilution, so that:

$$\varrho_i v_i = - kT \, grad \, (ln \, n_i) - e_i \, grad \, \varphi.$$

The diffusion may take place in one single direction, namely in the direction of the axis x. The charge e_i may be replaced by $z_i \varepsilon$. If we multiply by n_i, the equations become:

$$(32) \quad . \quad . \quad . \quad . \quad . \quad \varrho_i n_i v_i = - kT \frac{\partial n_i}{\partial x} - \varepsilon z_i n_i \frac{\partial \varphi}{\partial x}$$

Instead of (10) page 21 we now have to add the condition:

$$(33) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \Sigma_i z_i n_i = 0.$$

An exact integration of the system of equations obtained in this manner, has never been attained. It is true, that the approximations of Planck and of Henderson yield values for the diffusion-potentials, which have the right order of magnitude, but neither of the two theories is very convincing in itself. When criticizing the formulae of Planck and of Henderson one must bear in mind, that all observations concerning mixtures of electrolytes have been carried out at too large concentrations. The theory supposes ideal solutions, and all experiments have been carried out at concentrations 0.1 N. or more. Therefore one cannot even expect an exact agreement with theory. Moreover electrodepotentials play a part in almost all observations, and this always involves unknown ionactivities. It is true, that attempts have been made [1]), to take into account the

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[1]) K. J. Pedersen, Math. Fys. Medd. Kgl. Danske Vid. Selsk. XIV **9** (1937).

E. A. Guggenheim and A. Unmack, Math. Fys. Medd. Kgl. Danske Vid. Selsk. X **8** (1930), **14** (1931).

P. B. Taylor, J. Phys. Chem. **31**, 1478 (1927).

interionic forces; yet this would only mean a correction for concentrations under 0.05 N., and such calculations seem rather premature as long as there exists no well-founded theory for ideal solutions.

Finally it may be noted, that the theories, given so far, aimed exclusively at calculating the diffusionpotentials, while the picture of diffusion itself was thrust into the background or was even left out of consideration. Here we shall submit the calculations of Henderson, Planck, Sitte and Taylor to a more detailed discussion.

Conditions at the boundaries.

The diffusion takes place in the direction of the axis x. The usual conditions are:

$$\begin{array}{llllll} at -\infty: & n_i = c_i & \varphi = 0 & \partial n_i/\partial x = 0 & \partial n_i/\partial t = 0 & \partial \varphi/\partial x = 0 \\ at +\infty: & n_i = c'_i & \varphi = L & \partial n_i/\partial x = 0 & \partial n_i/\partial t = 0 & \partial \varphi/\partial x = 0 \end{array}$$

L is the diffusionpotential between $-\infty$ and $+\infty$. The condition: $\partial\varphi/\partial x = 0$ at the boundaries, expresses that no electric current exists.

The differential equations.

For convenience' sake we introduce the quantities:

$$(34) \quad \ldots\ldots\ldots \quad \frac{1}{\lambda_i} = \frac{\varrho_i}{kT}$$

$$(35) \quad \ldots\ldots\ldots \quad \Phi = \frac{\varepsilon}{kT}\varphi$$

Obviously λ_i is proportional to the ionmobility divided by the valency of the ion (compare page 21).

Now (32) becomes:

$$(36) \quad \ldots\ldots \quad \frac{1}{\lambda_i} n_i v_i = -\frac{\partial n_i}{\partial x} - z_i n_i \frac{\partial \Phi}{\partial x}$$

If now we consider a small space $d\tau = Sdx$ between two planes at x and $x + dx$ (S being the area of the planes), the number of ions i in this space amounts to $Sn_i dx$. In unit time $Sn_i v_i$ ions enter this space $d\tau$ at the left hand side and $S[n_i v_i + (\partial n_i v_i/\partial x)dx]$ leave it at the right hand side. So the increase of $Sn_i dx$ in unit time amounts to $-S(\partial n_i v_i/\partial x)dx$. Thus the so-called equation of continuity:

$$(37) \quad \ldots\ldots\ldots \quad \frac{\partial n_i}{\partial t} + \frac{\partial (n_i v_i)}{\partial x} = 0.$$

and the equations (36) can be written:

$$(38) \quad \frac{1}{\lambda_i}\frac{\partial n_i}{\partial t} = \frac{\partial^2 n_i}{\partial x^2} + z_i \frac{\partial}{\partial x}\left(n_i \frac{\partial \Phi}{\partial x}\right)$$

Multiplying by $z_i\lambda_i$ and adding, we get, on account of: $\Sigma_i z_i n_i = 0$,

$$\Sigma_i z_i \lambda_i \frac{\partial^2 n_i}{\partial x^2} + \Sigma_i z_i^2 \lambda_i \frac{\partial}{\partial x}\left(n_i \frac{\partial \Phi}{\partial x}\right) = 0.$$

Henceforth we abbreviate:

$$(39) \quad u = \Sigma_i z_i \lambda_i n_i \qquad v = \Sigma_i z_i^2 \lambda_i n_i$$

The values of these quantities at $-\infty$ and $+\infty$ respectively may be written U, V, and U', V'. Thus:

$$U = \Sigma_i z_i \lambda_i c_i \qquad V = \Sigma_i z_i^2 \lambda_i c_i \qquad U' = \Sigma_i z_i \lambda_i c_i' \qquad V' = \Sigma_i z_i^2 \lambda_i c_i'$$

With the aid of these definitions we find by integration:

$$\frac{\partial u}{\partial x} + v \frac{\partial \Phi}{\partial x} = f(t)$$

On account of the conditions at the boundaries: $f(t) = 0$, *so that:*

$$(40) \quad \frac{\partial u}{\partial x} + v \frac{\partial \Phi}{\partial x} = 0.$$

In connection with (36), remembering the definitions (39) of u and v, we see that (40) is nothing more than another way of saying that there is no electric current.

General Remarks.

1. From the equations (38) one can at once draw the conclusion, that none of the concentrations n_i can be constant, unless $\Phi \equiv 0$. When therefore, at the beginning of the diffusion, we have given to one of the n_i the same value for all x, this constant concentration cannot maintain itself, unless $\Phi \equiv 0$. This latter condition, however, generally gives rise to contradictions in the equations.
2. The equation (40) cannot be integrated without further assumptions, as was the case with the diffusion of a single electrolyte. Therefore one cannot say, if the potentialdifference between $-\infty$ and $+\infty$ remains constant or not.
3. If two mixtures are joined by a third one, the sum of the new diffusionpotentials need not be equal to the diffusionpotential between the two original solutions.

Formula of Henderson [2]).

Henderson simply supposed all concentrations linear in x. Then u and v are linearly related, so that

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[2]) P. Henderson, Z. physik. Chem. **59**, 118 (1907), **63**, 325 (1908).

$$\frac{\partial u}{\partial x} = \frac{U - U'}{V - V'} \frac{\partial v}{\partial x}, \text{ and (40) becomes: } \frac{U' - U}{V' - V} \frac{\partial v}{\partial x} + v \frac{\partial \Phi}{\partial x} = 0.$$

This can be integrated to:

$$\Phi = const. - \frac{U - U'}{V - V'} \ln v,$$

and the diffusionpotential becomes:

$$(41) \quad . \; . \; . \; . \; . \; . \quad L = \frac{kT}{\varepsilon} \frac{U - U'}{V - V'} \ln \frac{V}{V'}.$$

Independent of Henderson, Gouy[3]) has afterwards found this same formula a second time.

A linear dependence on x does not seem to agree too well with the usual picture of diffusion. For at $-\infty$ and at $+\infty$ the concentration-gradients must become zero. Planck[4]), however, already pointed out, that it is not necessary for Henderson's formula, that the concentrations n_i are linear in x. It is sufficient if they are related by a linear equation. And here we even saw, that it is already sufficient if there exists a linear relation between u and v (cf. also page 59). Of course the initial distribution can be chosen in such a way as to satisfy the condition of linearity. It can, however, easily be proved that it does not maintain itself, so that the Henderson-diffusionpotential need not maintain itself either.

Kramers*) proposed the following derivation of the formula. First write (40) in the form:

$$\frac{\partial \Phi}{\partial x} = \frac{\lambda}{v} \frac{\partial v}{\partial x} - \frac{1}{v} \frac{\partial}{\partial x} (\lambda v + u)$$

where λ is a constant; and now determine λ so as to make the last term as small as possible. It is plausible that we choose for λ such a number that $\lambda v + u$ has the same value at the left $(-\infty)$ as well as at the right hand side $(+\infty)$. Doing so, and then neglecting this term with regard to the other terms, one can easily be convinced that in this way the formula of Henderson is arrived at.

Formula of Planck[5]).

The approximation of Planck interferes very radically with the nature of the equations (38). For Planck replaces (38) by:

$$\frac{\partial^2 n_i}{\partial x^2} + z_i \frac{\partial}{\partial x} \left(n_i \frac{\partial \Phi}{\partial x} \right) = 0.$$

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*) Prof. H. A. Kramers (Leiden), private communication.

[3]) M. Gouy, J. Chim. physique **14**, 185 (1916).

[4]) M. Planck, Sitz. Ber. Berlin (1927) 285, (1929) 9, (1930) 367, (1931) 115, (1933) 362.

[5]) M. Planck, Wied. Ann. **40**, 561 (1890).

This means that the process is supposed stationary ($\partial n / \partial t = 0$), a supposition which does not agree with our boundary conditions which are those of the usual experiments. Integrating one finds:

$$\frac{\partial n_i}{\partial x} + z_i n_i \frac{\partial \Phi}{\partial x} = a_i$$

where a_i does not contain x. With the aid of the conditions (33) and (40) one can derive a transcendental equation for L, which must be solved by successive approximation. In case that all ions are univalent, Planck finds:

$$(42) \quad . \; . \; . \quad \begin{cases} L = \dfrac{kT}{\varepsilon} \ln \xi \\ \dfrac{\ln c'/c + \ln \xi}{\ln c'/c - \ln \xi} \cdot \dfrac{V + U - (V' + U')\xi}{(V - U)\xi - (V' - U')} = \dfrac{c - c'\xi}{c\xi - c'} \end{cases}$$

An extension to ions of different valency has been given by Pleyel[*]), Johnson[6]), Plettig[7]), Chang[8]), Guyot[9]), Gouy[10]). The formula supposes a stationary state, a condition which has not been fulfilled in the usual experiments. It is however valid in cases where the stationary state is guaranteed.

In some special cases the formulae of Planck and Henderson lead to the same result, e. g. when two electrolytes with a common ion diffuse into each other, provided the concentration of this common ion is the same in both electrolytes. The formulae are also identical when all concentrations at the left are proportional to those at the right, i. e. when the left hand solution can be obtained from the right hand one by a simple dilution only.

Formula of Sitte[11]).

As was explained on page 21, we take the condition (33) as a substitute for Poisson's formula:

$$\frac{\partial^2 \varphi}{\partial x^2} = - \frac{4 \pi \varepsilon}{D} \Sigma_i z_i n_i,$$

and we also proved why this is permissible. Now Sitte drew the wrong conclusion, that one could write as well:

$$\frac{\partial^2 \varphi}{\partial x^2} = 0, \text{ or: } \frac{\partial \varphi}{\partial x} = f(t)$$

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[*]) H. Pleyel, Z. physik. Chem. **72**, 1 (1910).

[6]) K. R. Johnson, Ann. Physik (5) **5**, 735 (1930), **14**, 995 (1904).

[7]) V. Plettig, Ann. Physik (5) **5**, 735 (1930).

[8]) Shu Tsu Chang, Ann. Physik (5) **16**, 513 (1933).

[9]) J. Guyot, J. Physique **6**, 530 (1907), **7**, 27 (1908).

[10]) cf. [3]).

[11]) K. Sitte, Z. Physik. **91**, 622 (1934).

Supposing all ions univalent, we have:

$$\Sigma_i \lambda_i n_i = \Sigma_i z_i^2 \lambda_i n_i = v$$

The equations (38) therefore yield:

$$(43) \quad . \; . \quad \frac{\partial}{\partial t}(\Sigma_i n_i) = \frac{\partial^2 v}{\partial x^2} + \frac{\partial}{\partial x}\left(u \frac{d\Phi}{\partial x}\right), \text{ in which} : \frac{\partial \Phi}{\partial x} = K(t).$$

For further calculation Sitte supposed the existance of a stationary state. It is, however, sufficient if the left member in (43) is zero. This can e.g. be approximately fulfilled if $\Sigma_i n_i$ has the same value at $-\infty$ as at $+\infty$. This leads to

$$(44) \quad . \; . \; . \; . \; . \quad L = \frac{kT}{\varepsilon} \; . \, ln \, \frac{V + U + V' - U'}{V - U + V' + U'} \, .$$

Properly speaking, the supposition $\partial\Phi/\partial x = K(t)$, means that the potentialgradient is approximated by a straight line. Notwithstanding the loosely founded theoretical background, the formula can therefore very well represent a useful approximation, especially in such cases, where $\Sigma_i \partial n_i / \partial t$ is small.

The process of diffusion.

The calculations, mentioned so far, only occupied themselves with the diffusionpotential. It was entirely left out of consideration, how it is brought about and how it maintains itself. Planck and Sitte even renounced the common boundary conditions expressing that $\partial\varphi/\partial x$ must become zero in infinity. So we get a quite different picture of the diffusion. Henderson avoids all these difficulties by assuming u proportional to v. One does not even know, however, if one can expect a relation between u and v, let alone a linear one (cf. page 59). In dealing with a single electrolyte, we already saw, how the velocity of the first ion is changed in a very radical way by the second. The electrolyte as a whole diffuses with a diffusioncoefficient, which lies between those of both ions (page 27). Likewise the average velocity of an ion in a mixture of electrolytes is strongly influenced by the presence of other ions, and this influence largely depends on the concentrations n_i of those ions. All this might only be traced by a more accurate integration of the equations (33, 38, 40). In this direction attempts have been made by Sitte[12]) and by Taylor[13]). Both authors imagine two mixtures, brought into contact in the plane $x = 0$ at $t = 0$.

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[12]) cf. [11]).

[13]) P. B. Taylor, J. Phys. Chem. **31**, 1478 (1927).

The equations (38) can also be written:

$$(45) \quad . \quad . \quad . \quad . \quad \frac{\partial^2 n_i}{\partial x^2} + z_i \frac{\partial \Phi}{\partial x} \frac{\partial n_i}{\partial x} - \frac{1}{\lambda_i} \frac{\partial n_i}{\partial t} + z_i \frac{\partial^2 \Phi}{\partial x^2} n_i = 0.$$

Now Sitte first solves the zero-order-approximation:

$$(46) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \frac{\partial^2 n_i^\circ}{\partial x^2} = \frac{1}{\mathfrak{D}_i} \frac{\partial n_i^\circ}{\partial t}$$

where $\mathfrak{D}_i$ are coefficients, which must be determined afterwards. With the aid of Poisson's equation the solution n^0_i yields a value for $\partial^2\Phi^0/\partial x^2$. Integrating one finds $\partial\Phi^0/\partial x$. One can put these values $\partial^2\Phi^0/\partial x^2$ and $\partial\Phi^0/\partial x$ into the equations (45):

$$(47) \quad . \quad . \quad . \quad . \quad \frac{\partial^2 n_i}{\partial x^2} + z_i \frac{\partial \Phi^\circ}{\partial x} \frac{\partial n_i}{\partial x} - \frac{1}{\lambda_i} \frac{\partial n_i}{\partial t} + z_i \frac{\partial^2 \Phi^\circ}{\partial x^2} n_i = 0,$$

and so obtain a first approximation for the n_i. To solve (47), Sitte makes use of a theory developed by Gevrey[14]). To obtain this first approximation, some very radical simplifications must be used already. To support his method, Sitte mentions the fact that the charge-densities, obtained in first approximation, are smaller than those obtained in zero approximation, but on closer examination it turns out that this is only the case for small *t*, as Sitte too admits. Because of the very circumstantial calculations we must refer to the literature concerned. Sitte does not proceed beyond the first approximation, and therefore his calculations are only important with respect to experiments, which only deal with the very first phase in the diffusionprocess.

