# THE THEORY OF CONCENTRATION POLARISATION.

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## 1. Introduction.

The velocity of electrochemical processes on the surface of an electrode immersed in a solution is governed by two factors : the velocity of approach of matter (ions or molecules) to the electrode and the velocity of the electrode processes proper.

In this paper we shall deal with the first factor. The molecular diffusion of ions in a liquid solution takes place extremely slowly. Therefore in practice the process is accelerated by artificially stirring the solution. It should be observed that if the solution is not purposely stirred then the irregular distribution of the density always gives rise to natural convection. The transport of ions to the surface of the electrode is thus brought about as a rule by convective diffusion.

The magnitude of the current flowing through the electrode depends to an extremely great degree on purely hydrodynamical factors. In a number of papers[1] we have discussed the influence of hydrodynamical factors on the velocity of heterogeneous reactions on interphase boundaries. The electrochemical reactions on the surface of an electrode are a particular case of such processes. The present communication will deal only with such reactions, it being first assumed that the electrode processes take place in the absence of noticeable overvoltage. To simplify the treatment we shall also limit ourselves to the case when the solution contains an excess of a neutral electrolyte.

The problem of the transport of matter in stirred solutions has been the subject of numerous theoretical and experimental investigations. Nernst[2] developed a qualitative theory of this process. He assumed that the main change in the concentration of the solution takes place in a very thin stationary layer contiguous to the electrode surface (Nernst's diffusion layer).

The diffusion current per unit surface area of the electrode is related to the concentration difference and the thickness of Nernst's diffusion layer $\delta'$ by the expression :

$$j_{\text{dif.}} = Dn_iF\frac{c_\infty - c_0}{\delta'} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[1] Levich, *Acta Physicochim.*, 1942, **17**, 257 ; *ibid.*, 1943, **19**, 117 ; *J. Physic. Chem.* (*Russ.*), 1944, **18**, 335 ; *ibid* (in press).

[2] Nernst, *Z. physik. Chem.*, 1904, **47**, 52 ; Nernst and Merriam, *ibid.*, 1905, **53**, 235.

where $D$ is the diffusion coefficient of the reacting particle, $n_i$ the change of valency during the electrochemical reaction and $c_\infty$ and $c_0$ are the concentrations of the solution far from the electrode and at its surface, respectively.

It is postulated in Nernst's theory that the thickness of the diffusion layer is independent of the nature of the electrochemical process on the electrode surface and of the character of the potential distribution. The absolute value of $\delta'$ depends on the régime of stirring, and must be found from experiment. In the usual practical cases of stirring, Nernst's diffusion layer has a thickness of the order of $10^{-3} - 10^{-5}$ cm., and depends on the régime of stirring according to the law :

$$\delta' = \frac{const.}{U^n}$$

where $U$ is the velocity of the liquid. The values of $n$ found by different authors[3] vary from $n = 0{\cdot}5$ to $n = 1$.

Although Nernst's theory was very fruitful in its time, it is now somewhat inadequate. In the first place this theory—at any rate, as usually formulated—contains the clearly unpermissible assumption that the liquid is stationary within the diffusion layer, which is contrary to the experimental data on the flow of liquids near solid surfaces.[4] Furthermore, the theory does not allow quantitative predictions to be made and it does not even offer any qualitative indications as to the dependence of $\delta'$ on the régime of stirring.

The inadequacy of Nernst's theory induced Eucken to reject the notion of a diffusion layer and attempt to develop a strictly hydrodynamical theory of the transport of matter in a moving solution.[5] Eucken did not, however, give a general theory of the transport of matter in a liquid, while the inaccuracy (see ref. (1)) of his initial equation invalidates his results for practical cases of stirring.

## 2. Equations of the Transport of Matter in a Moving Liquid.

In all cases of stirring of practical interest the Reynolds numbe $Re = \frac{Ul}{\nu}$ is great compared with unity ( and $Ul$ are, resp., the characteristic velocity and dimension, and $\nu$ is the kinematic viscosity of the liquid). The flow of the liquid, as is well known, can then be divided into a region of non-viscous flow and the Prandtl boundary layer contiguous to the surface of the solid.

We set ourselves the problem of studying the motion of ions or molecules in a liquid that is being stirred. To solve the problem of the transport of matter in a stirred solution it is necessary : (*a*) to solve the equations of convective diffusion and find the distribution of concentration in the solution, and subsequently (*b*) to find the distribution of the potential.

The equation of convective diffusion to the surface of a solid has the form :

$$U\frac{\partial c}{\partial x} + V\frac{\partial c}{\partial y} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \quad . \quad . \quad . \quad (2)$$

where $c$ is the concentration and $D$ the diffusion coefficient. The left-hand side expresses convective transport in the moving liquid, the right-hand side, ordinary diffusion. The boundary conditions of the problem are as follow. In the bulk of the solution far from the electrode, the concentration must have a constant value $c_\infty$. At the electrode surface the boundary conditions may vary. In the simplest case of constant potential

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[3] Brunner, *Z. physik. Chem.*, 1904, **47**, 56 ; Nernst and Merriam, *loc. cit.* ; Van Name, *ibid.*, 1910, **73**, 9, *Amer. J. Sci.*, 1910, **29**, 237 ; Wilderman, *Z. physik. Chem.* 1909, **66**, 445 ; King and Schack, *J. Amer. Chem. Soc.*, 1935, **57**, 1212.

[4] Fadge, *Proc. Roy. Soc. A*, 1932.

