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Introduction

When an ideally polarizable electrode, which by definition does not pass a faradaic current, is charged rapidly in a dilute solution, the concentration and charge distributions are disturbed at distances much greater than the equilibrium thickness of the diffuse double layer. For example, if such an electrode in a 0.001 M KCl solution is charged from zero to $-10\mu C/cm^2$, the disturbance reaches to about 5300 Å. The anions have been driven from this region, leaving the cations exposed and forming an extended region of charge. The cations are consequently driven, largely by their own charge, toward the electrode surface where they form a thin, diffuse layer.

As Gibbs has pointed out, such nonequilibrium, transient effects are important only when the solution is dilute and the change of surface concentration is large. The change should also be effected in a time short compared to the relaxation time for re-equilibration. Thus it is appropriate to consider charging the interface at $10\ A/cm^2$ for 1 μs in a millimolar solution. This paper treats the movement of charge and the decay of the observed potential after the charging period.

In the first approximation, these processes can be described with neglect of diffusion. The mathematical problem is then hyperbolic and can be solved exactly by the method of characteristics. Figure 1 illustrates the characteristic curves in terms of a dimensionless time τ and a dimensionless distance X from the surface. The surface was initially uncharged, and during the charging period the region with no anions increases linearly with time. Outside this region the initial, uniform