It is, however, not at all certain whether his results have a physical meaning or not, because quantities such as $\partial ni/\partial x$ do not exist at the boundary for $t = 0$; and it remains to be seen, whether they will soon be so small, that the differentialequations hold (cf. page 14). On the whole the initial distribution, here described, must be regarded as a schematic arrangement. The fact that this schematic arrangement yields a good reproduction of the process after a longer time, does not prove that it does so for very small times in the neighbourhood of the boundary.

As has been said, Taylor[13]) starts with the same initial distribution: two mixtures are brought into contact in the boundary $x = 0$ at time $t = 0$. The concentration of the ion *i* may be c_i at the left hand side, c'_i at the right hand side. If we abbreviate:

$$y = \frac{x}{2\sqrt{t}}$$

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[14]) F. Gevrey, J. Mathém. (6) **9**, 305 (1913).

we should have in the case of independent diffusion of all ions:

$$(48) \quad . \; . \; . \; . \quad n_i = \frac{c_i' + c_i}{2} + \frac{c_i' - c_i}{\sqrt{\pi}} \int_0^{\alpha_i y} e^{-w^2} dw$$

$$(49) \quad . \; . \; . \; . \quad \frac{\partial n_i}{\partial t} = \frac{c_i' - c_i}{\sqrt{\pi}} e^{-\alpha_i^2 y^2} . \, \alpha_i \frac{\partial y}{\partial t}$$

α^2_i being a reciprocal diffusioncoefficient.

In the case of real electrolyte-diffusion Taylor writes, instead of (49):

$$(50) \quad . \; . \; . \; . \; . \quad \frac{\partial n_i}{\partial t} = \Sigma_p \, a_{pi} \, (\alpha_i y)^p \, e^{-\alpha_i^2 y^2} . \, \alpha_i \frac{\partial y}{\partial t} \; .$$

where a_{pi} are coefficients, which must be determined afterwards. Integration yields:

$$n_i = b_i + \Sigma_p \, a_{pi} \int_0^{\alpha_i y} w^n \, e^{-w^2} dw \, .$$

$\partial\Phi/\partial x$ is determined by the equation: $\partial\Phi/\partial x = -1/v \, . \, \partial u/\partial x$, and we must have:

$$(51) \quad . \; . \; . \; . \; . \quad \frac{1}{\lambda_i} \int_{-\infty}^{x} \frac{\partial n_i}{\partial t} dx = \frac{\partial n_i}{\partial x} + z_i n_i \frac{\partial \Phi}{\partial x}$$

as can immediately be derived from (38). The left member can be obtained from (50), while the value found for $\partial\Phi/\partial x$ and the values of $\partial n_i/\partial x$, obtained from (48), are written on the right hand side. The equation, arrived at, must be an identity in y. An expansion of the various functions in (51) in powers of y can therefore yield conditions for the numbers a_{pi} and α_i. It appears, that the identity (51) contains t and x only as powers of $y = x/2\sqrt{t}$, as can indeed quite easily be proved. Taylor rightly concludes that a system of numbers a_{pi}, α_i, which satisfies once, will always satisfy. In other words: in that case the concentrations n_i and the electric potential can be written as functions of y only. An important sesult is, that the diffusionpotential is independent of time. For, eliminating y, one obtains the diffusionpotential between two points as a function of the concentrations in these points. As these concentrations do not alter at $-\infty$ and $+\infty$, the diffusionpotential too must remain constant.

This is the only real proof for the independence of time of the diffusionpotential, mentioned in literature, although this proof is restricted to the case of a very special initial distribution of the concentrations. On closer consideration, however, one cannot accept this proof either. For the whole theory is based upon the supposition, that the numbers a_{pi} and α_i are determined by the identity (51), and even determined in a single-valued way. Taylor does not prove that this is the case, and perhaps this cannot be proved at all. One must namely bear in mind, that the conditions, from which the numbers a_{pi} must be calculated, are quadratic in these numbers, because $\partial\Phi/\partial x$ is a fraction, which contains the a_{pi} in both the numerator and the denominator. It is still worse with respect to the α_i, for these enter in all possible powers. Therefore, we are not at all sure that a system of coefficients, which makes (51) an identity, can be found *).

Types of diffusion.

The question arises, whether it is possible, to choose the circumstances so as to guarantee the validity of the theories. This leads to a distinction in diffusion-types, a distinction which has first been made by Guggenheim 15).

1. *Continuous mixture layer* 16). In this case the mixture in each point of the diffusion layer between both solutions which diffuse into each other, can be obtained by simply mixing these solutions. This is nothing but a simple way to effectuate a linear relation between u and v. Because, if c_i and c'_i are respectively the concentrations of the ions i at the left and right hand side, we have, in a continuous mixture layer, on account of the definition itself: $n_i = \alpha c'_i + (1 - \alpha) c_i$, where α changes from 0 to 1. In other words: the concentrations are linearly related, and therefore u and v also. Thus the formula of Henderson holds for the diffusionpotential.

One must, however, raise serious objections to this opinion. The boundary is namely replaced by a series of solutions and consequently one is concerned with the sum of many small potentialdifferences. If the difference between the concentrations of these solutions is small, the potentialdifference concerned is also small, and it cannot differ much from Henderson's value. One should, however, choose the more terms, in proportion as one wishes to satisfy the condition better. And we have no reason at all, to suppose that the sum of these small potentialdifferences is exactly that of Henderson, for the errors too are added together.

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*) Notwithstanding our criticism of Taylor's treatment, it can readily be agreed that the possibility of writing $\epsilon\, n_1 n_2 \ldots\ldots$ as functions of y, is a very important principle, which is closely connected with the fact that the differential equations (38), when substituting $y = x/2\sqrt{t}$, reduce to:

$$\frac{-2y}{\lambda_i}\,\frac{dn_i}{dy} = \frac{d^2 n_i}{dy^2} + z_i\,\frac{d}{dy}\left(n_i\,\frac{d\Phi}{dy}\right),$$

which do not contain x or t explicitely. If it will be possible at all to demonstrate that L is independent of time, this demonstration probably will have to start from this principle.

15) E. A. Guggenheim, J. Am. Chem. Soc. **52**, 1315 (1930).

16) She so-called flowing junction where the two solutions flow along each other, is left out of consideration here (cf. page 76).

2. *Constrained diffusion junction.* The concentrations n_i are kept constant; the state is therefore stationary and the formula of Planck is valid. To realize this stationary state, Bjerrum [17]) proposed the use of membranes; along the outside of these membranes solutions of constant composition are made to flow.

3. *Free diffusion junction.* The solutions are brought into contact at time $t = 0$ in a plane $x = 0$; afterwards the ions diffuse in an undisturbed way. Of course one cannot entirely avoid a small mixing in the beginning, but in course of time the situation changes so that it looks as if one had started with a mathematical plane as boundary. It is the type of diffusion, to which Taylor's theory refers. Whereas from an experimental point of view this type has great advantage, and the concerning diffusionpotentials can be pretty well reproduced and are rather constant, the theory is as yet at an early stage.

B. THEORY FOR SMALL GRADIENT OF POTENTIAL.

We shall now examine, to what results the differential-equations lead when the gradients of potential and concentrations are supposed to be small. Motives are, in the first place the fact that the diffusion-potentials which occur, are as a rule rather small, and in the second place the reflection that, in the long run, the diffusionprocess will bring about a more and more flat slope of concentration. The results will then probably be best applicable to the so-called free diffusion, provided the process has been taking place for a long time; that means: a considerable time after both solutions have been brought into contact. For convenience' sake we shall write out the differential-equations once more.

$$(52) \quad . \quad . \quad . \quad . \quad \frac{1}{\lambda_i}\frac{\partial n_i}{\partial t} = \frac{\partial^2 n_i}{\partial x^2} + z_i \frac{\partial}{\partial x}\left(n_i \frac{\partial \Phi}{\partial x}\right)$$

$$(53) \quad . \quad . \quad . \quad . \quad \Sigma_i z_i n_i = 0$$

$$(54) \quad . \quad . \quad . \quad . \quad \frac{\partial u}{dx} + v\frac{\partial \Phi}{dx} = 0$$

Here λ_i is proportional to the mobility divided by the valency, Φ equals ε/kT times the electric potential; u and v are determined by (39) page 51.

The boundary conditions are:

$$\text{at } x = -\infty : n_i = c_i \quad \partial n_i/\partial x = 0 \quad \partial n_i/\partial t = 0 \quad \partial \Phi/\partial x = 0 \quad \Phi = 0$$

$$\text{at } x = +\infty : n_i = c_i' \quad \partial n_i/\partial x = 0 \quad \partial n_i/\partial t = 0 \quad \partial \Phi/\partial x = 0 \quad \Phi = \frac{\varepsilon}{kT} L$$

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[17]) N. Bjerrum, Z. physik. Chem. **53**, 428 (1905).

Differentiating (54) with respect to t, we find:

$$\frac{\partial^2 u}{\partial x \partial t} + \frac{\partial}{\partial t}\left(v\frac{\partial \Phi}{\partial x}\right) = 0,$$

which can be written in the form:

$$(55) \quad . \quad . \quad . \quad . \quad \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial t} + v\frac{\partial \Phi}{\partial t}\right) = \frac{\partial v}{\partial x}\frac{\partial \Phi}{\partial t} - \frac{\partial v}{\partial t}\frac{\partial \Phi}{\partial x}$$

The right hand member consist only of terms which are quadratic in the derivatives. The supposition, that these derivatives are small, may now be expressed in such a way, that the right hand member is neglected with regard to the left hand one.

So we have approximately:

$$\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial t} + v\frac{\partial \Phi}{\partial t}\right) = 0, \text{ or: } \frac{\partial u}{\partial t} + v\frac{\partial \Phi}{\partial t} = g(t)$$

Substituting the condition at the left hand boundary we find: $g(t) = 0$, in other words:

$$(56) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \frac{\partial u}{\partial t} + v\frac{\partial \Phi}{\partial t} = 0$$

From this equation we can immediately draw some important conclusions.

1. Substituting the condition at the right hand boundary, we find:

$$dL/dt = 0$$

In other words: the diffusionpotential remains constant in so far as our approximations hold.

2. From (54) and (56) taken together one can conclude, that u and v can be written as functions of Φ (and conversely) or also: u as a function of v. And the following relation holds for these quantities:

$$du = -v d\Phi.$$

So we know, that there exists a relation between u and v, which does not contain x or t explicitly. If we knew this relation, we could calculate the diffusionpotential by a simple integration. In the special case, that u and v are related by a linear equation, the formula of Henderson is found.

3. In consequence of the result thus obtained, the right hand member in (55) is not only small, but even zero. For this right hand member is nothing but the functional determinant $(v\Phi, xt)$. This result is not immediately evident, for the boundaryconditions were needed to arrive at it. We did not equate this right hand member to zero, but only neglected it with regard to the left hand one; and (56) could

only be arrived at afterwards by making use of the boundary-conditions. In the meantime one must not forget that all this is only a consequence of the proposed approximation. It is therefore only approximately true that $u(v)$ does not contain x or t explicitly. In other words: when x and t are changed, the functional relation $u = u(v)$ remains nearly the same.

4. From the fact that a functional relation $\Phi = \Phi(u)$ exists, one would be inclined to conclude, that the diffusionpotential L is not altered, when a third solution is added between two original ones. For one would think it does not matter how the value of u is arrived at Φ must always be determined by $\Phi(u)$. (The case that $\Phi(u)$ is a many valued function may be left out of consideration). One must, however, not forget that $\Phi(u)$ can contain the boundary-conditions. We may write $\Phi = \Phi(u, c', c)$, where c is an abbrevation for $c_2, c_1, \ldots.$ etc., c_i being the concentration of the i'th ion at the left ($-\infty$) and c'_i this concentration at the right hand side ($+\infty$). Conforming to this, we may write $L(c', c)$, for the diffusionpotential, so that:

$$L(c', c) = \Phi(U', c', c) - \Phi(U, c', c)$$

for U is the value of u at $-\infty$, U' is its value at $+\infty$. If we now add a third solution (with concentrations c''_i) between the original ones, we have to deal with the sum of two diffusionpotentials $L(c'', c)$ and $L(c', c'')$, and this sum need not be equal to $L(c', c)$.

5. Some special attention may be paid to the case of three ions, that is: two electrolytes with a common ion. In this case we have:

$$\begin{aligned} z_1 n_1 + z_2 n_2 + z_3 n_3 &= 0 \\ z_1 \lambda_1 n_1 + z_2 \lambda_2 n_2 + z_3 \lambda_3 n_3 &= u \\ z_1^2 \lambda_1 n_1 + z^2{}_2 \lambda_2 n_2 + z^2{}_3 \lambda_3 n_3 &= v \end{aligned}$$

From these three equations $n_1 n_2 n_3$ can be found as linear functions of u and v. If it is true that both u and v can be written as functions of Φ, it follows than all n_i can be regarded as functions of Φ, and vice versa. From this general conclusion we can deduce some particular properties of the diffusion layer. It means i. e. that several (at least two) extrema must occur in Φ after some time.

For definiteness, the concentration n_1 may be larger at $-\infty$ than at $+\infty$, n_2 however larger in $+\infty$ than in $-\infty$. No matter how the diffusion takes place, the result will be at all events, that a given concentration n_1 is found farther to the right after some time, and a given concentration n_2 farther to the left.

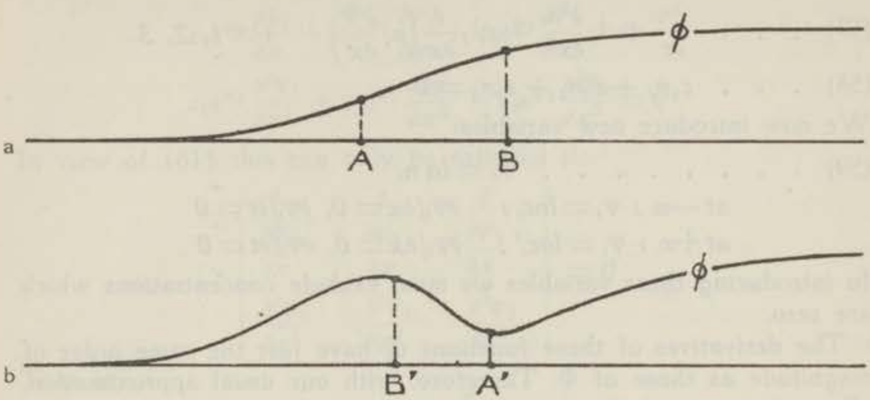

Fig. 6.