[5] Eucken, *Z. Elektrochem.*, 1932, **38**, 341.

the concentration at the electrode surface should have a constant value $c = c_0$. In particular for the régime of the limiting current, $c = 0$ on the electrode surface.

If equation (2) is compared with the equations of motion of a viscous liquid they are seen to be similar, the unknown concentration taking the place of the unknown velocity components in the equations of motion, and the diffusion coefficient that of the viscosity. Hence equation (2) can be solved in the same way as the Navier-Stokes equations in hydrodynamics.

The ratio of the two terms in (2) is in order of magnitude equal to

$$Pe = \frac{U\left|\frac{\partial c}{\partial x}\right|}{D\left|\frac{\partial^2 c}{\partial x^2}\right|} = \frac{Ul}{D}.$$

This dimensionless number is called the Pekle number. It corresponds to the Reynolds number for the flow of a liquid, and the régime of transport of matter is determined by the value of the Pekle number. If this number is great compared with unity, molecular diffusion can be neglected in comparison with the convective transport of matter; if it is small, on the contrary, molecular diffusion predominates.

The ratio of the Pekle and Reynolds numbers is a dimensionless number called the Prandtl number:

$$\frac{Pe}{Re} = \frac{\nu}{D} = Pr.$$

In liquids the Prandtl number is always large compared with unity; for water it is usually of the order of $10^3$. In gases, on the contrary, the Prandtl number is of the order of unity.

Due to the smallness of the diffusion coefficient, the Pekle number is large for the lowest values of the velocity, even when the corresponding Reynolds number is still small compared with unity. Molecular diffusion in liquids can therefore almost always be neglected in comparison with the convective transport of matter. When the Pekle number is large convective diffusion can be treated in a manner analogous to that applied in hydrodynamics to the flow past a body at large Reynolds numbers. Thus if the Pekle number is large compared with unity, then the term due to molecular diffusion in (2) can be dropped and the solution of the equation will be $c = \text{const.} = c_\infty$.

The concentration of matter will thus be constant throughout the volume of the liquid. However, this solution of the equation cannot be valid on the electrode surface where the condition $c = c_0$, or $c = 0$, must be satisfied. There should therefore be a thin layer of liquid near the surface of the electrode in which the concentration varies rapidly. In this layer the derivatives of the concentration with respect to the co-ordinates are very large and as a result the term in the right-hand side of (2) expressing molecular diffusion becomes comparable to the term in the left-hand side, despite the smallness of the diffusion coefficient.

Thus, at large Pekle numbers, as at large Reynolds numbers, the entire liquid can be divided into two parts; a region of constant concentration far from the surface of the reaction and a region of rapid variation of the concentration in the immediate vicinity of this surface. The latter extremely narrow zone is analogous to the Prandtl boundary-layer. In the Prandtl layer the viscosity of the liquid must be taken into account, whereas in the main volume of the flow it does not come into play. Similarly, in the liquid layer contiguous to the surface of the electrode molecular diffusion must be considered. This layer will therefore be called the diffusion boundary-layer.

The concept of the diffusion boundary-layer is evidently a generalisation of Nernst's layer. However, the two concepts are fundamentally different in that the velocity of flow of the liquid in the diffusion boundary-layer is not necessarily equal to zero. On the contrary, the diffusion and convection currents of matter are of the same order of magnitude. The diffusion boundary-layer is an analogue of the thermal boundary-layer in the theory of the transport of heat in liquids, but there is an important quantitative difference between the two: the diffusion boundary-layer is several times thinner than the thermal layer and hence its properties (e.g. the spatial distribution of matter) differ from the analogous properties of the thermal layer. We shall return further to the problem of the limits of applicability of the concept of the diffusion boundary-layer.

On this basis it was possible to develop a qualitative theory of the boundary-layer for an electrode of arbitrary form, using considerations of dimensions and to calculate the diffusion currents and the distribution of potential for a number of geometrically simple cases of flow. Only a short summary of the main results arrived at will be set forth here.

## 3. Diffusion Currents.

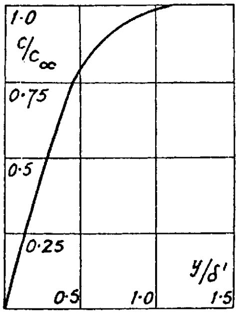

FIG. 1.—Dependence of the concentration on the distance from the electrode surface.

We have found the exact solution of the equations of convective diffusion of ions to an electrode having the form of a large disc revolving about an axis passing through its centre. The c.d. on the electrode is given by an interpolation formula, which coincides with that of Nernst's theory (I), if for the thickness of the diffusion layer we put:

$$\delta' = 1{\cdot}62\left(\frac{D}{\nu}\right)^{\frac{1}{3}}\left(\frac{\nu}{\omega}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (3)$$

where $\omega$ is the angular velocity of the electrode.

In Fig. 1 is represented the dependence of the concentration of the solution on the distance to the disc (in units of $\delta'$). We see that the main change in the concentration takes place at a distance of unit length so that in this sense $\delta'$ really represents the thickness of the diffusion boundary-layer. Comparing $\delta'$ and $\delta$, the thickness of the hydrodynamical boundary-layer in which the revolving disc exercises the main drag on the liquid, it can be shown that with an accuracy up to a factor of the order of unity, $\delta'$ equals the thickness of the layer dragged along divided by $\left(\frac{D}{\nu}\right)^{\frac{1}{3}}$, i.e. by the Prandtl number $Pr$ to the power $\frac{1}{3}$. The velocity of the liquid at the boundary of the diffusion layer is equal approximately to 10 % of the total velocity of flow and falls off gradually to zero at the solid surface.