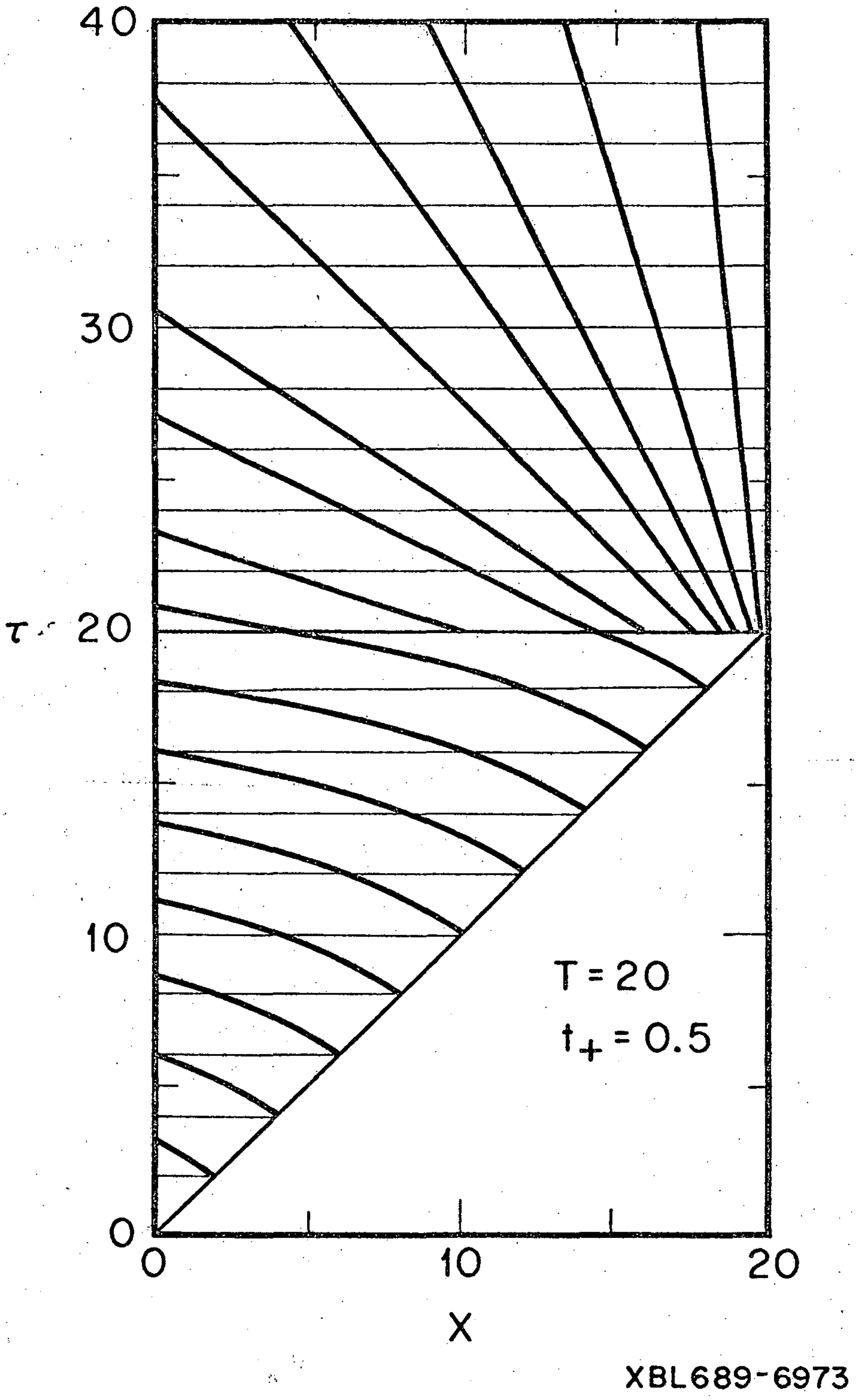

Figure 1. Characteristic curves for the charging and decay periods.

concentration of both anions and cations prevails, and there is no net charge density. After the charging period, here taken to be $\tau = T = 20$, this region no longer increases in thickness. One set of characteristic curves is the lines of constant τ. The other set shown on the figure is the paths of the cations as they move toward the electrode.

With neglect of diffusion, the cations accumulate at the electrode surface. One can, as a second approximation, treat the diffuse nature of this charge distribution. During the charging period it is also possible to treat the diffuse nature of the boundary between the charged and charge-free regions. At long times it is necessary to treat the back-diffusion of the electrolyte, not as a second approximation, but as a primary factor in determining the decay of the potential. An analysis along these lines thus is not exact, but it does give considerable insight into the factors involved and a semi-quantitative prediction of the decay of the observed potential.

Mathematical Formulation

For a symmetric electrolyte with $z_+ = -z_- = z$, the fluxes of cations and anions in the direction x normal to the surface are

$$N_+ = -D_+ \partial c_+/\partial x + (zD_+F/RT)\, c_+ \mathcal{E} \,, \tag{1}$$

$$N_- = -D_- \partial c_-/\partial x - (zD_-F/RT)\, c_- \mathcal{E} \,, \tag{2}$$

the conservation equations take the form

$$\frac{\partial c_+}{\partial t} = D_+ \frac{\partial^2 c_+}{\partial x^2} - \frac{zD_+F}{RT} \frac{\partial c_+ \mathcal{E}}{\partial x} \,, \tag{3}$$

$$\frac{\partial c_-}{\partial t} = D_- \frac{\partial^2 c_-}{\partial x^2} + \frac{zD_-F}{RT} \frac{\partial c_- \mathcal{E}}{\partial x} \,, \tag{4}$$

and Poisson's equation is

$$\partial \mathcal{E}/\partial x = (zF/\epsilon)(c_+ - c_-) \ . \tag{5}$$

For charging a large planar electrode at a constant current density, the electric field $\mathcal{E}$ approaches a constant -B far from the electrode, where B is positive for the charging process considered here, which drives cations toward the electrode. It is convenient to use this constant in forming dimensionless variables and parameters:

$$\left.\begin{aligned} &C = \frac{c_+ + c_-}{2c_\infty} , \quad Q = \frac{c_+ - c_-}{2c_\infty} , \quad E = \frac{\mathcal{E}}{B} , \quad X = \frac{2zc_\infty F}{\epsilon B} x , \\ &\tau = \frac{\kappa_\infty t}{\epsilon} = \frac{z^2 F^2 c_\infty (D_+ + D_-)}{RT\epsilon} t, \quad A = \frac{2c_\infty RT}{\epsilon B^2} \end{aligned}\right\} \tag{6}$$

The equations then become

$$\frac{\partial C}{\partial \tau} = A \frac{\partial^2 C}{\partial X^2} - \frac{\partial EQ}{\partial X} + (t_+ - t_-) \left(A \frac{\partial^2 Q}{\partial X^2} - \frac{\partial EC}{\partial X}\right) , \tag{7}$$

$$\frac{\partial Q}{\partial \tau} = A \frac{\partial^2 Q}{\partial X^2} - \frac{\partial EC}{\partial X} + (t_+ - t_-) \left(A \frac{\partial^2 C}{\partial X^2} - \frac{\partial EQ}{\partial X}\right) , \tag{8}$$

$$\partial E/\partial X = Q , \tag{9}$$

where $t_+ = 1 - t_- = D_+/(D_+ + D_-)$.