Suppose Φ has a form like fig. 6a, without a maximum or a minimum. When after some time the concentration $n_1(A)$ is now found in A', the value $\Phi(A)$ must also be found in A', because Φ can be written as a function of n_1. A similar consideration holds for the concentration $n_2(B)$. Obviously Φ must show a maximum and a minimum. On account of the equation: $\partial n_i/\partial x = dn_i/d\Phi \,.\, \partial\Phi/\partial x$, the concentrations too show an extremum, unless by coincidence $d\Phi/dn_i = 0$. So it appears, that the diffusion soon offers a rather irregular picture: the concentrations do not remain monotonic in x. And the direction, in which an ion of a given species moves at a given time, need neither be the same for all x. Temporary accumulations of some ionspecies can occur, which will disappear afterwards. And, of course, it can be expected, that these considerations are all the more effectual in the case of more than three ions.

For the special case of two electrolytes with a common ion, — provided the concentration of this ion is the same at $-\infty$ as at $+\infty$ —, Planck[18]) and Taylor[19]) already predicted these extrema. Plettig[20]) also calculated from Planck's theory, that the concentration of the chlorine-ions shows a maximum when 0.01 N. HCl diffuses into 0.1 N. KCl.

C. "LOGARITHMIC" SOLUTION FOR THREE IONS.

I. Simplification of the equations.

For three ions, that is two electrolytes with a common ion, one has:

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[18]) cf. [4]).

[19]) cf. [13]).

[20]) cf [7]).

$$(57)\quad \dots \quad \frac{\partial n_i}{\partial t} = \lambda_i \frac{\partial^2 n_i}{\partial x^2} + z_i \lambda_i \frac{\partial}{\partial x}\left(n_i \frac{\partial \Phi}{\partial x}\right) \qquad i = 1,\ 2,\ 3.$$

$$(58)\quad \dots \quad z_1 n_1 + z_2 n_2 + z_3 n_3 = 0$$

We now introduce new variables:

$$(59)\quad \dots\dots\dots \quad \varphi_i = \ln n_i$$

$$\text{at} -\infty : \varphi_i = \ln c_i ; \quad \partial\varphi_i/\partial x = 0,\ \partial\varphi_i/\partial t = 0$$

$$\text{at} +\infty : \varphi_i = \ln c_i' ; \quad \partial\varphi_i/\partial x = 0,\ \partial\varphi_i/\partial t = 0$$

In introducing these variables we must exclude concentrations which are zero.

The derivatives of these functions φ_i have just the same order of magnitude as those of Φ. Therefore, with our usual approximation, all expressions which are quadratic in these derivatives, can be neglected compared with these derivatives themselves. From a physical point of view this approximation is based on the same assumption as that on which we based our calculations on page 59, i. e. the assumption that the gradients of concentrations and potential are small. This does not involve, however, that both approximations are entirely equivalent. For on page 59 we started from the equation (54):

$$\partial u/\partial x + v\partial\Phi/\partial x = 0,$$

while here all equations of motion are approximated separately.

Dividing (57) by n_i we get:

$$\frac{1}{n_i}\frac{\partial n_i}{\partial t} = \frac{\lambda_i}{n_i}\frac{\partial^2 n_i}{\partial x^2} + z_i\lambda_i\left(\frac{1}{n_i}\frac{\partial n_i}{\partial x}\frac{\partial \Phi}{\partial x} + \frac{\partial^2 \Phi}{\partial x^2}\right)$$

which can easily be reduced to:

$$\frac{\partial \varphi_i}{\partial t} = \lambda_i \frac{\partial^2 \varphi_i}{\partial x^2} + z_i\lambda_i \frac{\partial^2 \Phi}{\partial x^2} + \lambda_i \left(\frac{\partial \varphi_i}{\partial x}\right)^2 + z_i\lambda_i \frac{\partial \varphi_i}{\partial x}\frac{\partial \Phi}{\partial x}\,.$$

Here the two last terms are quadratic while the remaining terms are linear. Therefore approximately:

$$(60)\quad \dots\dots \quad \frac{\partial \varphi_i}{\partial t} = \lambda_i \frac{\partial^2 \varphi_i}{\partial x^2} + z_i\lambda_i \frac{\partial^2 \Phi}{\partial x_2}\,.$$

Compared with (57) these equations have the great advantage that they are linear and homogeneous in $\varphi_1\varphi_2\varphi_3\Phi$. A disadvantage, however, is that now (58) takes the form:

$$(61)\quad \dots\dots \quad z_1 e^{\varphi_1} + z_2 e^{\varphi_2} + z_3 e^{\varphi_3} = 0$$

Therefore we wish to replace this latter equation by another, which is approximately equivalent to it. To that end we differentiate (61) two times with respect to x, neglecting $(\partial\varphi/\partial x)^2$ with regard to $\partial^2\varphi/\partial x^2$. So we find:

$$z_1 e^{\varphi_1} \frac{\partial \varphi_1}{\partial x} + z_2 e^{\varphi_2} \frac{\partial \varphi_2}{\partial x} + z_3 e^{\varphi_3} \frac{\partial \varphi_3}{\partial x} = 0$$

$$z_1 e^{\varphi_1} \frac{\partial^2 \varphi_1}{\partial x^2} + z_2 e^{\varphi_2} \frac{\partial^2 \varphi_2}{\partial x^2} + z_3 e^{\varphi_3} \frac{\partial^2 \varphi_3}{\partial x^2} = 0$$

In view of (61) this can only be satisfied if:

$$\begin{vmatrix} 1 & 1 & 1 \\ \frac{\partial \varphi_1}{\partial x} & \frac{\partial \varphi_2}{\partial x} & \frac{\partial \varphi_3}{\partial x} \\ \frac{\partial^2 \varphi_1}{\partial x^2} & \frac{\partial^2 \varphi_2}{\partial x^2} & \frac{\partial^2 \varphi_3}{\partial x^2} \end{vmatrix} = 0$$

That is:

$$\frac{\partial(\varphi_1 - \varphi_3)}{\partial x} \cdot \frac{\partial^2(\varphi_2 - \varphi_3)}{\partial x^2} = \frac{\partial(\varphi_2 - \varphi_3)}{\partial x} \cdot \frac{\partial^2(\varphi_1 - \varphi_3)}{\partial x^2}$$

And by integrating: $\varphi_1 - \varphi_3 = \alpha(t) \cdot (\varphi_2 - \varphi_3) + \beta(t)$.
This can be written in a symmetric form:

(62) . . . . . $A_1\varphi_1 + A_2\varphi_2 + A_3\varphi_3 = K$.

(63) provided $A_1 + A_2 + A_3 = 0$.

According to this deduction the quantities $A_1 A_2 A_3 K$ might depend on *t*. It will, however, be proved that this is not the case. *K* is determined directly by means of the boundary-condition at the left hand side:

(64) . . . . . $K = A_1 lnc_1 + A_2 lnc_2 + A_3 lnc_3$

A similar condition can, however, be deduced from the other boundary-condition, and therefore the numbers A_i must satisfy the condition:

$$\Sigma_i A_i lnc_i = \Sigma_i A_i lnc_i'$$

Henceforth we abbreviate:

(65) . . . . $\Theta_i = ln\, c_i / c_i'$

And so we have for A_i:

(66) . . . . . $A_1\Theta_1 + A_2\Theta_2 + A_3\Theta_3 = 0$.

Together with (63) this suffices for the calculation of the ratio of the numbers A_i, and apparently these ratios do not depend on *t*. If, however, all A_i are proportional to one and the same function of *t*, *K* is also proportional to it (on account of 64), and therefore we can divide (64) by this function, the result being that there remain numbers A_i, *K*, which do not depend on *t*.

As only the ratios matter, we write:

(67) . . . $A_1 = \Theta_2 - \Theta_3 \quad A_2 = \Theta_3 - \Theta_1 \quad A_3 = \Theta_1 - \Theta_2$

II. Expression for the diffusionpotential.

With the aid of (62) we easily deduce from (60):

$$\Sigma_i \lambda_i A_i \frac{\partial^2 \varphi_i}{\partial x^2} + \Sigma_i z_i \lambda_i A_i \frac{\partial^2 \Phi}{\partial x^2} = 0.$$

Integrating, and taking into account the boundary-conditions:

$$\Phi = \frac{1}{\Sigma_i z_i^2 \lambda_i A_i} \left\{ \Sigma_i \lambda_i A_i \ln c_i - \Sigma_i \lambda_i A_i \varphi_i \right\}$$

Using (65) and remembering (35, page 50) we then find for the diffusionpotential:

$$(68) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad L = \frac{kT}{\varepsilon} \frac{\Sigma_i \lambda_i A_i \Theta_i}{\Sigma_i z_i \lambda_i A_i}$$

We shall postpone the discussion of this expression for L and first proceed with the equations of motion.

III. Further examination of the differential equations.

For convenience' sake we introduce the symbols:

$$D = \frac{\partial}{\partial x} \qquad D' = \frac{\partial}{\partial t}$$

The equations (60) then run:

$$(D' - \lambda_i D^2) \varphi_i = z_i \lambda_i D^2 \Phi$$

Henceforth we shall apply the notation which is usual in the theory of symmetric functions. So an expression like $\Sigma z_1 \lambda_1$ stands for $z_1\lambda_1 + z_2\lambda_2 + z_3\lambda_3$, $\Sigma z_1\lambda_2\lambda_3$ for $z_1\lambda_2\lambda_3 + z_2\lambda_3\lambda_1 + z_3\lambda_1\lambda_2$, and so on. Then, with the aid of (62) we can deduce the following differential equation for Φ:

$$(69) \quad . \; . \; . \; . \quad \Sigma z_1 \lambda_1 A_1 (D' - \lambda_2 D^2)(D' - \lambda_3 D^2) D^2 \Phi = 0.$$

We abbreviate:

$$(70) \quad . \; . \; P = \Sigma z_1 \lambda_1 A_1 \qquad Q = \Sigma z_1 \lambda_1 (\lambda_2 + \lambda_3) A_1 \qquad R = \Sigma z_1 \lambda_1 \lambda_2 \lambda_3 A_1$$

and can therefore write (69) in the form:

$$(PD'^2 - QD'D^2 + RD^4) D^2 \Phi = 0.$$

We now integrate twice with respect to x, taking into account the fact that Φ = constant = 0 at $-\infty$, and find:

$$(PD'^2 - QD'D^2 + RD^4) \Phi = 0.$$

In non-symbolic notation:

$$(71) \quad . \; . \; . \; . \quad P \frac{\partial^2 \Phi}{\partial t^2} - Q \frac{\partial^3 \Phi}{\partial t \, \partial x^2} + R \frac{\partial^4 \Phi}{\partial x^4} = 0$$

If α and β are the roots of the quadratic equation:

$$72) \quad . \; . \; . \; . \; . \; . \; . \quad Ps^2 - Qs + R = 0,$$

we can also write:

(73) . . . . $(D' - \alpha D^2)(D' - \beta D^2)\Phi = 0$

If we apply this result to the equations of motion $(D' - \lambda_i D^2)\varphi_i = z_i \lambda_i D^2 \Phi$, we find:

(74) . . . $(D' - \lambda_i D^2)(D' - \alpha D^2)(D' - \beta D^2)\varphi_i = 0.$

The solution of (74) is a sum of the solutions of the following three equations:

$$(D' - \lambda_i D^2)\varphi_i = 0 \quad (D' - \alpha D^2)\varphi_i = 0 \quad (D' - \beta D^2)\varphi_i = 0.$$

As to the solutions of the first of these three equations, only the trivial solution φ_i = constant can be used, because the functions φ_i must satisfy (62). This can readily be seen if one writes down the solutions of $(D' - \lambda_i D^2)\varphi_i = 0$ in the form $exp(px + \lambda_i p^2 t)$. It is, of course, impossible that an expression of the form:

$$\Sigma_i \Sigma_p a_i(p) \,.\, exp\,(px + \lambda_i p^2 t)$$

would disappear for all x and t, unless all a_i are zero. Only in the special case that two "mobilities" λ_i are equal, does this break down. This case will therefore be discussed seperately.

So one can conclude that each of the functions $\varphi_1 \varphi_2 \varphi_3 \Phi$ "diffuses" according to (73). The whole motion is a superposition of two diffusions, one with a diffusion-coefficient α and the other with a diffusion-coefficient β. These α and β are the roots of the quadratic equation (72), and thus, on account of (70), functions of the ratios between the numbers A_i. According to (63) and (66) these ratios are, however, determined by the boundary-conditions.

IV. The case $\lambda_1 = \lambda_2 = \lambda$.

As has already been said, the theory must be modified, when two of the λ_i are equal. For instance $\lambda_1 = \lambda_2 = \lambda$.

We need not take into consideration, the case that they are also equal to λ_3, for in that case we have in (40) page 51 : $u = 0$, and thus $\Phi = 0$; and all ions diffuse as if they were uncharged.

Now write μ for the third "mobility" $\lambda_3 (\mu \neq \lambda)$. The equations of motion become:

$$(D' - \lambda D^2)\varphi_1 = z_1 \lambda D^2 \Phi$$
$$(D' - \lambda D^2)\varphi_2 = z_2 \lambda D^2 \Phi$$
$$(D' - \mu D^2)\varphi_3 = z_3 \mu D^2 \Phi$$

With the aid of (62) one can easily deduce:

$$(D' - \sigma D^2)\Phi = 0 \qquad (D' - \lambda D^2)(D' - \sigma D^2)\varphi_1 = 0$$
$$(D' - \lambda D^2)(D' - \sigma D^2)\varphi_2 = 0 \quad (D' - \mu D^2)(D' - \sigma D^2)\varphi_3 = 0$$

Here:

$$\sigma = \frac{(z_1A_1 + z_2A_2 + z_3A_3)\lambda\mu}{(z_1A_1 + z_2A_2)\lambda + z_3A_3\mu}$$

Now, by a similar consideration as mentioned before it is easily understood that φ_3 and Φ carry out a "simple diffusion" with diffusioncoefficient σ while the diffusion of φ_1 and φ_2 is a superposition of two diffusions with diffusion-coefficients λ and σ. For again the solutions of $(D' - \mu D_2)\varphi_3 = 0$ cannot be used, because they can never satisfy (62). Not so the solutions of

$$(D' - \lambda D_2)\varphi_1 = 0 \text{ and } (D' - \lambda D_2)\varphi_2 = 0,$$

provided one takes care that these solutions satisfy the condition: $A_1\varphi_1 + A_2\varphi_2 = 0$.

We can easily indicate the physical meaning of this result. Suppose first that $z_1 = z_2 = z$. As far as the electrolytic diffusion is concerned, the ions 1 and 2 do not differ in this case. As $A_1 + A_2 = -A_3$, we find:

$$\sigma = \frac{(z_3 - z)A_3\lambda\mu}{-zA_3\lambda + z_3A_3\mu} = \frac{(w_1 + w_3)\,\lambda\mu}{w_2\lambda + w_3\mu}$$

Here the valencies $w = |z|$ have been introduced. Obviously σ is nothing but Nernst's diffusioncoefficient (page 27) for the electrolyte [1.3] or [2.3]. In other words: we have a superposition of two diffusions, the first is an ordinary Nernst diffusion, the other is a diffusion with diffusion-coefficient λ, which means nothing but a continual exchange of ions 1 and 2, which can take place because they do not differ from the point of view of electrolytic diffusion. When z_1 and z_2 are different, this exchange remains possible provided the ions 3 take part in it. Therefore σ is no longer equal to the Nernst diffusion-coefficient, while nevertheless Φ is uneffected by this exchange and "diffuses" with the diffusion-coefficient σ only.