The second case to be analysed in detail was that of an electrode in the form of a plate set in a laminar flow of liquid. For the limiting current régime when the concentration of the reacting ion at the electrode surface is zero, the density of the limiting current on the electrode is:

$$j_{\text{lim.}} = 0,\ 33\ n_i F D c_\infty \left(\frac{D}{\nu}\right)^{-\frac{1}{3}} b\left(\frac{U}{\nu x}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad (7)$$

where $U$ is the velocity of the liquid, $b$, the cross-section of the plate, $x$, the co-ordinate along the plate counting from the edge. The thickness of the diffusion layer is:

$$\delta' = 3\left(\frac{D}{\nu}\right)^{\frac{1}{3}}\left(\frac{\nu x}{U}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (5)$$

In the case of a plate the thickness of the diffusion boundary-layer increases as the square root of the distance $x$ from the edge of the plate and as the inverse square root of the velocity of the liquid. The diffusion boundary-layer is in this case too geometrically similar to the Prandtl boundary-layer, only thinner by a factor of $\left(\frac{D}{\nu}\right)^{\frac{1}{3}}$.

In addition to forced convection we have also considered the case of natural convection to a vertical plate. We furthermore calculated the diffusion current to the surface of an electrode in the form of a plate for the case of turbulent flow in the hydrodynamical boundary layer. The following expression was found for the total diffusion current in a plate of area S at $Pe \gg 1$ :

$$J_{\text{turb.}} \simeq C_f^{\frac{1}{2}} n_i F c_\infty (Pr)^{-\frac{2}{3}} US \quad . \quad . \quad . \quad . \quad (6)$$

The coefficient of resistance $C_f$ depends on the velocity of flow past the plate, so that $J_{\text{turb.}}$ is a complicated function of the velocity. $C_f$ is first proportional to $Re^{-\frac{1}{5}}$ and then varies with $Re$ logarithmically. Thus $J_{\text{turb.}} \sim Pr^{-\frac{2}{3}} U^{0.9}$ and at very great $Re$, $J_{\text{turb.}}$ is almost proportional to $U \; Pr^{-\frac{2}{3}}$.

The case of turbulent flow is important above all because, in order of magnitude, the results obtained can be applied to electrodes of non-streamlined form (sphere, cylindrical wire), and also to electrodes having a rough surface or angles, and to the case when the interior of a tube serves as electrode. In such conditions turbulent motion sets in comparatively easily in the boundary-layer and is the most frequent case encountered. It follows from the preceding results that although the properties of the boundary-layer depend on the régime of the motion and on the properties of the diffusing substance, nevertheless the limiting diffusion current can always be represented in a standard form (I).

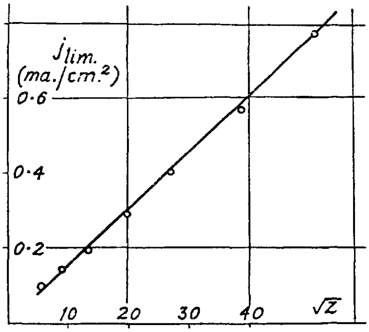

FIG. 2.—Relation between density of limiting current on a revolving disc and number of rotations per min.

Full curve—calculated from eqn. (3) and (1) ; circles—experimental values (according to Kabanov and Siver).

The author and Meiman recently considered the more general case when the velocity of the electrochemical reaction on the electrode surface is comparable with the velocity of transport of matter to the surface, and also the case when the c.d. on the electrode surface is artificially kept constant (e.g. by introducing a large resistance, which is the same for all the paths of the current).[6] It appeared that for a given régime of stirring and given properties of the ions the thickness of the diffusion boundary layer depends on the velocity of the electrochemical process or on the distribution of potential on the electrode. This circumstance brings out especially clearly the conventional nature of the notion of the diffusion layer which merely represents a convenient and illustrative form of describing the phenomenon and shows that the thickness of this layer is no real physical constant.

The agreement of the theory developed by the author with experiment was checked in the laboratory of Prof. A. Frumkin by Kabanov and Siver for the case of a limiting current on a disc. The electrochemical reaction was the reduction of dissolved oxygen to $H_2O_2$ on an amalgamated copper electrode. Fig. 2 shows the theoretical curve obtained with the help of

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[6] Levich and Meiman, *Acta Physicochim.* (in press).

eqn. (3) and the experimental points. We see that there is complete agreement between theory and experiment.

In the paper cited under ref. (1), the theory was compared with published experimental data on limiting currents. It was shown there that the disagreement between the data of different authors relating to the dependence of $n$ on the velocity, which was mentioned at the beginning of the present paper, is evidently to be attributed to the varying degree of turbulence of the liquid in the different experiments. The dependence of the limiting current on the diffusion coefficient of the ions ($J_{\text{lim.}} \sim D^{\frac{2}{3}}$) and the viscosity of the liquid $\left(J_{\text{lim.}} \sim \frac{D}{\nu}\left(\frac{\nu}{D}\right)^{\frac{1}{3}} \sim \frac{1}{\nu^{\frac{5}{6}}}\right)$ is found to agree with experiment. It is at present impossible to make a quantitative comparison of the formula for the current in the case of turbulent flow in the boundary-layer with the existing experimental data in view of their incompleteness.

In addition to the above calculation of diffusion currents to the surface of a solid electrode we calculated the diffusion to a liquid-liquid interface for a number of cases too.