The initial conditions are

$$C = 1 \quad \text{and} \quad Q = 0 \quad \text{at} \quad \tau = 0 , \tag{10}$$

implying a zero charge on the electrode and no specific adsorption. Far from the electrode,

$$E \rightarrow -1, \quad C \rightarrow 1, \quad \text{and} \quad Q \rightarrow 0 \quad \text{as} \quad X \rightarrow \infty \tag{11}$$

during the charging period. At the end of the charging period when the current is interrupted, the electric field E increases everywhere by 1 while the concentration and charge distributions remain unchanged. At the surface, which may be taken to be the inner limit of the diffuse layer, the fluxes of anions and cations are zero

$$A\,\partial C/\partial X = QE \quad \text{and} \quad A\,\partial Q/\partial X = CE \quad \text{at} \quad X = 0-, \tag{12}$$

implying the absence of faradaic reactions and specific adsorption of cations. The last conditions can be replaced by

$$\int_0^\infty (C-1)dX = (t_+-t_-)\tau \quad \text{and} \quad \int_0^\infty Q dX = \tau\ . \tag{13}$$

Neglect of Diffusion

As a first approximation, let us neglect diffusion and treat the system behavior when the anions and cations move by migration alone. Far from the electrode the concentration remains uniform, and the anions and cations move with constant velocities. This depletes the solution of anions near the electrode, and in the absence of diffusion there is a growing region in which anions are virtually absent. In this region, which extends to $X = 2t_-\tau$, we thus have $C = Q$. The remaining cations form a region of extended charge where the electric field increases by Poisson's equation 9. Hence the cation speed increases as the cations approach the electrode surface. Then at $X = 0$, the cations pile up and in the absence of diffusion form a surface charge density σ. In the region of extended charge and without diffusion, the electric field and charge density obey the equations

$$\frac{\partial Q}{\partial \tau} = -2t_+\frac{\partial EQ}{\partial X} \quad \text{and} \quad \frac{\partial E}{\partial X} = Q\ . \tag{14}$$

During the charging period $\tau < T$, the solution is

$$E = [t_- - (1-t_+X+2t_+t_-\tau)^{\frac{1}{2}}]/t_+ \,, \tag{15}$$

$$Q = 1/2(1-t_+X+2t_+t_-\tau)^{\frac{1}{2}} \,, \tag{16}$$

which satisfies the boundary conditions $E = -1$ and $Q = 1/2$ at $X = 2t_-\tau$. When the current is interrupted at $\tau = T$, the electric field E increases by 1 and takes the value $E = 0$ for $X > 2t_-T$. Subsequently, the region of extended charge no longer increases but has the constant thickness of $2t_-T$. During the decay period $\tau > T$, the charge density and electric field in this region are

$$t_+E = 1 + t_+\tau' - [(1+t_+\tau')^2 - t_+(X-2t_-T)]^{\frac{1}{2}} \,, \tag{17}$$

$$Q = 1/2[(1+t_+\tau')^2 - t_+(X-2t_-T)]^{\frac{1}{2}}, \tag{18}$$

where $\tau' = \tau - T$. This satisfies the condition at $\tau = T$ prescribed by equation 16 and the condition that $E = 0$ at $X = 2t_-T$. The details of the derivation by the method of characteristics are interesting in themselves but are not essential to an understanding of the processes of charging and decay.

For $t_+ = 0.5$, the charge distribution is sketched in figure 2 for the charging period and in figure 3 for the decay period. During the charging period, Q is maintained at a value of 0.5 at $X = 2t_-\tau$ by the arrival of cations from the bulk solution. The presence of the free charge density increases the electric field and hence increases the speed of the cations as they move through this region. This results in a decrease in the concentration of cations, since they arrive at the electrode surface sooner. The cation trajectories are indicated in figure 1.