V. The case of a single electrolyte viewed in retrospect.

The theory of the diffusion of three ions, developed in this dissertation makes use of two different approximations. The first replaces (57) by (60); the other (58) by (62, 63). Both make use of the supposition that the gradients of potential and concentrations are small. If there are only two ion species, we can again approximate (57) by (60), and find:

$$(75) \quad \ldots\ldots \quad \left\{ \begin{aligned} \frac{\partial\varphi_1}{\partial t} &= \lambda_1 \frac{\partial^2\varphi_1}{\partial x^2} + z_1\lambda_1 \frac{\partial^2\Phi}{\partial x^2} \\ \frac{\partial\varphi_2}{\partial t} &= \lambda_2 \frac{\partial^2\varphi_2}{\partial x^2} + z_2\,\lambda_2 \frac{\partial^2\Phi}{\partial x^2} \end{aligned} \right.$$

The condition (62, 63) can here be written:

(76) . . . . $\varphi_1 = \varphi_2 + K$

In this case, however, (76) is not an approximation for (58), but exactly the same equation in another form. With the aid of (76) we easily deduce from (75):

$$\Phi = -\frac{\lambda_1 - \lambda_2}{z_1\lambda_1 - z_2\lambda_2}(\varphi_2 - \ln c_1)$$

This is nothing but Nernst's equation for the diffusionpotential. Apparently the approximation (75) doet not change this result in the case of a single electrolyte.

On the other hand, eliminating Φ, one finds:

$$\frac{\partial \varphi_1}{\partial t} = \frac{z_2 - z_1}{z_2\lambda_2 - z_1\lambda_1}\lambda_1\lambda_2 \cdot \frac{\partial^2 \varphi_1}{\partial^2 x_1}$$

This is an equation of diffusion for the logarithm of the concentration instead of the concentration itself. The meaning of this approximation, which replaces the concentration by its logarithm, will now be submitted to a closer investigation.

VI. The replacement of the concentration by its logarithm.

An equation of diffusion

$$\frac{\partial n}{\partial t} = \mathfrak{D}\frac{\partial^2 n}{\partial x^2}$$

can be reduced to the form:

(77) . . . . $\dfrac{\partial n}{\partial t} = \dfrac{\partial^2 n}{\partial x^2}$

by a convenient choice of the independent variables, e.g. by introducing a new variable $t' = Dt$. If $u(x, 0)$ is the initial distribution, the solution of (77) runs:

(78) . . . . $n(x,t) = \dfrac{1}{\sqrt{\pi}}\displaystyle\int_{-\infty}^{\infty} u(x + 2\omega\sqrt{t}, 0)\, e^{-\omega^2}\, d\omega.$

In particular, when $u(x, 0) = p$ for $-\infty < x < o$ and $u(x, o) = q$ for $o < x < \infty$ one finds:

$$n(x,t) = \frac{q+p}{2} + \frac{q-p}{\sqrt{\pi}}\int_{o}^{x/2\sqrt{t}} e^{-\omega^2}\, d\omega$$

Henceforth we abbreviate:

$$\chi(\xi) = \frac{2}{\sqrt{\pi}}\int_{o}^{\xi} e^{-\omega^2}\, d\omega$$

And so:

$$(79) \quad . \quad . \quad . \quad n(x,t) = {}^1/_2\,(q+p) + {}^1/_2\,(q-p)\,\chi\,(x/2\sqrt{t})$$

If now a new variable $\varphi = ln\ n$ is introduced, one finds instead of (77):

$$\frac{\partial\varphi}{\partial t} = \frac{\partial^2\varphi}{\partial x^2} + \left(\frac{\partial\varphi}{\partial x}\right)^2$$

With the approximation for small concentration-gradient, which has been proposed in this dissertation, this becomes:

$$(80) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \frac{\partial\varphi}{\partial t} = \frac{\partial^2\varphi}{\partial x^2},$$

which has entirely the same form as (77).

Now we also wish to compare the *integral* of (80) with that of (77), and want to prove that both integrals practically lead to the same result if the circumstances are chosen appropiately. This demonstration cannot be regarded as superfluous, for even if (80) represents a good approximation of (77), one should not forget that the interval of integration where this approximation is applied, is extended from $x = -\infty$ to $x = +\infty$. Moreover, there are certainly points where the approximation (80) is bad, namely those points where $\partial^2\varphi/\partial x^2$ is zero or does not differ much from zero. Now we must take into account that (80) represents an approximation for small concentration-gradient. Therefore, we must choose an initial distribution which satisfies this condition. In that case we can prove that the integral of (80) represents an approximation to the integral of (77), for times which are not too large.

Now the original distribution which is easiest and most plausible, is the one which has come into existence by bringing two solutions with concentrations p and q into contact. Suppose therefore, that this diffusionprocess has begun at time $-\ t_0$. The distribution at time $t = 0$ is then determined by (79):

$$(81) \quad . \quad . \quad . \quad n(x,o) = {}^1/_2\,(q+p) + {}^1/_2\,(q-p)\,\chi\left(\frac{x}{2\sqrt{t_0}}\right)$$

So that:

$$(82) \quad . \quad . \quad . \quad \varphi(x,o) = ln\left[\frac{q+p}{2} + \frac{q-p}{2}\,\chi\left(\frac{x}{2\sqrt{t_0}}\right)\right]$$

t_0 is supposed to be large so as to guarantee a small concentration-gradient. Now it can be proved that the integral of (80) which satisfies the condition (82), is indeed an approximation to the integral of (77) which satisfies the condition (81), provided one restricts oneself to times which are small compared with t_0.

If one substitutes the expression (81) for $n(x, o)$ in (78), the solution of (77) becomes:

$$n(x,t) = \frac{q+p}{2} + \frac{q-p}{2\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\omega^2}\, \chi\left(\frac{x + 2\,\omega\sqrt{t}}{2\sqrt{t_0}}\right) . \, d\omega$$

As, however, $n(x,t)$ has come into existence by means of a diffusion during the time $t_0 + t$, after the solutions with concentrations p and q have been brought into contact, one also has:

$$n(x,t) = \frac{q+p}{2} + \frac{q-p}{2}\, \chi\left(\frac{x}{2\sqrt{t_0+t}}\right)$$

This yields a relation which shall be used later:

$$(83) \quad . \quad . \quad \int_{-\infty}^{\infty} e^{-\omega^2}\, \chi\left(\frac{x + 2\,\omega\sqrt{t}}{2\sqrt{t_0}}\right) . \, d\omega = \sqrt{\pi} \, . \, \chi\left(\frac{x}{2\sqrt{t_0+t}}\right)$$

On the other hand the solution of (80) runs:

$$\varphi(x,t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} ln\left[\frac{q+p}{2} + \frac{q-p}{2}\, \chi\left(\frac{x + 2\,\omega\sqrt{t}}{2\sqrt{t_0}}\right)\right] . \, e^{-\omega^2} . \, d\omega$$

As t is here small compared with t_0, $\omega\sqrt{t/t_0}$ can only differ much from zero when ω is large. On account, however, of $e^{-\omega^2}$ in the integrand, such terms practically do not count. Therefore, when we write

$$\chi\left(\frac{x + 2\,\omega\sqrt{t}}{2\sqrt{t_0}}\right) = \chi\left(\frac{x}{2\sqrt{t_0}}\right) + s(\omega)$$

we are only concerned with small absolute values of s, an approximation which is allowed because $e^{-\omega^2}$ very rapidly becomes zero when ω increases. Now expanding the logarithm under the integral-sign in powers of s and breaking off after the first power, we find:

$$\varphi(x,t) = ln\left[\frac{q+p}{2} + \frac{q-p}{2}\, \chi\left(\frac{x}{2\sqrt{t_0}}\right)\right] + \frac{\dfrac{q-p}{2\sqrt{\pi}}}{\dfrac{q+p}{2} + \dfrac{q-p}{2}\, \chi\left(\dfrac{x}{2\sqrt{t_0}}\right)} \int_{\infty}^{\infty} s(\omega) e^{-\omega^2} d\omega.$$

On account of the definition of s we have:

$$\int_{-\infty}^{\infty} s(\omega)\, e^{-\omega^2}\, d\omega = \int_{-\infty}^{\infty} e^{-\omega^2}\, \chi\left(\frac{x + 2\,\omega\sqrt{t}}{2\sqrt{t_0}}\right) d\omega - \sqrt{\pi} . \chi\left(\frac{x}{2\sqrt{t_0}}\right).$$

With the aid of (83) this can be reduced to:

$$\sqrt{\pi} . \chi\left(\frac{x}{2\sqrt{t_0+t}}\right) - \sqrt{\pi} . \chi\left(\frac{x}{2\sqrt{t_0}}\right).$$

Finally we get:

$$\varphi(x,t) = \ln\left[\frac{q+p}{2} + \frac{q-p}{2}\,\chi\left(\frac{x}{2\sqrt{t_0}}\right)\right] + \frac{q-p}{2}\cdot\frac{\chi\left(\frac{x}{2\sqrt{t_0+t}}\right) - \chi\left(\frac{x}{2\sqrt{t_0}}\right)}{\frac{q+p}{2} + \frac{q-p}{2}\,\chi\left(\frac{x}{2\sqrt{t_0}}\right)}$$

The numerator of the last term is small, and therefore, calculating e^{φ}, one can expand to powers of this numerator. This leads to:

$$n = e^{\varphi} = \frac{q+p}{2} + \frac{q-p}{2}\,\chi\left(\frac{x}{2\sqrt{t_0+t}}\right).$$

This, however, agrees exactly with the solution of (77).

VII. The diffusionpotential.

We shall now discuss the expression (68) for the diffusionpotential. Substituting the values (67) for the numbers A_i, we find:

$$(84)\ L = -\frac{kT}{\varepsilon}\cdot\frac{(\lambda_2-\lambda_3)\,\Theta_2\Theta_3 + (\lambda_3-\lambda_1)\,\Theta_3\Theta_1 + (\lambda_1-\lambda_2)\,\Theta_1\Theta_2}{(z_2\lambda_2 - z_3\lambda_3)\,\Theta_1 + (z_3\lambda_3 - z_1\lambda_1)\,\Theta_2 + (z_1\lambda_1 - z_2\lambda_2)\Theta_3}$$

In discussing this formula one must always bear in mind that the quantities $\Theta_1\Theta_2\Theta_3$ are connected with each other. For one has:

$$\Sigma_i z_i c_i = 0 \qquad and \qquad \Sigma_i z_i c_i' = 0.$$

Some particular properties of the formula (84) shall now be examined in detail.

a. When the concentration-ratios c_i/c'_i are the same for all ions, one has: $\Theta_1 = \Theta_2 = \Theta_3 = \Theta$. In that case the expression (84) for L becomes indefinite. This is connected with the fact that the condition (66) page 63 for the numbers A_i becomes identical with (63), so that these numbers remain undetermined. Nevertheless one can easily ascertain to what limit L approaches when the concentration-ratios become equal to each other.

Suppose at the right hand side: $n_1 = c'_1$, $n_2 = c'_2$. This determines n_3 to $c'_3 = -1/z_3(z_1c'_1 + z_2c'_2)$. The fact that the proportions c_i/c'_i are nearly equal, can be expressed in the following general way: At the left hand side: $n_1 = c_1 = \alpha c'_1$; $n_2 = c_2 = (1+p)\alpha c'_2$; p *small*, and thus $n_3 = c_3 = -\alpha/z_3[z_1c'_1 + (1+p)z_2c'_2]$. If we neglect powers of p, higher than the first, we find:

$$\Theta_1 = \ln c_1/c_1' = \ln\alpha$$
$$\Theta_2 = \ln c_2/c_2' = \ln\alpha + p$$
$$\Theta_3 = \ln c_3/c_3' = \ln\alpha + p\,\frac{z_2c_2'}{z_1c_1' + z_2c_2'}$$

Substituting in (84), and again neglecting all powers of p except the first, we find:

$$L = kT/\varepsilon \,.\, ln\, \alpha \,.\, \frac{(\lambda_1 - \lambda_3)z_1c_1' + (\lambda_2 - \lambda_3)z_2c_2'}{(z_1\lambda_1 - z_3\lambda_3)z_1c_1' + (z_2\lambda_2 - z_3\lambda_3)z_2c_2'}$$

This can also be written:

$$L = kT/\varepsilon \,.\, ln\, \alpha \,.\, \frac{z_1\lambda_1c_1' + z_2\lambda_2c_2' + z_3\lambda_3c_3'}{z_1^2\lambda_1c_1' + z_2^2\lambda_2c_2' + z_3^2\lambda_3c_3'}$$

This is exactly the same expression as yielded by the formula of Henderson (page 52) in this case. Moreover, Planck's formula (42, page 53) yields the same result here.

b. It is, of course, impossible that the diffusionpotential should be considerably altered if a very small number of ions in a single electrolyte is replaced by a third species. Yet c/c' can differ considerably from unity while n is small. And to all appearances the formula (84) would lead to entirely wrong conclusions.

We meet this circumstance, for instance, in the diffusion of an acid in water. Besides the ions H and Z of the acid there are also OH-ions. And, when e. g. the acid-concentration on the left is ten times as large as that on the right, the OH-ion-concentration on the left is about ten times as small as that on the right, owing to mass-acion. We have something similar in the case of the diffusion of a base. Therefore, we must prove that the formula (84) reduces in such cases to the formula of Nernst for two ions.

Suppose at $-\infty : n_1 = c \quad n_2 = pc$ (p very small)

$$n_3 = -1/z_3 \,.\, (z_1 + pz_2)c.$$

at $+\infty : n_1 = c' \quad n_2 = qc'$ (q very small)

$$n_3 = -1/z_3 \,.\, (z_1 + pz_2)c'.$$

As p and q are small, Θ_3 and Θ_1 practically become equal to $ln\, c/c'$. So:

$$L = \frac{kT}{\varepsilon}\frac{(\lambda_1 - \lambda_3)(\Theta_2 - \Theta_1)\,\Theta_1}{(z_1\lambda_1 - z_3\lambda_3)(\Theta_2 - \Theta_1)} = \frac{kT}{\varepsilon}\frac{\lambda_1 - \lambda_3}{z_1\lambda_1 - z_3\lambda_3}\, ln\, \frac{c}{c'},\ \text{q. e. d.}$$

c. Finally one might wonder if the denominator in (84) can become zero. It can, however, easily be proved that this denominator can only be zero when $\Theta_1 = \Theta_2 = \Theta_3$, a case which has already been discussed. To prove this, we have only to reduce this denominator to a slightly different expression. We shall assume that two of the three ions (e. g. 1 and 2) have a positive charge, the third ion a negative. This does not impose any restriction, for L only changes its sign when z_1 and z_2 are supposed negative and z_3 positive. We have:

$$\Theta_1 = ln\, c_1/c_1' \qquad \Theta_2 = ln\, c_2/c_2' \qquad \Theta_3 = ln\, \frac{z_1c_1 + z_2c_2}{z_1c_1' + z_2c_2'}$$

And we notice that all three Θ_i must equal each other as soon as two of them do so. We can reduce the denominator of (84) to

$$N = (z_1\lambda_1 - z_3\lambda_3)\, ln\, \frac{c_1}{c_1'}\, \frac{c_2'}{c_2} + (z_1\lambda_1 - z_2\lambda_2)\, ln\, \frac{z_1 + z_2 \,.\, c_2/c_1}{z_1 + z_2 \,.\, c_2'/c_1'}$$

If now we introduce the symbols:

$$\varrho = \frac{c_1}{c_2} \qquad \sigma = \frac{c_1'}{c_2'}$$

N becomes:

$$N = (z_2\lambda_2 - z_3\lambda_3)\, ln\, \frac{\varrho}{\sigma} + (z_1\lambda_1 - z_2\lambda_2)\, ln\, \frac{z_1\varrho + z_2}{z_1\sigma + z_2}$$

This is zero for $\varrho = \sigma$. In that case, however, $\Theta_1 = \Theta_2$ and so equal to Θ_3. Therefore we only need to prove that *N* cannot become zero unless $\varrho = \sigma$. If we define the function

$$f(x) = (z_2\lambda_2 - z_3\lambda_3) lnx + (z_1\lambda_1 - z_2\lambda_2) ln(z_1x + z_2)$$

we have: $N = f(\varrho) - f(\sigma)$, and it can easily be shown that $f(x)$ cannot have the same value for two different values of *x*. This is evident from the fact that $f(x)$ is a monotonic function as long as *x* is positive (and negative *x* need not be taken into account). In fact we have: $f'(x) = (z_2\lambda_2 - z_3\lambda_3)/x + z_1\lambda_1 - z_2\lambda_2)/(z_1x + z_2)$. This expression vanishes only when $x = -z_2(z_2\lambda_2 - z_3\lambda_3)/z_1\,(z_1\lambda_1 - z_3\lambda_3)$. As, however, z_1 and z_2 are supposed to be positive and z_3 negative, this value of *x* is negative. Negative *x* having no physical meaning, it follows that $f'(x)$ has always the same sign, in other words: $f(x)$ is monotonic, q.e.d.