Diffusion to a liquid electrode presents electrochemical interest in connection with the existence of a tangential motion of the surface of dropping mercury described by Krjukova.[7] This tangential motion stirs up the liquid and gives rise to a current on the dropping electrode which under suitable conditions can be comparable to, or even exceed, the current on a radially growing drop, as calculated by the Ilkovič-Rideal-MacGillavry equation. Hence when tangential motion of the drop is possible the current on the drop increases. This phenomenon has been given the name of a polarographic maximum of the second kind.

Convective diffusion to a liquid interface differs fundamentally from the discussed case of diffusion to a solid surface. This difference results from the change in the hydrodynamical conditions : at a liquid interface the tangential component of the velocity remains continuous and does not vanish as it does at a solid wall. Due to this, the conditions of stirring are much more favourable, and the current is greater than at a solid surface.

A calculation of the current to the surface of the drop yields the following expression for the total current $J$ on the drop : [8]

$$J = 8\sqrt{\frac{\pi}{2}}\left(\frac{DV}{a}\right)^{\frac{1}{2}}(c_{\infty} - c_0)a^2$$

where $V$ is the velocity of the liquid at the surface of the drop and $a$ the radius of the drop. This theory rests on the assumption that the interface is completely mobile, which is not so in the presence of a double electrical layer or of a layer of adsorbed molecules. In this case a number of new phenomena appear which, however, cannot be treated here (effect of a double-layer on the mobility of a liquid-liquid interface),[9] influence of surface-active substances.[10]

The above investigations were undertaken at the suggestion of Prof. A. Frumkin. In the course of the work the author had valuable discussions with Prof. A. Frumkin and Prof. L. Landau, to whom he expresses his sincere gratitude.

## Résumé.

On considère la vitesse à laquelle des corps (ions ou molécules) s'approchent d'une électrode, la réaction électrochimique à la surface de l'électrode étant regardée comme un cas particulier de l'influence de

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[7] Krjukova, *J. Physic. Chem.* (*Russ.*), 1946, **20**, 1179 ; *Acta Physicochim.* (in press).

[8] Levich, *Acta Physicochim.* (in press).

[9] Frumkin and Levich, *ibid.*, 1945, **20**, 769 ; 1946, **21**, 193.

[10] Frumkin and Levich, *ibid.* (in press).

facteurs hydrodynamiques sur la vitesse des réactions hétérogènes aux interfaces. Le traitement suppose qu'il n'y a pas de survoltage notable et que la solution contient un excès d'un électrolyte neutre. On donne la solution des équations qui se rapportent aux deux convections, naturelle et forcée, vers différents types d'électrodes et on compare la théorie avec les données expérimentales connues.

## Zusammenfassung.

Unter der Annahme, dass die elektrochemische Reaktion an der Elektrodenoberfläche als ein besonderer Fall des Einflusses von hydrodynamischen Faktoren auf die Geschwindigkeit von heterogenen Reaktionen an Phasengrenzflächen betrachtet werden kann, wurde die Geschwindigkeit, mit der sich Materie (Ionen oder Moleküle) der Elektrode nähern kann, theoretisch untersucht. Es wird dabei weiters angenommen, dass keine Überspannung vorhanden ist und dass die Lösung überschüssigen Neutralelektrolyt enthält. Die Gleichungen werden für natürliche und Zwangskonvektion zu verschiedenen Elektroden gelöst und die Theorie mit in der Literatur befindlichen experimentellen Daten verglichen.

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*Moscow.*

## *GENERAL DISCUSSION*

**Dr. A. K. Holliday** (*Liverpool*) said : In the paper of Grimley and Mott, reference is made to the experimental work of Julien, who found a negative $\zeta$-potential at the surface of capillaries of fused AgBr, in the presence of appreciable concentrations of $Ag^+$ ions. Julien also found that AgBr, freshly precipitated in the presence of excess $AgNO_3$, has a positive $\zeta$-potential, which decreases with time and becomes negative after a few hours ; thus the precipitated AgBr must undergo ageing before it can acquire the negative potential required by the theory of Grimley and Mott. For colloidal AgBr, determinations of the electrophoretic mobility of the particles which I have made indicate that a well-aged and dialysed AgBr sol acquires immediately an appreciable *positive* charge when $AgNO_3$ is added ; for example, 0·01 M. $AgNO_3$ gives a value of $\zeta$ not less than +45 mv. Moreover, AgBr particles, in the presence of a saturated solution of AgBr only, have a $\zeta$-potential of practically zero, as against the value of − 40 mv. given by Grimley and Mott. Clearly the assumption that the $\zeta$-potential of AgBr is always negative does not hold for the colloidal state, though it may be true for macroscopic crystals. The *immediate* appearance of a positive charge when $AgNO_3$ is added to an initially neutral AgBr sol seems to preclude any possibility that the charge can arise within the solid phase (e.g. by an increase of the concentration of interstitial $Ag^+$ ions inside the lattice). The conventional explanation, that $Ag^+$ ions are adsorbed at the surface of the AgBr, is discounted by Grimley and Mott, and I should like to know if they have any suggestion to make regarding the means by which AgBr particles do acquire a positive charge in the presence of an excess of $Ag^+$ ions.