VIII. Calculation of the diffusion-coefficients α, β (σ).

It may be demonstrated by some examples that the theory leads to plausible values for the diffusion-coefficients α and β (or σ in the case that two λ_i are equal). We need no absolute values for these diffusion-coefficients; it will suffice if we compare them with the quantities λ_i, and therefore we shall simply write the mobility divided by the valency for these λ_i (compare page 58).

a. A mixture of HCl and NaCl in water at 25°. Mobilities: $l_H = 350$; $l_{Cl} = 76.3$; $l_{Na} = 50.1$. Suppose to simplify calculations, that the concentration of the Cl-ions at the left hand side is the same as at the right hand side. For instance on the left: $c_H = a$, $c_{Na} = b$, $c_{Cl} = a + b$. On the right $c_H = b$, $c_{Na} = a$, $c_{Cl} = a + b$. Thus: $\Theta_1 = ln\, a/b$; $\Theta_2 = ln\, b/a$; $\Theta_3 = 0$. The numbers A_i become (as only the ratio is important):

$$A_1 = 1 \qquad A_2 = 1 \qquad A_3 = -2.$$

In the quadratic equation $Ps^2 - Qs + R = 0$; $P = 552.7$; $Q = 126652$; $R = 5351700$. And therefore $\alpha = 173.3$; $\beta = 55.9$.

In pure HCl the diffusion-coefficient, if expressed in units of mobility, would have been (23, page 27):

$$\frac{l_H \, l_{Cl}}{l_H + l_{Cl}} = 125.3$$

and, in the same way, in pure NaCl: 60.5. So we have the very plausible, and even symmetric, sequence

Na	mixture	NaCl	Cl	HCl	mixture	H
50.1	$\beta = 55.9$	60.5	76.3	125.3	$\alpha = 173.3$	350

b. If a small amount of the ion 1 in an electrolyte [1.3] is replaced by the ion 2, the diffusion-coefficient must be approximately equal to

$$\frac{w_1 + w_3}{w_1\lambda_1 + w_3\lambda_3} \lambda_1\lambda_3$$

Here one hase: on the left $n_1 = c \quad n_2 = pc$ (p very small)
on the right $n_1 = c' \quad n_2 = qc'$ (q very small)

And so:

$$\Theta_1 = \ln c/c' \qquad \Theta_2 = \ln c/c' + \ln p/q \qquad \Theta_3 \cong \ln c/c'$$

Therefore the numbers A_i become: $A_1 \cong 1$, $A_2 \cong 0$, $A_3 = -1$.

For the coefficients P, Q, R we find:

$$P = z_1\lambda_1 - z_3\lambda_3 \quad Q = z_1\lambda_1(\lambda_2 + \lambda_3) - z_3\lambda_3(\lambda_1 + \lambda_2) \quad R = \lambda_1\lambda_2\lambda_3(z_1 - z_3)$$

And finally the roots of the quadratic equation for s are:

$$\alpha = \lambda_2 \qquad \beta = \frac{z_1 - z_2}{z_1\lambda_1 - z_3\lambda_3} \lambda_1\lambda_3 = \frac{w_1 + w_3}{w_1\lambda_1 + w_3\lambda_3} \lambda_1\lambda_3 \text{ . q.e.d.}$$

c) Also in the case $\Theta_1 = \Theta_2 = \Theta_3$, the coefficients α and β are entirely determined. In that case one has, as has already been pointed out: on the right $n_1 = c'_1 \quad n_2 = c'_2$
on the left $n_1 = \alpha c'_1 \quad n_2 = (1 + p)\alpha c'_2$,

where p is very small and approaches zero. Expanding in powers of p we get:

$$\Theta_1 = \ln\alpha \, ; \qquad \Theta_2 = \ln\alpha + p \, ; \qquad \Theta_3 = \ln\alpha + \frac{z_2 c_2' p}{z_1 c_1' + z_2 c_2'} \, .$$

$$A_1 = z_1 c_1' p \, ; \; A_2 = z_2 c_2' p \, ; \qquad A_3 = -(z_1 c_1' + z_2 c_2')p.$$

As only the proportions of these numbers is important, we can divide by p, and the numbers A_i are obviously entirely determined for $p \to 0$.

d. To get an idea of the influence of the ion-charge, one can e. g. compare the following cases:

A. on the left $n_1 = a$ $n_2 = b$ $n_3 = a + b$
on the right $n_1 = b$ $n_2 = a$ $n_3 = a + b$
$z_1 = -1$ $z_2 = -1$ $z_3 = 1$
$\lambda_1 = 34$ $\lambda_2 = 34$ $\lambda_3 = 64.4$
ion: JO_3 $C_2H_3O_2$ K , all at 18°.
One finds $A_1 = 1$ $A_2 = 1$ $A_3 = -2$ $\underline{\overline{\sigma = 44.5}}$.

B. on the left $n_1 = a$ $n_2 = \frac{1}{2}b$ $n_3 = a + b$
on the right $n_1 = b$ $n_2 = \frac{1}{2}a$ $n_3 = a + b$
$z_1 = -1$ $z_2 = -2$ $z_3 = 1$
$\lambda_1 = 34$ $\lambda_2 = 34$ $\lambda_3 = 64.4$
ion: JO_3 SO_4 K , all at 18°.
One finds $A_1 = 1$ $A_2 = 1$ $A_3 = -2$ $\underline{\sigma = 47.4}$.

(For convenience' sake we have chosen $\lambda_1 = \lambda_2 = \lambda$).

The second case is different from the first insofar as the acetate-ions have been replaced by an equivalent quantity of SO_4-ions. The double charge of the SO_4-ion results in a greater diffusion-coefficient σ. This was to be expected because K_2SO_4 also diffuses more swiftly than $KC_2H_3O_2$. The diffusion-coefficients of these salts are namely 49.6 and 44.5 respectively, as can readily be calculated from the ion-mobilities.

IX. Critical review of the theory.

Zero concentrations had to be excluded from the "logarithmic" solution for three ions. The theory would lose all sense, if one tried to apply it to the diffusion of one electrolyte AZ into antother BZ. The expression (84) for the diffusionpotential would even become infinite. Therefore one must expect that deviations will occur in the case of large concentration-ratios, i. e. large Θ_i. Considering more closely the approximation introduced, this becomes quite clear. For if the diffusion extends itself over a distance l, the quantity $\partial\varphi_i/\partial x$ has the order of magnitude Θ_i/l and $\partial^2\varphi_i/\partial x^2$ the order Θ_i/l^2. So, if one neglects $(\partial\varphi_i/\partial x)^2$ with respect to $\partial^2\varphi_i/\partial x^2$, this means properly speaking that one neglects Θ_i with respect to unity. In the limits of very small Θ_i the expression for L becomes identical with that of Henderson. From a theoretical point of view our theory has no advantages over Henderson's for the present, except insofar as Henderson's theory does not yield any information about the diffusionprocess, while our theory does.

It is possible that in the case of larger Θ the results of this theory agree better with experiments than those of Henderson's. (Compare for hat purpose the observations which will be discussed further on). The fact that the formula lead to right conclusions in special cases where, however, Θ is not small, speaks in favour of this possibility. Moreover it may be remarked that the above estimation of the quantities $\partial\varphi_i/\partial x$ and $\partial^2\varphi_i/\partial x^2$ is only provisional. In reality there are points where $\partial^2\varphi_i/\partial x^2$ is small or even zero and others where $\partial^2\varphi_i/\partial x^2$ is large. The solution of an equation of diffusion like (77) page 67 with the boundary conditions of page 67, is represented by (79):

$$n(x,t) = {}^1/_2\,(q+p) + {}^1/_2\,(q-p)\,\chi\left(\frac{x}{2\sqrt{t}}\right)$$

Thus

$$\frac{\partial n}{\partial x} = \frac{q-p}{\sqrt{\pi}}\,\frac{1}{2\sqrt{t}}\,e^{-\frac{x^2}{4t}}$$

$$\frac{\partial^2 n}{\partial x^2} = \frac{q-p}{\sqrt{\pi}}\,\frac{-x}{4t\sqrt{t}}\,e^{-\frac{x^2}{4t}}$$

and one can easily convince oneself that the ratio: $\dfrac{\dfrac{1}{n}\dfrac{\partial^2 n}{\partial x^2}}{\left(\dfrac{1}{n}\dfrac{\partial n}{\partial x}\right)^2}$

has the order of magnitude $x\sqrt{t}\,.\,exp(x^2/4t)$. This is small for small $|x|$ but increases very rapidly for increasing $|x|$. Thus the approximation is bad for small values of $|x|$, but much better as soon as $|x|$ becomes larger. Now the question remains, what part of the axis x is most important. The fact that the potential shows two or more extrema might possibly mean that the slope at small x contributes but little to the whole diffusionpotential L. In the end the experiments will have to decide, and they will indeed show that the formula (84), (page 70) reproduces the observations better than Henderson's formula for concentrationratios which are not too large. It could not be seen, what L does when the concentrationratios become larger and larger, because L no longer reaches a constant value in such cases.

Recapitulating, it can be said that (84) represents an expression which surely does not hold in all cases and which, from a theoretical point of view, cannot be regarded as more exact than Henderson's formula, but which seems to yield a better reproduction of the observations in a certain interval. And finally the fact that the theory is able to picture in a very plausible way the diffusionprocess, can be regarded as a great advantage.

DIFFUSION OF A MIXTURE OF ELECTROLYTES

II. Experimental Part.

Introduction.

The various opinions mentioned in the literature, about the reproducibility of measurements and the usefulness of the theoretical formulae, diverge very much.

Mc. Innes and Yu Liang Yeh[1]) give a review of older measurements, remarking that their predecessors rarely found a constant diffusionpotential. Generally the largest value of L was considered as the "right one". Walpole[2]) was the first to state that more reproducible values of L could be obtained, when both solutions flow along each other (flowing junction). The conditions which hold for this diffusion, are, however, difficult to formulate theoretically. For instance, one is not sure if there exists a well-defined concentration-gradient everywhere, and if it does, whether it is small enough for the application of the differential equations (compare page 14). Obviously some stationary state will occur, but will it be similar to that of Planck's theory or will the diffusion layer show a structure which resembles that of Henderson's theory for the mixing of both solutions?

Further L appears to be independent of the velocity of flow within rather restricted limits only, and the rather complicated technique of the measurements is, of course, a serious objection too. Moreover Scatchard and Buehrer[3]) found that the diffusionpotential of flowing junctions differs from that of ordinary diffusion in the case of a single electrolyte (where the structure of the diffusion layer should be of no importance for the value of L) and is less reproducible.

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[1]) D. A. Mc. Innes and Yu Liang Yeh, J. Am. Chem. Soc. **42,** 229 (1920); **43,** 1217, 2563 (1921).

[2]) G. S. Walpole, J. Chem. Soc. London **105,** 2501, 2521 (1914).

[3]) G. Scatchard and T. F. Buehrer, J. Am. Chem. Soc. **53,** 574 (1931).

The difference is not large and is attributed by Hamer[4]) to the heat of mixing. It is, however, also possible that the differential equations of the process or their integration have to be reconsidered. Anyhow it seems clear that one cannot be quite sure about the significance of the measured potential-differences in the case of flowing junctions. In this dissertation the flowing junction may be left out of consideration. One can find literature about it in Dole[5]), Brighton[6]), Mc. Innes[7]), Martin and Newton[8]).

Another method to obtain values which are more constant, has recently been indicated by Szabó[9]), who makes use of a closed cock to avoid convection. The diffusion itself and the boundary-conditions remain unaltered. Szabó's experiments, however, have only been carried out at large concentrations and generally the diffusionpotentials can be reproduced much better in that case. An extension of his method to smaller concentrations seems desirable.

Most authors have compared their results with the formulae of Planck or Henderson or both. Sometimes they agree very well, sometimes very badly. For instance, six out of eight observations, mentioned by Lovén[10]), agree with the formula of Planck with an accuracy of 1 to 2 mV (that is 3 to 7 %), while two other observations show deviations of 20 %. Wilke and Kieningen[11]) reproduce L by experimental formulae which cannot in the least be brought into accord with the theory of Planck or Henderson. An entirely deviating result was also obtained by Loomis and Acree[12]), and by Fales and Vosburgh[13]). The observations of these experimentalists have been repeated and confirmed by Chanoz, Florence and Perrottet[14]). Szabó[9]) found values for the diffusionpotential which are much larger than Henderson's.

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[4]) W. J. Hamer, J. Am. Chem. Soc. **52**, 662 (1935).

[5]) M. Dole, J. Am. Chem. Soc. **54**, 2120, 3100 (1932).

[6]) D. A. Mc. Innes and T. B. Brighton, J. Am. Chem. Soc. **47**, 994 (1925).

[7]) D. A. Mc. Innes, J. Am. Chem. Soc. **45**, 2249 (1923), **53**, 1357 (1931).

[8]) F. D. Martin and R. F. Newton, J. Phys. Chem. **39**, 485 (1935).

[9]) Z. Szabó, Z. physik. Chem. (A) **174**, 22 (1935).

[10]) J. M. Lovén, Z. physik. Chem. **20**, 593 (1896).

[11]) E. Wilke and O. Kieningen, Z. physik. Chem. **116**, 215 (1925), **125**, 421 (1927), **160**, 39 (1932).

[12]) N. E. Loomis and S. F. Acree, Am. Chem. J. **46**, 585 (1911).

[13]) H. A. Fales and W. Vosburgh, J. Am. Soc. **40**, 1291 (1918).

[14]) M. Chanoz, G. Florence and P. Perrottet, Arch. Phys. biol. **12**, 238 (1935).

[15]) E. A. Guggenheim, J. Am. Chem. Soc. **52**, 1315 (1933). E. A. Guggenheim and A. Unmack, Math. Fys. Medd. Kgl. Vid. Selsk. X **8** (1930), **14** (1931).

On the other hand Guggenheim[15]) mentions values which fairly well agree with theory. As the diffusion here involved is that of HCl into KCl, while the concentration of the chlorine-ions is the same at the left as at the right hand side, the formulae of Planck and Henderson yield the same result. Büchi[16]) found Henderson's formula confirmed for a short time after he had brought both solutions into contact. After some time the diffusion-potential decreases and sometimes reaches a minimum value, to mount slightly afterwards. Planck supposes that this minimum value would agree with his own formula, and thinks this verified by experiments of Chang[17]). It must, however, be remarked that the minimum value does not always occur. Moreover, the experimental differences between the maximum and the minimum value do not agree with its theoretical value $E_H - E_P$. In Chang's experiments, for instance, they amounted to 10.0; 13.5 and 7.3 instead of 5.3; 6.3 and 4.0 mV.

Finally, at a suggestion of Einstein's, Plettig[18]) worked out a method to decide between the formula of Planck and that of Henderson. To that end he replaced the diffusion layer by a "Henderson-series" of solutions as described on page 57. As one can calculate from Planck's theory how the concentrations vary in the diffusion layer in the case of the stationary state, one can do the same for a "Planck-series" of solutions. Plettig now compared the e.m.f. of such chains with the potential-difference of "free" diffusion. As only the difference is important, the electrode-potentials play no part at all, which, of course, is very important when judging the results. On the other hand these differences are rather small (in the cases examined by Plettig, never more than 3 mV) and therefore it is difficult to know whether concentration-effects (which, of course, occur in the diffusionpotentials too) play a part in the results or not. Moreover, we already stated on page 57, that a series of solutions, as described here, cannot without more ado be compared with a diffusion layer of similar structure. In any case, Plettig concluded from his measurements, that the potential-difference of free diffusion is in better agreement with that of a "Henderson-series" than with that of a "Planck-series".

Observations.

The object of our observations was, to see whether the formula (84) page 70 yields better values than Henderson's. We therefore deliberately examined cases, where the results of both formulae show

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[16]) F. Büchi, Z. Elektrochem. **30**, 443 (1924).

[17]) Shu Tsu Chang, Ann. Physik (5) **16**, 513 (1930).

[18]) V. Plettig, Ann. Physik (5), **5**, 735 (1930).

a large difference. In the formula (84) we had to restrict ourselves to the diffusion of two electrolytes with a common ion, none of the concentrations becoming zero. All measurements are therefore restricted to such cases.

We examined mixtures of NaCl and HCl, and sometimes mixtures of KCl and HCl. Solvent: water at 25°. Ionmobilities:

$l_H = 349.7 \quad l_{Na} = 50.1 \quad l_{Cl} = 76.3 \quad l_K = 73.5$ *).

Besides the tube described on page 35, we often used another of the same form and dimensions, except for the junction of both ends, which had a diameter of 1 mm. Similar tubes were used by Chang[17]). The run of the potential was, as a rule, observed for about six days, sometimes even longer. The electrodes were AgCl-electrodes, prepared as described on page 35. They were not replaced by others during the measurements. We always took care that the solution with the greatest density remained beneath the other.

1. *An attempt to extrapolate to infinite dilution.*

In both electrodepotential and diffusionpotential concentration-effects due to deviations from the behaviour in ideal solutions, can occur. In calculating the electrode-potential from the Nernst formula and the diffusionpotential from (84) page 70 or (41) page 52, one can therefore expect errors. In a special case, namely 0.1 HCl/0.1 KCl, Guggenheim[15]) estimated this error at about 1 mV, but it can, of course, be greater in other cases. We therefore tried to eliminate this error in the following way.

When all concentrations are reduced in the same proportion, the concentration-effect decreases, while the calculated electrode- and diffusionpotentials remain unaltered. Possibly one might be able to find the accurate diffusionpotential by extrapolating to infinite dilution. This appeared, however, to be impossible with our experiments. For the uncertainty in the measured potentialdifference itself amounted to 1 or 2 mV, and seemed even to increase at higher dilutions.

The concentrations were (g/mol per l):

at the left: $c_H = 0.0111 \quad c_{Na} = 0.0816 \quad c_{Cl} = 0.0927$
at the right: $c_H = 0.0997 \quad c_{Na} = 0.00906 \quad c_{Cl} = 0.1088$

According to Nernst the electrodepotential becomes: 51.1 $\log_{10}$ 1088/927 = 4.1 mV. From Henderson's formula one finds a diffusionpotential of 25.0 mV. The sum is 29.1 mV. On the other hand (84) yields 31.2 mV. Sum: 35.3 mV.

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*) D. A. Mc. Innes, Th. Shedlovsky and L. G. Longsworth, J. Am. Chem. Soc. **54**, 2758 (1932).

The potential-difference showed the following course:

first observation.

t in hours:	0	0.5	1.0	2.0	4	6	10
E in mV.	46.0	40.5	37.0	36.6	36.0	36.6	37.2

t in hours:	23	28	33	48	73	98	120
E in mV	36.2	37.6	38.0	36.0	38.2	38.2	38.0

second observation.

t in hours:	0.5	1.0	3.5	5.5	9.5	10.5
E in mV.	43.9	44.1	41.6	40.8	39.1	38.8

t in hours:	12.0	16	24	40	52	72	85	97
E in mV.	38.5	38.0	37.6	36.2	36.8	37.0	37.0	37.1

t in hours:	125	144	150
E in mV.	33.2	30.8	29.6

According to the first observation E has the value 36.0—38.0. According to the second: 36.2—37.6 mV. Now both solutions were diluted five times, so that the following solutions diffuse into each other:

at the left: $c_H = 0.00222$ $c_{Na} = 0.01632$ $c_{Cl} = 0.01854$
at the right: $c_H = 0.01994$ $c_{Na} = 0.00181$ $c_{Cl} = 0.02175$

t in hours:	2	6	8	12	24	52	72	120
E in mV.	51.2	47.8	47.0	42.0	39.6	38.5	37.0	36.2

t in hours:	145	148	156
E in mV.	38.8	36.0	36.2

Thus E = 36.0—38.8.

Finally ten times diluted:

at the left: $c_H = 0.00111$ $c_{Na} = 0.00816$ $c_{Cl} = 0.00927$
at the right: $c_H = 0.00997$ $c_{Na} = 0.000906$ $c_{Cl} = 0.01088$

t in hours:	2	5	8	24	28	37	48	62
E in mV.	40.8	40.8	40.2	39.6	39.0	39.0	38.0	36.0

t in hours:	75	96	120	128	134	144	146
E in mV.	37.2	39.0	39.0	38.2	37.1	33.8	33.0

Thus E = 37.0—39.0 mV.

It can be concluded from these measurements, that the concentration-effect practically remains within the limits of attainable reproducibility, so that an extrapolation to infinite dilution, as aimed at above, is impossible.

After some time the e.m.f. reaches a rather constant value. This value does not agree with Henderson's formula but rather well with the formula (84). In opposition to Büchi's experience, L

deviates even more from Henderson's value in the beginning than at the end. Finally it may be remarked that, according to Sitte's formula (44) page 54, the diffusionpotential in this case would be $L = 34.5$ mV, $E = 38.6$. This value agrees still better with the experimental E.

2. *Mixtures of NaCl and HCl.*

To facilitate a comparison of the theoretical formulae, we henceforth only examined the case where the concentration of chlorine ions was the same both on the left- and on the right hand side. In that case the formulae of Planck, Henderson and Sitte all simplify to:

$$L_H = kT/\varepsilon \,.\, log\ V/V'.$$

That is, at 25°:

(85) . . . . . $L_H = 59.1\ log_{10}\ V/V'\ mV.$

The Nernst electrode-potential is now zero. Further in formula (84) we have $\Theta_{Cl} = 0$, so that:

$$L' = 59.1 \frac{(l_H - l_{Na})\ \Theta_H\ \Theta_{Na}}{(l_{Na} + l_{Cl})\ \Theta_H - (l_H + l_{Cl})\ \Theta_{Na}}$$

Instead of lnc/c', Θ here means: $\log_{10} . c/c'$. Finally this expression for L' can be simplified by taking the H-concentration at the right hand side equal to the Na-concentration at the left hand side, and vice versa. Thus:

on the left: $c_H = a \quad c_{Na} = b \quad c_{Cl} = a + b$
on the right: $c_H = b \quad c_{Na} = a \quad c_{Cl} = a + b$

$$\Theta_H = -\ \Theta_{Na} = log_{10}\ a/b.$$

With the ionmobilities, mentioned above:

(86) . . . . $L' = 33.9\ log_{10} . a/b$

On the other hand we have in (85): $V = (l_H + l_{Cl})a + (l_{Na} + l_{Cl})b$ and $V' = (l_H + l_{Cl})b + (l_{Na} + l_{Cl})a$. And therefore (85) can be written:

(87) . . . . $L_H = 59.1\ log_{10} \dfrac{426 + 126.4\ a/b}{426\ a/b + 126.4}$

L' increases much more rapidly with a/b than L_H and should even become infinite (logarithmically) when a/b becomes infinite. This cannot be true, of course, but the question is, if there exists an interval where (86) is better than (87).

In fig. 7 the theoretical values of L' and L_H have been reproduced. The observations are also represented in it.

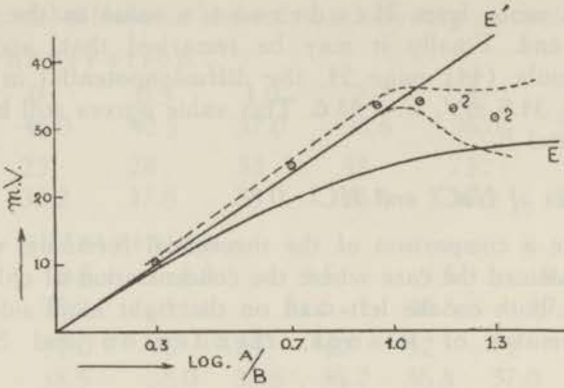

Fig. 7.

The concentration $a + b$ always amounted to 0.1108 g/mol. per *l*. All the times are expressed in hours, E in mV.

$a/b = 2 \quad E' = 10.2 \quad E_H = 9.4$

t:	0	2	4	24	28	48	52	56	73	77	80
E:	11.6	10.6	10.6	9.9	9.8	9.8	10.2	10.6	9.8	10.0	10.0

t:	96	99	120	145
E:	10.2	10.0	9.7	10.5

Result: E = 9.8 — 10.6

$a/b = 5 \quad E' = 23.7 \quad E_H = 19.5$

t:	0	2	4	6	24	36	72	84	88	96
E:	30.6	28.2	26.0	25.0	23.9	24.2	24.7	24.5	24.5	24.5

Result: E = 24.0 — 24.6

$a/b = 5 \quad E' = 23.7 \quad E_H = 19.5$

t:	1	7	25	28	37	48	75	84	100	104	124
E:	24.2	22.7	23.8	23.8	24.0	24.2	24.2	24.6	24.4	24.2	24.2

t:	134	146	150	154
E:	24.8	24.7	23.0	22.2

Result: E = 24.0 — 24.6.

$a/b = 9 \quad E' = 32.4 \quad E_H = 23.9$

t:	8	24	28	32	46	60	76	101	122	144
E:	22.2	28.4	28.6	33.0	32.9	33.2	34.2	34.0	34.0	33.0

t:	148	150	156
E:	33.0	33.0	33.7

Result: E = 33.0 — 34.0

$a/b = 12 \quad E' = 36.6 \quad E_{\mathrm{H}} = 25.5$

t:	0	2	4	8	26	52	84	120	146	172	192	244	268	270	272	284
E:	40.1	42.1	40.3	38.2	34.0	31.8	32.2	32.6	35.0	35.9	35.2	32.8	33.7	32.8	30.0	24.5

Result: E = 32.5 — 35.7

$a/b = 12 \quad E' = 36.6 \quad E_{\mathrm{H}} = 25.5$

t:	0	2	8	10	24	28	30	32	36	38	48	62	68	80	98	120	126	146
E:	26.0	26.7	26.7	26.9	27.3	27.5	28.9	30.3	32.2	32.7	34.8	34.6	35.2	32.3	34.2	35.0	34.8	34.0

Result: E = 32.3 — 34.8

$a/b = 15 \quad E' = 39.9 \quad E_{\mathrm{H}} = 26.5$

t:	0	4	8	24	30	49	52	74	96	125	146	168	200	104	206	207
E:	22.0	24.6	27.8	28.2	28.5	33.7	35.8	29.1	33.5	36.0	28.2	28.5	26.4	25.6	25.6	25.0

Result: E = 28.2 — 36.0

$a/b = 15 \quad E' = 39.9 \quad E_{\mathrm{H}} = 26.5$

t:	2	8	26	50	52	56	75	79	96	124	144	168
E:	41.2	40.3	35.6	35.1	33.0	33.0	30.3	28.7	27.9	34.5	35.7	35.2

Result: E = 28.0 — 35.7

$a/b = 20 \quad E' = 44.1 \quad E_{\mathrm{H}} = 27.6$

t:	0	24	28	32	50	72	96	120
E:	51.2	40.8	44.5	48.0	38.2	35.5	30.2	39.6

Result: E = ?

$a/b = 20 \quad E' = 44.1 \quad E_{\mathrm{H}} = 27.6$

t:	0	2	4	24	32	50	72	96	120	144	168	192	240	244	248
E:	22.2	26.8	35.1	40.2	48.0	52.3	45.1	40.2	40.6	34.6	34.6	46.7	44.8	30.0	25.6

Result: E = ?

3. *Mixtures of KCl and HCl.*

Some observations with HCl and KCl in water at 25° yielded similar results. With the mobilities $l_{\mathrm{H}} = 349.7$, $l_{\mathrm{Cl}} = 76.3$ and $l_{\mathrm{K}} = 73.5$ the formulae for the diffusionpotentials become:

$$L_H = 59.1 \; \log_{10} \frac{426 + 150\, a/b}{426\, a/b + 150}$$

$$L' = 28.4 \; \log_{10} a/b$$

$a/b = 10$ $E' = 28.4$ $E_H = 21.3$

t:	0	4	8	24	49	73	99	120	124	168
E:	25.4	27.0	28.8	29.0	29.5	28.5	28.5	28.7	28.9	29.4

Result: E = 28.5 —29.5

$a/b = 10$ $E' = 28.4$ $E_H = 21.3$

t:	26	49	75	98	124	168	192	240	248	266
E:	27.8	28.0	28.0	29.2	29.0	28.7	28.4	28.0	27.8	29.0

Result: E = 28.0 — 29.2

$a/b = 15$ $E' = 33.4$ $E_H = 23.0$

t:	0	1	20	24	43	66	71	72	95	163
E:	26.0	27.8	28.3	28.5	31.2	38.8	38.7	39.2	41.8	40.7
t:	169	186	188	240	244	248				
E:	29.5	43.0	33.5	25.2	24.0	22.6				

Result: E = ?

General Conclusions.