**Mr. C. A. McDowell** (*Liverpool*) said : (1) With regard to the results just quoted by Holliday I should like to point out that Julien[1] found that though the negative charge on capillaries of fused AgBr was not reversed by silver nitrate, reversal was obtained when capillaries coated with colloidal AgBr were used. Similar results were observed by Kruyt. He[2] has shown that while the $\zeta$-potential of crushed barytes (as calculated

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[1] Julien, *Thesis* (Utrecht, 1933), see Butler, *Electrocapillarity* (Methuen, 1939), p. 121.

[2] Kruyt and Ruyssen, *Proc. Acad. Wetenschappen Amsterdam*, 1934, **37**, 624.

from electroendosmosis experiments) is always negative and is not reversed by $BaCl_2$, the $\zeta$-potential of precipitated $BaSO_4$ is positive in the presence of $BaCl_2$. It seems, therefore, that the $\zeta$-potential of a heteropolar surface depends on the origin of the material. It may be that the theory outlined by Mott and Grimley applies to fairly large and reasonably perfect crystals but not to particles of colloidal dimensions.

(2) There has been considerable [3, 4] discussion amongst colloid chemists as to the correct value of $D$, the dielectric constant of water, to use in calculations involving Poisson's equation and I should like to know if Professor Mott or Mr. Grimley would care to make any remarks about this.

**Prof. N. K. Adam** (*Southampton*) said: If the silver halide surface is always negatively charged, even in presence of an excess of silver ions over halide in the solution, we shall have to find another explanation of the action of fluorescent indicators, whose coloured anions are generally supposed to become adsorbed when an excess of silver ions in solution charges the surface positively.

**Dr. J. A. V. Butler** (*London*) said: There is another aspect of concentration polarisation. It is well known that it frequently happens that the substance concerned in the electrode process becomes so reduced in concentration that the potential must change until an alternative process can occur. The time at which this happens, the *transition time*, can be varied enormously by varying the current and is proportional to either $1/i$ or $1/i^2$ according to the circumstances.[5] The calculation of transition times when they are so short that a uniform diffusion layer can hardly be established is a very difficult problem and I should like to ask Dr. Agar if his calculations would be applicable to these circumstances.

**Dr. J. N Agar.** (*Cambridge*) (*communicated*): Proportionality between the transition time, $\tau$, and $1/i^2$ follows from the well-known treatment of diffusion at an electrode due originally to Sand.[6] This treatment assumes that there is no convection, but the results should be applicable to moving liquids provided $\tau \ll \delta^2/D$, where $\delta$ is the thickness of the diffusion layer and $D$ the diffusion coefficient. Under these conditions the concentration changes occurring during the interval $\tau$ are restricted to a thin zone of nearly stationary liquid in contact with the electrode, and supply of solute by convection should be negligible. The $1/i^2$ law is, in fact, commonly observed when $\tau$ is small.

There does not seem to be any satisfactory explanation of the linear relation between $i$ and $1/\tau$ found at higher values of $\tau$. The problem has been discussed recently by Levich,[7] for the case of a disc rotating at a steady speed. I do not think that dimensional methods would give much help.

**Dr. J. Weiss** (*Newcastle*) (*communicated*): In a paper which is in the press I have attempted to give an exact treatment of certain cases of mass transfer in heterogenous systems under conditions of (i) laminar flow, (ii) turbulent flow. Although a number of simplifying assumptions had to be introduced to make the mathematical treatment possible the results obtained show a close resemblance to certain empirical and dimensional equations.

**Dr. W. F. Berg** (*Wealdstone*) (*communicated*): This note is to draw attention to an experimental method for studying concentration distributions, due to Mr. T. R. Scott, then of I.C.I. Alkali Div., Ltd., which allows a close study of two-dimensional diffusion problems. Such studies seem to be called for in electrode chemistry, since there is much speculation and little detailed knowledge on the concentration distribution of

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[3] Rideal, *Surface Chemistry* (Cambridge, 1926).

[4] Lewis, *Trans. Faraday Soc.*, 1932, **28**, 597.

[5] Butler and Armstrong, *ibid.*, 1934, **30**, 1173; 1938, **34**, 806; *Proc. Roy. Soc. A*, 1933, **139**, 406.

[6] Sand, *Phil. Mag.*, 1900, **1**, 45.

[7] Levich, *Acta physicochim.*, 1944, **19**, 133.

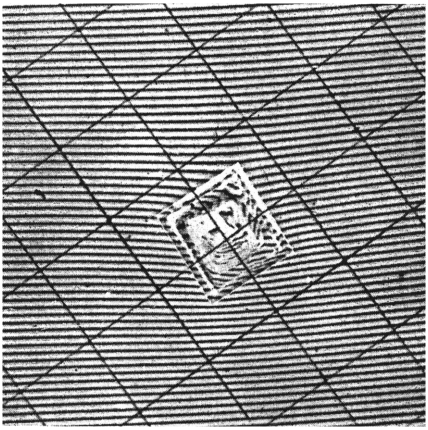

FIG. 1.

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ions. An example of the method is shown in Fig. 1.[8] The growing crystal with its surrounding supersaturated solution is held between two heavily surface-silvered optical flats. The system is placed on a microscope stage and illuminated with "parallel" light from a very small source of monochromatic light. The resulting fringes would be straight if the concentration of the solution were constant; the deflection of the fringes allows the concentration distribution to be worked out. The method would seem to be directly applicable to electrode problems, provided that the silver layers on the flats can be insulated from the electrolyte. This should be possible, for example, by evaporating a thin silica layer on top of the silver surface.