1. From $a/b = 2$ to $a/b = 10$ a rather constant diffusionpotential is found, and its value can be pretty well reproduced. In proportion as the concentrationratio a/b increases, E becomes more and more uncertain. At $a/b = 15$ or 20 no plausible value of E can be deduced from the measurements. In such cases E sometimes changes more than 5 mV. in the course of a few hours. We do not know whether this fact in due to accidental (experimental) errors or to a real property of these e.m.f.'s. It may be reminded that E is not at all constant in the case of small a/b neither, only the deviations are much less important in that case. It is very remarkable that the course of E with time resumes its normal behaviour when we pass to the diffusion of pure HCl into pure KCl (a/b infinite), as can be seen from the following experiment.

on the left: HCl 0.1108 n.
on the right: KCl 0.1108 n.

t:	0	8	24	26	30	32	38	48	52	58
E:	26.2	29.3	30.1	30.3	29.6	29.1	28.7	29.2	28.8	28.7
t:	78	80	98	122						
E:	29.2	29.3	29.2	28.7						

Result: E = 28.7 — 29.2

In view of this result it seems most reasonable to suppose that the above mentioned deviations in the case of large *a/b* are due to experimental errors. Perhaps the influence of small convections (e. g. caused by small changes in temperature) is particularly large when small amounts of an electrolyte are added to the solution of another one.

2. Generally the run of the potentialdifference in time cannot be reproduced. The manner in which the constant value of E is reached, is always different. Sometimes E decreases, sometimes it increases, and the time required to attain the constant value, varies between 6 or 8 hours and 24 hours or more. To be sure, one gets more or less the impression that it generally takes a little longer in proportion as *a/b* is larger. This would be in accordance with theory, because, in the case of larger difference in concentration, a state which satisfies the condition that gradients of potential and concentrations are *small*, can only be arrived at after a longer time. In this respect, however, the measurements are not convincing at all.

3. In several cases E shows a small decrease towards the end. Chang[19] and Szabó[20] too, attribute this phenomenon to the fact that the diffusion begins to extend outside the capillary. Whether this conception is true or not, probably cannot be concluded from potential-differences only.

4. The measurements concerning mixtures of HCl and NaCl are recapitulated in table XI.

Table XI.

Diffusionpotentials in mixtures of HCl and NaCl, in water at 25°.

a/b	E'	E_H	E (exp)
2	10.2	9.4	9.7—10.5
5	23.7	19.5	24.0—24.6
9	32.4	23.9	33.0—34.0
12	36.6	25.5	32.5—35.7
15	39.9	26.5	?
20	44.1	27.6	?

5. As to the immediate practical importance of the theory and measurements, mentioned in this thesis, about the diffusion of a mixture of electrolytes, we may make the following observations.

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[19] Shu Tsu Chang, Ann. Physik (5) **16**, 513 (1930).

[20] Z. Szabó, Z. physik. Chem. A **174**, 22 (1935).

Apparently the diffusionpotential reaches a rather constant value only after a long time (even amounting to 24 hours or more). Generally this time is too long to have direct applications in such measurements where the diffusionpotential has only importance as a disturbing, unknown factor. In such cases one must be satisfied with devices which further a more rapid adjustment of a constant potential, such as a concentrated solution of potassiumchloride[21]). In that case one will, of course, have to be content with an unknown value of the diffusionpotential.

In case a long time would be no paramount objection, the result of the theory remains nevertheless rather uncertain, as was the case with all preceding theories, except that of Planck. In this thesis it may be especially pointed out that, in cases where the knowledge of diffusionpotentials is of great importance, one had best make use of stationary diffusion for the time being. For Planck's theory is the only one which integrates exactly the differential equations under the supposed conditions. It cannot yet be judged if such measurements will be practically feasible. Perhap one might use two tubes, joined by a capillary, provided the electrodes are placed in the immediate neighbourhood of the ends of this capillary. Whether a layer of gelatine can render service, depends a.o. on whether the ionmobilities are influenced by the gelatine. In this respect experiments of France and Moran[22]) and of Richter[23]) too, may be mentioned. These authors found transportnumbers in gelatine, which differ from those in water.

In this thesis the possibilities of direct application, in so far as the diffusion of a mixture of electrolytes is concerned, are provisionally thrust into the background. We only tried to throw some light on the general problems of electrolytic diffusion, and to give a solution of some of these problems.

Experimental Proof for the extrema in the concentrations.

On page 61 we obtained, in a very general way, the result that the concentration of a given ion-species can in the course of time show extrema if this ion participates in the diffusion of a mixture of electrolytes. It is evident that this conclusion can be of great importance for processes in which the diffusion of electrolytes plays a part.

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[21]) N. Bjerrum, Z. physik. Chem. **53**, 428 (1905).

[22]) W. G. France and W. H. Moran, J. Am. Chem. Soc. **46**, 19 (1924).

[23]) P. Richter, Z. physik. Chem. **80**, 449 (1912).

1. It is, for instance, very well possible that this phenomenon is an important or even determining factor in the formation of Liesegang rings during the diffusion of electrolytes into each other. For the present we must restrict ourselves to this indication. Whether this supposition holds can only be settled by a further examination both theoretical and experimental. On the one hand, the fact that Liesegang rings have also been observed in the case of diffusion of (entirely dry) gases into each other [1]), and in the case of reactions between organic substances [2]), where ions do not occur, would indicate that the extrema which occur during electrolyte diffusion, do not play a determining role. On the other hand the experiments of Kisch [3]) and of Shikata and Hukuwatari [4]) point to a great influence of external electric fields on the formation of Liesegang rings in electrolytic mixtures.

2. Straub [5]) suggested that this formation of maxima and minima — which might rightly be called "anomalous diffusion" — might be akin to the so-called "anomalous osmosis", the only difference being that in the latter case the diffusion takes place through a membrane. By anomalous osmosis is meant the motion of certain substances through the membrane from lower towards higher concentration; it would then have to be considered as caused by the potential-difference across the membrane, just as the "anomalous diffusion" is caused by the diffusionpotential. According to Straub the anomalous osmosis has indeed only been established in solutions of electrolytes.

If one succeeded in giving an experimental proof for the existence of extrema, this would mean a direct confirmation of the theory, and moreover one would then have more confidence in applying its results. As far as we know, no experiments which describe such extrema, have been mentioned in the litterature. There only remained an experiment of Thovert to be called attention to, which has already been done in the introduction of this thesis (page 10). We have tried to give a convincing proof for this phenomenon with simple means. It is clear that one can expect the best results in cases where

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[1]) Koenig, J. Phys. Chem. **24**, 466 (1920); Hedges, J. Chem. Soc. London (1926) 2580, (1929) 1028, 1849, (1927) 1077. Koll. Z. **52**, 219 (1930).

[2]) Handowsky and du Bois Reymond, Koll. Z. **33**, 347 (1933); S. Veil, C. R., **195**, 781 (1932).

[3]) Kisch, Koll. Z. **49**, 433 (1929).

[4]) Shikata and Hukuwatari, J. Soc. Chem. Ind. Japan **35**, 25 (1932).

[5]) J. Straub (Amsterdam); this suggestion was made at a meeting of the Nederl. Chem. Vereen. 29 Dec. 1936.

the diffusionpotential is large. Now this condition is best fulfilled when the concentrationratios are large, and when, moreover, the ions which take part in the diffusion, differ much in mobility. Therefore, we must examine the diffusion of a rather concentrated solution of a salt into a much dilute solution of an acid or a base, or conversely: the diffusion of a concentrated acid or base into the dilute solution of a salt. In both cases a positive result was obtained.

I. The diffusion of concentrated NaCl into dilute NaOH.

A tube of 60 cm with a diameter of 4 mm was half-filled with a solution of NaCl in a 1 % solution of agar-agar. The concentration of the NaCl amounted to 0.1 g/mol. per L; to this solution phenolphtalein had been added (0.1 gram per L). After cooling down, a solution of NaOH in water was poured on it. This solution contained 0.1 gram phenolphtalein per L and 10^{-3} to 10^{-4} g/mol. NaOH per L. Then the upper end of the tube is sealed air-tight; the diffusion of the NaCl into the NaOH (and vice versa) sets in. After a few days one observes a red layer in the upper solution, some centimeters above the agar-agar. This layer is distinctly more intense in colour than the original solutions above it. It slowly moves upwards, broadening in the meantime; it can maintan itself for four or five days but it finally disappears. We even succeeded a few times in choosing the circumstances so that we attained a discolouring of the whole upper solution with the exception of a red layer in the middle.

The circumstances in which the experiments takes place, can be varied within wide limits.

1. The phenomenon could also be established in tubes of about 100 cm with a diameter of 10 mm.

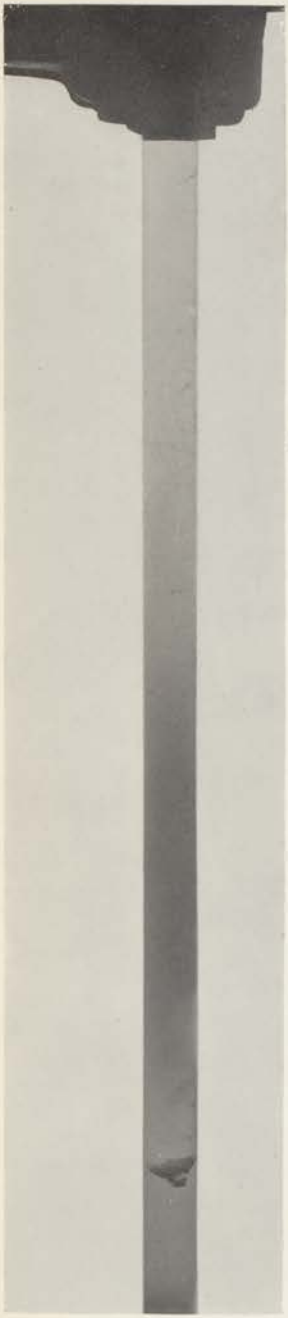
2. With a concentration 0.01 n. of the NaCl a similar result was observed though less distinctly.

3. As a matter of course the concentration of the phenolphtalein had little or no influence.

4. The agar-agar was only used to avoid disturbing currents.

5. We never took particular precautions with respect to temperature. The diffusion took place at roomtemperature, but this temperature slowly varied, being somewhat lower at night than by day.

6. Finally the concentration of the NaOH was so chosen as to obtain a colouring suitable for observation. When this concentration is too large the effect does not occur. This does not prove, of course, that the concentration of the OH-ions does not show a maximum in



Diffusion of NaCl 0.1 into NaOH ± 10^{-4} with phenolphtalein (0.3 gram per 1) as an indicator.

The photograph has been made by W. K. L. Rameau, photographer at the Library of the University, Leiden.

that case. It only means that one is too far at the alcaline side to observe differences in the concentrations. On the other hand, when the concentration of the NaOH is chosen too small, the colouring is too weak even in the maximum to yield a clearly visible difference from its surroundings. A photograph of the phenomenon is printed here. It was taken with transmitted light obtained from an incandescent lamp behind a milk-glass plate. The photographic plate was sensitive to green light; the exposure was made with the aid of a yellow filter.

II. The diffusion of concentrated HCl into dilute indigo-carmine.

When a solution of indigo-carmine in water (2.10^{-4} g/mol. per L) is poured upon a cold solution of HCl in 2 % agar-agar (0.1 g/mol. HCl per L), a distinct minimum in the concentration of the blue coloured ion [6]) of indigo-disulfonic-acid is observed after a few days.

It can easily be seen that the direction in which these phenomena take place, is indeed as was to be expected. We shall show this for both cases separateley.

I. *The diffusion of concentrated NaCl into NaOH.* For difiniteness suppose the NaCl at the left and the NaOH at the right hand side. The first question which we must answer is the question at which side the potential is the largest, in other words: is L positive or negative? We cannot use the formula (84), page 70, because zero concentrations have not been excluded. The formula of Henderson, however, yields a very large negative diffusionpotential, and it is therefore practically excluded that some other theory would find a positive L. Indeed, the concentration of the NaCl is large compared with that of the NaOH. In the beginning the diffusion of the NaCl is therefore the determining factor for the potentialgradient. The chlorine-ions have greater mobility than the sodium-ions, and thus a potentialgradient originates which slows down the chlorine-ions and accelerates the sodium-ions, in other words: the potential at the left hand side becomes higher than that at the right hand side (L is negative).

In the first phase of the diffusionprocess the form of the potential Φ is, therefore, that of fig. 6a, page 61, reflected in the ordinate. Instead of fig. 6b we get after some time a potentialgradient with a

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[6]) The author is indebted to Dr. J. van Alphen (Leiden) at whose suggestion this ion was chosen.

minimum at the left hand side (in the agar-agar) and a maximum at the right hand side (in the solution of NaOH in water). It is clear that the diffusion of the OH-ions will be disturbed by this maximum of Φ in such a way as to yield a maximum in the concentration. For the negative OH-ions will show a tendency towards points of higher potential.

II. *The diffusion of concentrated HCl into indigo-carmine.* Again we shall imagine the agar-agar at the left hand side. Here the course of potential is reversed because the rapid H-ions overtake the slower Cl-ions. The picture of Φ becomes that of fig. 6a, page 61. It is true that the theory of page 60 cannot be applied here without more ado, because we have to deal with the diffusion of *four* ions (H, Cl, Na and indigodisulfonic acid). Nevertheless we may very probably conclude that a distribution of potential will originate after some time, with a minimum at the right hand side (in the solution of indigo-carmine), in analogy with fig 6b, page 61. The negative ions seek points of higher potential and will therefore show a tendency to form a minimum in the concentration.

SAMENVATTING.

I.

Wanneer twee verschillend geconcentreerde oplossingen van een electrolyt met elkaar in aanraking worden gebracht, treedt diffusie in en ontstaat een potentiaalverschil tusschen de beide oplossingen: de diffusiepotentiaal. Men heeft veelal gemeend, dat deze diffusiepotentiaal thermodynamisch kon worden berekend op een wijze die analoog is aan de manier waarop de E.M.K. van een electrolytische cel-in-evenwicht door thermodynamische redeneering kan worden verkregen. Deze thermodynamische behandeling leidde tot de onjuiste gevolgtrekking dat in de uitdrukking voor de E.M.K. van een concentratie-element met diffusie, de aktiviteiten der respectieve ionen slechts in den vorm van de *gemiddelde* aktiviteit voorkomen, zoodat men door metingen van zulke elektromotorische krachten nooit iets over de ionenaktiviteiten zou kunnen te weten komen.

In de inleiding van dit proefschrift wordt aangegeven waarom de thermodynamische behandeling van diffusiepotentialen niet geoorloofd is, en dat dus ook de bovengenoemde conclusie niet dwingend is. De diffusie is in wezen een *kinetisch* probleem, en slechts van een nauwkeurige kinetische theorie kan men een goede beschrijving van het diffusieproces en een juiste berekening van de diffusiepotentiaal verwachten.

Voor ideale oplossingen is door Nernst¹) (1889) de kinetische theorie der elektrolyt-diffusie ontwikkeld. Nu men, vooral sinds het werk van Debije en Hückel, een goed inzicht heeft verkregen in de structuur van verdunde elektrolytoplossingen, is het mogelijk om Nernst's theorie tot het geval van niet-ideale oplossingen uit te breiden. Aan deze taak is het eerste theoretisch gedeelte van dit proefschrift gewijd (p. 11—28).

Twee correcties moesten worden aangebracht. Eenerzijds moest in rekening worden gebracht, dat de neiging van de ionen om zich naar punten van lager concentratie te begeven, geringer is in niet-ideale dan in ideale oplossingen. Elk ion is n.l. omgeven door een Debije-Hückelsche „ionenwolk", en bezit daardoor een negatieve elektrostatische energie t.o.v. zijn omgeving, waarvan de absolute waarde des

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¹) W. Nernst, Z. physik. Chem. 4, 129 (1889).

te grooter is naarmate de concentratie van de elektrolyt grooter is. Als een ion zich naar een punt van kleinere concentratie beweegt, wordt zijn energie dus grooter; m.a.w. er zullen elektrische krachten zijn die zich tegen de beweging verzetten.

Anderzijds wordt de beweging van elk ion beïnvloed door die der andere ionen. In eerste benadering kan men dit effekt aldus beschrijven, dat de (osmotische en elektrische) krachten die op de ionenwolk aangrijpen, een hydrodynamische strooming veroorzaken. Het door de ionenwolk omgeven ion beweegt zich dus in een medium, dat een eigen snelheid bezit; deze snelheid wordt eenvoudig op die van het ion gesuperponeerd. Dit hydrodynamische effekt is reeds eerder berekend door Debije en Hückel[2]) en later door Onsager[3]). In dit proefschrift is echter direkt gebruik gemaakt van eenige algemeene resultaten der hydrodynamica, een methode die tegelijk aanschouwelijk is en zeer algemeen.

Berekeningen over de diffusie van een elektrolyt werden reeds eerder uitgevoerd door Onsager en Fuoss[4]). Men vergelijke daartoe echter de opmerkingen op p. 19. De bovengeschetste theorie kan volledig worden doorgevoerd, wanneer men zich beperkt tot de eerste macht van $\sqrt{c}$ (c = concentratie). De theorie van andere eigenschappen der elektrolytoplossingen (geleidingsvermogen, aktiviteit, inwendige wrijving, oppervlaktespanning) moet zich evenzeer tot de eerste macht van $\sqrt{c}$ beperken. De eenige uitzondering tot nu toe vormt de berekening der aktiviteit, welke door Gronwall, La Mer en Sandved[5]) met succes in hoogere benadering is doorgevoerd, terwijl trouwens ook hier nog verschillende onzekerheden bestaan. Voor de andere eigenschappen is men er veelal in geslaagd de experimenten tot aanzienlijke concentraties (soms tot 1 n. of hooger) door half-empirische formules weer te geven, die zich voor kleine concentratie aan de theoretische grenswet aansluiten. Een overeenkomstige werkwijze stuit echter in het onderhavige geval der diffusiepotentialen voorloopig op onoverkomelijke moeilijkheden. De meting van diffusiepotentialen kan n.l. niet direkt geschieden. Men moet gebruik maken van concentratie-elementen met diffusie, en in de E.M.K. van zulke elementen treden de potentialen oplossing/electrode op, die bepaald worden door de aktiviteit van het ion ten opzichte waarvan de betreffende elektrode omkeerbaar is. Empirisch is echter

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[2]) P. Debije en E. Hückel, Physik. Z. **25**, 49 (1924).

[3]) L. Onsager, Physik. Z. **27**, 388 (1926).

[4]) L. Onsager en R. Fuoss, J. Phys. Chem. **36**, 2689 (1932).

[5]) T. H. Gronwall, V. K. La Mer en K. Sandved, Physik. Z. **29**, 358 (1928).

slechts de aktiviteit van de elektrolyt als geheel, d. i. de gemiddelde aktiviteit der beide ionsoorten, bekend. Men vindt de discussie van deze moeilijkheid op p. 25. Voor het oogenblik zou dan ook de uitbreiding van de formule voor de diffusiepotentiaal tot grootere concentraties op al te speculatieve grondslagen moeten geschieden, zoodat in dit proefschrift slechts de $\sqrt{c}$-wet werd onderzocht.

Een vergelijking met in de literatuur vermelde waarnemingen (dit proefschrift p. 28—33) bewijst, dat de theoretische formule voor de diffusiepotentiaal binnen de bereikbare nauwkeurigheid der waarnemingen wordt bevestigd, en wel tot aan een concentratie van bijna 0.03 N. bij NaCl en bij HCl in water, en vermoedelijk 0.01 N. bij $BaCl_2$ in water. Bij deze laatste elektrolyt waren de beschikbare waarnemingen echter zeer onvolledig. Enkele weinige metingen betreffende LiCl, die eveneens in de literatuur vermeld zijn, blijken niet met de theorie in overeenstemming. Deze metingen werden echter bij te groote concentratie verricht om goede overeenstemming te mogen verwachten, terwijl de theoretische $\sqrt{c}$-correctie in dit geval bijzonder klein uitvalt, zoodat wellicht spoedig termen van hoogere orde een rol gaan spelen.

Eigen metingen (p. 34—48) zijn toegevoegd. Zij betreffen de elementen: Ag . AgCl/NaCl c_1/NaCl c_2/AgCl. . Ag. Oplosmiddel: water bij 18°.
Ag . AgCl/$BaCl_2$ c_1/$BaCl_2$ c_2/AgCl . Ag. Oplosmiddel: water bij 25°.
Ag . AgCl/HCl c_1/HCl c_2/AgCl . Ag. Oplosmiddel: 40 mol.% alkohol
Pt . H_2/HCl c_1/HCl c_2/H_2 . Pt. en 60 mol.% water bij 25°.

De gebruikte AgCl-elektroden bestonden uit verzilverd platina, dat daarna werd gechloreerd volgens een voorschrift van Elema[6]. In het alkohol-water-mengsel werden bovendien elektroden van geplatineerd platina gebruikt.

Daar de loopsnelheden l_H en l_{Cl} in het betreffende alkohol-watermengsel niet bekend waren, werden tevens het geleidingsvermogen en het transportgetal van HCl in dit mengsel gemeten. Het geleidingsvermogen werd bepaald voor concentraties varieerend van 0.00016 tot 0.0335 n., het transportgetal (volgens een analytische methode) van 0.007 tot 0.14 n. Van 0.0008 tot 0.01 n. bleek het geleidingsvermogen te kunnen worden voorgesteld door de uitdrukking: $\lambda = 99.4 - 92.9 \sqrt{c}$, in goede overeenstemming met de theoretische formule van Onsager. Het transportgetal is niet in overeenstemming te brengen met de formule die Longsworth[11] uit de theorie van Debije en Hückel afleidde. Een grafische extrapolatie leverde voor het transportgetal bij oneindige verdunning: $t_{Cl}^\circ = 0.231$.

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[6] B. Elema, Diss. Utrecht 1930.

[11] L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).

II.

Bij de toepasisng der kinetische theorie op de diffusie van een *mengsel* van elektrolyten stuit men reeds in het geval van ideale oplossingen op een moeilijkheid, die tot nu toe slechts in een bijzonder geval (n.l. het stationnaire), en wel door Planck[7]) volledig kon worden opgelost. De theorie van Planck kan echter niet worden toegepast op het diffusieproces met de gebruikelijke randvoorwaarden, waarbij twee oplossingen vrij in elkaar diffundeeren, terwijl op grooten afstand van de diffusielaag de concentraties praktisch konstant blijven en de gradienten dier concentraties evenals het potentiaalverval nul zijn. Dit probleem kon tot nu toe slechts met behulp van speciale benaderingen worden behandeld.

In dit proefschrift zijn de methoden van Henderson[8]) en van Sitte[9]) aan een kritiek onderworpen, terwijl ook de Plancksche theorie der stationnaire diffusie werd besproken (p. 49—54). Terwijl deze theorieën zich uitsluitend toeleggen op de berekening der diffusiepotentiaal en het diffusieproces zelf buiten beschouwing laten, zijn daarnaast eenige berekeningen uitgevoerd door Sitte[9]) en door Taylor[10]), die zich met het diffusie-beeld bezig houden. Een kritiek van deze berekeningen (p. 54—57) toont aan, dat men aan de resultaten van deze onderzoekers slechts geringe waarde kan hechten.

Op grond van de overweging dat de meeste diffusiepotentialen die in mengsels van elektrolyt-oplossingen optreden, tamelijk klein zijn, en het diffusieproces tot gevolg heeft, dat het concentratie- en potentiaalverloop steeds meer vervlakt, werd nu in dit proefschrift getracht een theorie der diffusie van elektrolyt-mengsels te ontwikkelen, die gebruik maakt van het feit, dat de genoemde gradienten klein zijn. Dit gebeurt in dien zin, dat quadraten van potentiaal- en concentratie-gradienten worden verwaarloosd tegenover uitdrukkingen, die in deze gradienten lineair zijn (p. 58). Voor zoover deze benadering geldt, blijkt de diffusiepotentiaal tusschen twee elektrolytmengsels onafhankelijk van den tijd te zijn. Tevens kan men uit de algemeene theorie eenige belangrijke gevolgtrekkingen maken omtrent de struktuur der diffusielaag. Het blijkt n.l., dat na verloop van tijd maxima en minima in de concentraties zullen optreden. Het ontstaan van dergelijke extrema kon experimenteel worden aangetoond (zie beneden).

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[7]) M. Planck, Wied. Ann. **40**, 561 (1890).

[8]) P. Henderson, Z. physik. Chem. **59**, 118 (1907), **63**, 325 (1908).

[9]) K. Sitte, Z. physik. **91**, 622 (1934).

[10]) P. B. Taylor, J. Phys. Chem. **31**, 1478 (1927).

Een overeenkomstige benadering kon worden toegepast op het speciale geval van twee elektrolyten met één gemeenschappelijk ion, waarbij echter concentraties nul moesten worden uitgesloten. Deze theorie (p. 61—70) leidt tot een uitdrukking voor de diffusiepotentiaal en geeft tevens een zeer plausibele beschrijving van het diffusieproces. De formule voor de diffusiepotentiaal werd aan de hand van experimenten getoetst (zie beneden). Een nader onderzoek van de theoretische resultaten (p. 70—75) leert, dat men in bijzondere gevallen tot plausibele uitkomsten geraakt.

Experimenten betreffende de diffusiepotentialen die in elektrolytmengsels optreden, zijn dikwijls in de literatuur vermeld. In dit proefschrift vindt men een korte bespreking van deze experimenten (p. 76). Al deze waarnemingen zijn bij tamelijk groote concentraties verricht (0.1 n. of hooger), terwijl de theorie de oplossingen ideaal onderstelt. De experimenteele moeilijkheden zijn echter ook bij deze concentraties reeds zeer aanzienlijk, en de verschillende onderzoekers zijn het zelden geheel eens.

Eigen experimenten werden verricht met mengsels van HCl en NaCl in water van 25°, en eenige malen met mengsels van HCl en KCl. Deze metingen zijn beschreven op p. 78—86. In die gevallen waarin de concentratieverhouding der elektrolyten in de beide in elkaar diffundeerende oplossingen niet te groot is, bleken de experimenten beter in overeenstemming met de in dit proefschrift verkregen formule dan met die van Henderson. De elektromotorische kracht van de betreffende elementen is echter steeds slechts bij benadering konstant, en de waarde der diffusiepotentiaal kan dan ook niet zeer nauwkeurig worden bepaald.

Naarmate men de genoemde concentratieverhoudingen grooter kiest, vertoonen de gemeten potentiaalverschillen hoe langer hoe grooter schommelingen, en tenslotte is geen betrouwbare waarde meer uit de metingen af te leiden.

Tenslotte konden in enkele gevallen de bovenbesproken extrema in de concentraties worden aangetoond (p. 86). En wel kon een zichtbaar maximum worden verkregen bij de diffusie van NaCl 0.1 n. in zeer verdunde NaOH-oplossing, waarbij phenolphtaleine als indicator dienst deed, terwijl een zichtbaar minimum optrad bij de diffusie van HCl 0.1 n. in een verdunde oplossing van indigokarmijn.

STELLINGEN.

I.

De meening van Gilman en Marple, als zou het intermediaïr optreden van organo-aluminium-verbindingen bij de synthese van Friedel en Crafts zeer onwaarschijnlijk zijn, moet worden verworpen.

H. Gilman en K. E. Marple, Rec. trav. chim. **55**, 134 (1936).

II.

De uitwisselingssnelheid van chloor tegen radioaktieve chloorionen is aanmerkelijk grooter dan de snelheid waarmee acetanilid met chloor reageert.

F. A. Long en A. R. Olson, J. Am. Chem. Soc. **58**, 2214 (1936).

III.

De gebruikelijke wijze waarop de regressievergelijkingen eener empirische twee-dimensionale frequentie-verdeeling worden bepaald, is niet van een zekere willekeur vrij te pleiten, en is niet in overeenstemming met de historische beteekenis van het begrip regressie.

Vergelijk: A. A. Tschuprow, Grundbegriffe und Grundprobleme der Korrelationstheorie, Leipzig—Berlin 1925, p. 68. J. B. D. Derksen, Inleiding tot de correlatie-rekening, Acad. Proefschr., Leiden 1935, p. 21.

IV.

De door Koenig aangegeven groepentheoretische klassificatie der thermodynamische vergelijkingen heeft slechts gering didactisch belang.

F. O. Koenig, Chem. Physics **3**, 29 (1935).

V.

Hoewel de gelijktijdige meting van het Maxwell-effect en het Kerr-effekt in oplossingen van hoog-molekulaire stoffen een middel kan zijn om uit te maken of men met eigen dubbelbreking dan wel met deformatie-dubbelbreking van de opgeloste deeltjes te doen heeft, wordt dit verschijnsel door minder eenvoudige regels bepaald dan Taylor aangeeft.

A. M. Taylor, Trans. Far. Soc. **32**, 307 (1936).

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A. M. Taylor, Trans. Far. Soc. 32, 307 (1936).

VI.

De dampspanning en de osmotische druk van zeer verdunde oplossingen wordt niet bepaald door specifieke oplos-krachten.

K. Fredenhagen, Z. Elektrochem. **43**, 28 (1937).
K. F. Herzfeld, Physik. Z. **38**, 58 (1937).

VII.

De golfmechanische theorie der Liesegangsche ringen, zooals die is ontworpen door Nikiforov en door Christiansen, kan een nauwkeurige kritiek niet doorstaan.

J. A. Christiansen en Inger Wulf, Z. physik. Chem. B **26**, 187 (1934).
W. K. Nikiforov, J. Chim. physique **32**, 585 (1935).

VIII

Het is ten zeerste gewenscht, dat de theorie der detonatiegolven van Jouguet—Hugoniot met behulp van nauwkeurig geschifte experimenteele gegevens wordt getoetst.

IX.

De experimenten van Gribnau, Krom en Kruyt kunnen niet als een dwingend bewijs gelden, dat een directe invloed van de lichtdruk bij de photophorese in colloidale oplossingen, afwezig is.

F. B. Gribnau, C. J. Krom en H. R. Kruyt. Rec. trav. chim. **56**, 565 (1937).

X.

De afwijkingen van de Debije—Hückel-grenswetten in elektrolytoplossingen treden op bij ongeveer dezelfde ionale concentratie als waar de optische eigenschappen van de concentratie afhankelijk beginnen te worden. Kortüm's conclusie, dat daarom deze verschijnselen aan dezelfde invloeden moeten worden toegeschreven, behoeft een nader bewijs.

G. Kortüm, Das opt. Verh. gelöster Elektrolyte, Samml. chem. und chem. techn. Vorträge **26**, 97 1936); Z. Eletrochem. **42**, 287 (1936).

XI.

Het is onwaarschijnlijk, dat het individueele gedrag van elektrolytoplossingen in zoo hooge mate door de polariseerbaarheid der ionen wordt bepaald, als Lange dit aannemelijk tracht te maken.

J. Lange, Z. physik. Chem. A **168**, 147 (1934), **177**, 193 (1936).

XII.

Aan de practische opleiding in qualitatieve analytische chemie dient vooraf te gaan een korte vóóropleiding in enkele eenvoudige manipulaties der quantitatieve analyse.