**Dr. A. F. H. Ward** (*Manchester*) (*communicated*): In connection with the papers of J. N. Agar and J. E. B. Randles which involve a consideration of diffusion to an electrode, it may be useful to draw attention to a recent rigorous treatment of this aspect of diffusion.[9] If the solute diffuses, from a constant concentration in bulk, to an interface such as an electrode, the differential equation of diffusion is easily soluble for the simple case when the concentration equals zero at the surface and may also be soluble if the variation of surface concentration with time can be expressed analytically. The new treatment allows the amount of diffusion to be calculated when the concentration at the surface varies with time in any manner whatsoever, provided that values of surface concentration are known at various times. An expression is derived which is amenable to graphical evaluation.

**Dr. B. Ershler** (*Moscow*) (*communicated*): I should like to make a few remarks concerning the interesting paper of Randles.

Formulæ (16), (17), (18) derived by Randles are identical with formula (2) in my paper [10] and the derivation are identical too. The value $R_2$ in (18) is equal to $r$ in (2). By comparing Randles' formulæ with (2) one should bear in mind that (16), (17), (18) give the resistance of the electrode without the double-layer and (2) the conductance of the electrode with the double-layer. Therefore by comparing (17) and (2) it is necessary to substitute $\bar{C}$ in (2) by $\bar{C}-C_1$ from formula (1) of my paper, and to calculate the resistance of the scheme consisting of the capacitance $\bar{\bar{C}} - C_1$, and the conductance $\bar{\bar{\Pi}}$ connected in parallel.

It should be mentioned that a theory of the behaviour of an electrode under applied alternating voltage in which the resistances due to concentration polarisation and to retarded electrode reaction are taken in series, was first developed by Frumkin, Dolin and Ershler [11] for the case of a reversible platinum hydrogen electrode. The formulæ derived in this paper were somewhat more complicated since in this case there are two stages of the electrode reaction itself, the discharge of the $H^+$ ion and the formation of the $H_2$ molecule.

It is interesting to note that the influence of the nature of the anions present in the solutions on the kinetics of the cation discharge found by Randles can be explained on the basis of Frumkin's correction of the theory of retarded discharge according to which the rate of the cation discharge should increase with increasing negative $\zeta$-potential values.[12] The latter as is known from electrocapillary data actually increases in the series

$$NO_3^- < Cl^- < Br^- < CNS^- < I^-.$$

For the case of the $H^+$ ion discharge such an influence of the anion was already demonstrated experimentally.[13]

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[8] From *Proc. Roy. Soc. A*, 1938, **164**, 79.

[9] Ward and Tordai, *J. Chem. Physics*, 1946, **14**, 453.

[10] *This vol.*, p. 269.

[11] *Acta Physicochim.*, 1940, **13**, 793.

[12] Frumkin, *Z. Physik. Chem. A*, 1933, **164**, 121.

[13] Jofa, Kabanov, Kuchinski, and Chistyakov, *Acta Physicochim.*, 1939, **10**, 317.

**Dr. J. H. Baxendale** (*Leeds*) (*communicated*) : When introducing his interesting paper on the kinetics of rapid electrode reactions, Mr. Randles said that further work on the temperature dependence of the rate constant $k$ had led to the evaluation of activation energies for the reactions. In the experiments reported in the paper the conditions are such that the rate constants of forward and reverse reactions are equal and presumably this applies also to the experiments at higher temperatures. Thus the activation energy measured is apparently that for both the forward and the reverse reactions. But unless the reactions are thermoneutral these cannot be equal, and it appears that the measured activation energy is not in fact the true activation energy. It does involve the heat of the electrode reaction as can be seen from the following.

As stated in the paper the rate constants measured are those for the electrode at *the equilibrium potential.* Using the kinetic picture of electrode reactions[14] we have that, if the electrode is at some potential $E$ with respect to the solution the rate constant for the forward reaction

$$M^{n+} + ne \underset{k_2}{\overset{k_1}{\leftrightarrows}} M(\text{Hg}) \quad . \quad . \quad . \quad . \quad (1)$$

is given by $k_2 = A_2 \exp. (Q_2 + \alpha E)/RT$ and for the back reaction $k_1 = A_1 \exp. (Q_1 - (1 - \alpha)E)/RT$ where $Q_1$ and $Q_2$ are the activation energies for the reactions when the electrode is at the same potential as the solution, and $\alpha E$ is the extent to which an applied potential $E$ affects the activation energy of the forward reaction. Now when $k_1 = k_2$, $E$ is the equilibrium potential of the electrode, so that the measured rate constants are functions of the equilibrium potential. Thus the temperature dependence of $k_2$ is given by

$$\frac{\mathrm{d}\log k_2}{\mathrm{d}(1/T)} = -\frac{Q_2}{R} - \frac{\alpha}{R}\,\frac{\mathrm{d}(nFE/T}{\mathrm{d}(1/T)}$$

We have for the temperature dependence of the electrode potential

$$\frac{\mathrm{d}(nFE/T)}{\mathrm{d}(1/T)} = -\Delta H,$$

where $H(= Q_2 - Q_1)$ applies to the forward reaction (1) so that the observed activation energy $Q$ is given by

$$Q = Q_2 - \alpha\Delta H = (1 - \alpha)Q_2 + Q_1$$

and it can easily be seen that the temperature dependence of $k_2$ leads to the same value. It therefore seems that it is not possible to obtain $Q_1$ and $Q_2$ from the observed activation energy without a knowledge of $\alpha$.

**Mr. J. E. B. Randles** (*Birmingham*) (*communicated*) : Breyer and Gutmann[15] derive an expression for the " Dynamic Resistance " and " Dynamic Capacitance " of an electrode on the implicit assumption that the expression relating current to electrode potential for a steady state of the diffusion layer determines the current changes due to an alternating potential of the electrode. It has been pointed out by Ershler and by myself in papers contributed to this Discussion (with reference to an earlier publication[16] by Breyer and Gutmann) that this assumption is inadmissible for alternating potentials of ordinary frequencies since no steady state of the diffusion layer is attained. This will certainly be the case, as stated by Ershler, at all frequencies down to a few C.P.S. It may be worth while to mention that this criticism is supported by the obvious non-correspondence of Breyer and Gutmann's theoretical results with experiment. For instance in their paper expression (4) for $R_D$ makes it independent of frequency which is not true in practice, $C_D$ should be

[14] Glasstone, Laidler and Eyring, *Theory of Rate Processes.*

[15] *This vol.*, p. 19.

[16] Breyer and Gutmann, *Trans. Faraday Soc.*, 1946, **42**, 645.

proportional to $1/\sqrt{\omega}$ which is not shown by expressions (16) and (17), and the statement (p. 25) that "in an ideal perfectly reversible reaction there appears no dynamic resistance" is untrue and is not even in agreement with their expression (4). Elaboration is unnecessary except to remark that the significance of the agreement between experimental and calculated results (Table I) is lessened by the presence of the arbitrary quantity "*d*" in the latter.

In reply to the useful point made by Dr. Baxendale, I feel it necessary to raise an objection to his implied definition of the "true activation energy" as that which exists when the electrical potentials of the electrode and solution are the same, since this state of equal potential cannot be satisfactorily determined or thermodynamically defined. At the equilibrium potential used experimentally the activation energies of both forward and reverse electrode reactions are equal, apart from any small difference due to difference in the frequency factors $A_1$ and $A_2$. These activation energies are equal to Baxendale's expression $Q = (1 - \alpha)Q_2 + \alpha Q_1$ and since it is impossible at present to known $Q_1$ and $Q_2$ precisely we must be content with determining $Q$.

**Dr. J. O'M. Bockris** (*London*) (*communicated*): The fundamental equations (1) and (8) of Breyer and Gutmann's paper appear to the present author to be quite inapplicable to the dynamic analysis needed for reactions in A.C. fields. The equations given are valid for steady states only.

**Dr. B. Breyer and Dr. F. Gutmann** (*Sydney*) (*communicated*): Ershler[17] and Randles[18] raised objections as to the applicability of the reversible electrode equation to processes involving superimposed alternating potentials. Ershler states that the general applicability of the equations derived by the present authors is "questionable, in so far as they have been derived from the assumption that at each value of the potential, arising on A.C. charging, a current flows through the electrode equal in strength to the steady state current at this potential. . . . Only on very violent stirring of the solution and at very low A.C. frequencies can the relations obtained by Breyer and Gutmann be valid." Randles states that "That equation refers to what is, in effect, a steady state of the diffusion layer, and is not applicable to the alternating current process."

In the last analysis, Ershler's and Randles' objections centre on the questions, (1) whether the electrode process itself, involving the supply or uptake of an electron by the electrode, is sufficiently fast to allow the application of the reversible electrode equation and (2) whether the diffusion equilibrium would not be disturbed to such an extent as to demand the introduction of some corrections to that equation. It is obvious that of the two processes the second will be the slower.

Randles' own derivations indicate that the ionic distribution round the electrode *can* follow the changes in instantaneous potential at the low frequencies considered. He assumes that the impressed alternating potential will lead to a *harmonic* variation in the concentrations of the ions facing the electrode, with a frequency equal to that of the A.C. and with a *constant* phase angle relative thereto. Randles' experimental results are in accord with the derivations obtained under these assumptions, which therefore can be accepted as justified.

It seems to the present authors, however, that the question raised is important enough to warrant closer investigation. It has to be proved that an ion under the influence of a potential gradient such as exists near the electrode, due to the alternating component of the field, moves fast enough in order to re-establish diffusion equilibrium within $\frac{1}{4}$ of an alternating cycle.

The mobility of, say, Cd ions is approx. $5 \times 10^{-4}$ cm./sec. for unity field, i.e. for a gradient of 1 v./cm. Nearly the whole of the applied potential appears across the electric double layer formed by the ions facing

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[17] Ershler, *this vol.*, p. 45.

[18] Randles, *this vol.*, p. 46.

the electrode. This is especially true in the presence of a supporting electrolyte. The bulk of the solution is substantially equipotential. It is generally assumed that the electrochemical processes take place within a space of a few ionic diameters in thickness. From the author's results, however,[19] it follows that the ionic concentration differs markedly from that in the bulk of the solution within a layer always less than $4 \cdot 5 \times 10^{-6}$ cm. thickness. Assuming this latter value, which is the least favourable for the present deliberation, and an R.M.S. value of the superimposed alternating potential of 45 mv., as used by the authors, gives an average field of about $10^4$ v./cm. Under this field, an ion will attain an average velocity of approx. 5 cm./sec. At a frequency of 50 C.P.S. therefore, an ion will be able to cover a distance of approx. $2 \cdot 5 \times 10^{-2}$ cm. This distance is about 20,000 times the thickness of the layer, wherein the electrochemical process makes itself felt.

There is also direct experimental evidence justifying the application of the reversible electrode equation to the A.C. processes under consideration. Matheson and Nichols [20, 21] adopted the cathode-ray tube to polarography. They linearly increased the potential applied to the electrode from zero to − 2·4 v. within 1/60th of a second at a repetition-rate of 30 per sec. Synchronising the dropping rate of the capillary to the repetition-rate yields current-voltage curves exactly in concordance to those obtained in ordinary polarography, on the screen of the cathode-ray tube. These authors also come to the conclusion that "these particular electrode reactions require not more than a few thousandths of a second to attain a steady state." This is in conformity to the present authors' considerations as outlined above. It should be pointed out, moreover, that the rate of change of potential in Matheson and Nichols' case is 144 v./sec., whereas in the present authors' case $|de/dt| = \omega V \sin \omega t$, i.e. a highest rate of 20 v./sec. The mean rate of change will be only 12·7 v./sec. There can be little doubt, therefore, as to the applicability of the reversible electrode equation to the reactions considered.

Referring to Prof. Frumkin's remark [22] as to the lack of a connection between the anomalous trend on his capacity curves and the maxima observed and calculated by the authors, it is desired to state that they accept his point of view.

**Dr. B. Ershler** (*Moscow*) (*communicated*): As it was shown by Frumkin [23] the electrocapillary zero point can be determined by measuring the capacity of the electrode in dilute electrolyte solutions, the zero point corresponding to the minimum capacity. The minimum capacity values determined experimentally in the case of a mercury electrode (7·8 μF./cm.² in a 0·001 N. solution) are somewhat larger than the theoretical values calculated from Stern's theory.[24] Thus the minimum value 5·75 μF./cm.² found by Breyer and Gutmann, although it agrees with the theoretical value calculated by Frumkin and Vorsina is almost certainly too low.

**Dr. B. Breyer and Dr. F. Gutmann** (*Sydney*), (*communicated*): In a communication to this Discussion Randles first reiterates his objection to our treatment of electrode reactions in alternating fields on the assumption that the reaction would be too slow to allow attainment of an equilibrium state at the frequency employed (50 c./sec.). We have shown in a communication to this discussion (which probably had not been printed at the time Randles wrote his comment) from theoretical considerations as well as from experimental evidence that this objection cannot be maintained.

[19] Breyer and Gutmann, *this vol.*, p. 24.

[20] Matheson and Nichols, *Trans. Amer. Electrochem. Soc.*, 1938, **73**, 193.

[21] Kolthoff and Lingane, *Polarography* (New York, 1941), p. 236.

[22] Frumkin, *this vol.*, p. 57.

[23] *Trans. Faraday Soc.*, 1940, **36**, 124.

[24] Vorsina and Frumkin, *Compt. Rend.*, *U.R.S.S.*, 1939, **24**, 915.

In his second comment, Randles states that our theoretical results are not in accord with his experimental evidence, since our theory would make the dynamic resistance $R_D$ independent of frequency, which is not true in practice. We wish to point out that Randles has expressed his results in terms of an equivalent *series* circuit while we have treated our case in terms of a parallel arrangement of the dynamic resistance and the dynamic capacitance. If our parallel circuit is transformed into the series arrangement employed by Randles, then by virtue of the well-known transformation equation :

$$R_S = \frac{R_D}{1 + \omega^2 C_D{}^2 R_D{}^2},$$

(where $R_S$ is the equivalent series resistance and $R_D$ and $C_D$ the dynamic resistance and capacitance, respectively), the resulting equivalent dynamic series resistance $R_S$ becomes a function of frequency.

Randles furthermore criticises our treatment because it yields an expression for the dynamic capacitance $C_D$ which is not proportional to $1/\sqrt{\omega}$, as required by Randles' work. In reply to this we wish to point out that the reactions studied by Randles and those treated by ourselves, while closely related, are by no means identical.

Our theory is based upon the continuous passage of direct current. In Randles' experiments there is no direct current present. Therefore the *average* flux of diffusing substance integrated over a whole cycle will be zero in Randles' case, while having a finite value in the processes which we are considering. For zero direct current our theory is inapplicable by its very derivation from the assumption of a steady current flow, exactly as Randles' theory is inapplicable to our case in view of his basic assumption of the absence of a D.C. component. If, in Randles' eqn. (1), a steady term were superimposed upon the alternating one, his solution of the diffusion equation would no longer apply. In Randles' case the flux of diffusing substance is exclusively determined by the alternating current flow. Its average is zero and the reaction rate is governed by the instantaneous alternating potential. In our case, due to the passage of a direct current, the rate of the reaction will be decisively dependent on the rate of diffusion to the dropping-mercury electrode from the bulk of the solution (Ilkovic equation). In other words, in the presence of D.C. the charge density in the proximity of the electrode is primarily governed by the steady current flow and, therefore, less dependent on frequency than in Randles' case.

As to Randles' criticism of our statement, that " in an ideal perfectly reversible reaction there appears no dynamic resistance," we desire to point out that any energy expended in the resistive part of an impedance obviously represents an irreversible loss in contradistinction to that part of the energy which is electrostatically stored in the ionic field and which gives rise to the dynamic capacitance. Our statement referred to an idealised electrode without resistance, a system which certainly cannot be realised in our physical world. In any real experiment the resistance effects have to be considered, as has been done in our eqn. (4) and in the reactions studied by Randles in his eqn. (16).

Our quantity $d$, which Randles considers arbitrary, has in the meantime been given what we think a rather firm theoretical foundation as the thickness of the " active space " wherein the electrode process occurs. A theoretical treatment giving a mathematical derivation based upon the Debye equation has now been completed by us with the view to publication at an early date.