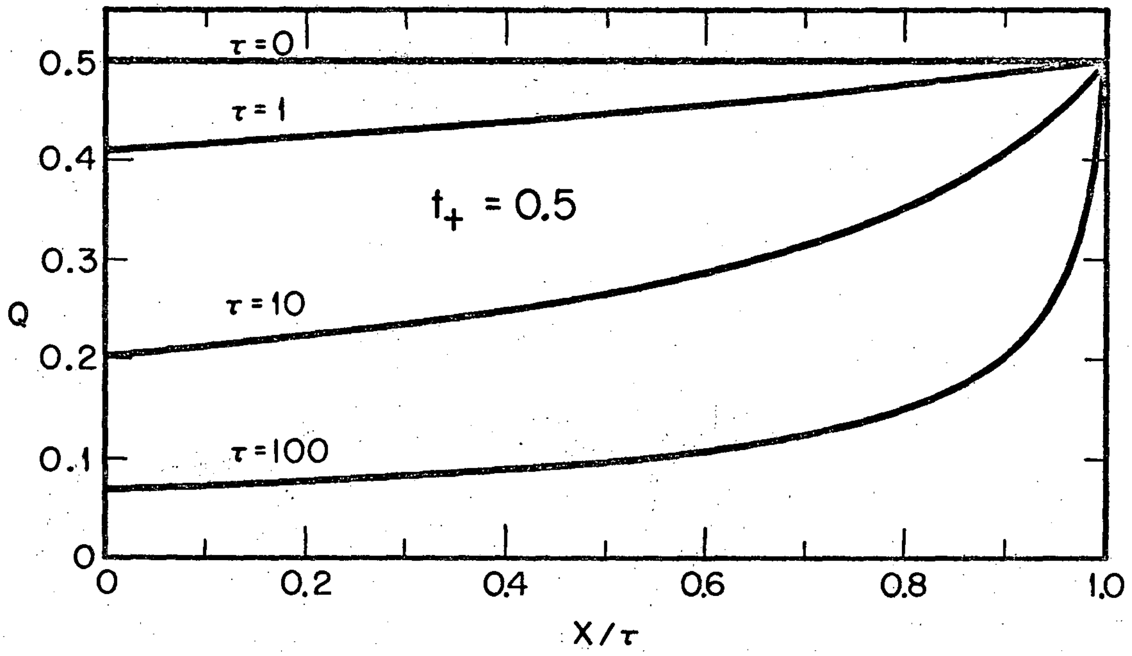

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Figure 2. Distribution of extended charge during the charging period.

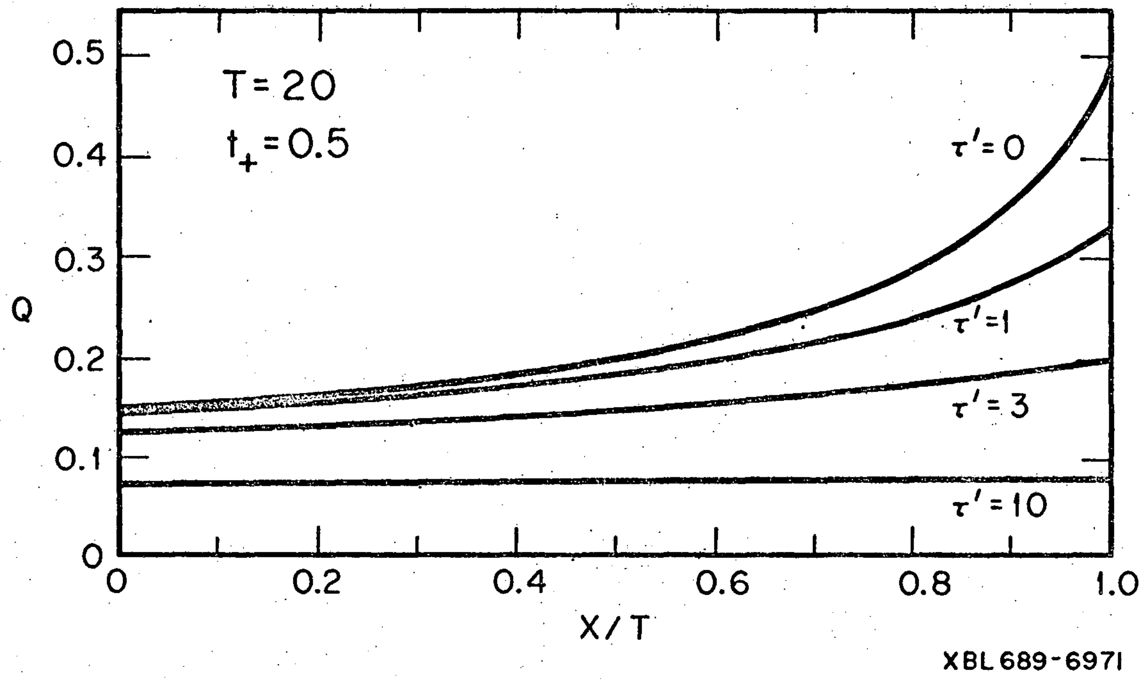

Figure 3. Distribution of extended charge after the charging period. (T=20)

During the decay period an electric field continues to exist due to the presence of the cations themselves. Hence the cations continue to migrate from the region of extended charge toward the electrode surface, as indicated in figure 3.

The (dimensionless) potential at $X = 0$, relative to the bulk solution but corrected for the ohmic drop which would exist if there were no charge layer, will be denoted by Φ. The contribution to this potential due to the extended charge is

$$\Phi_1 = \int_0^\infty (E+1)dX = \frac{2}{3t_+^2}\left[3t_+t_-\tau + 1 - (1+2t_+t_-\tau)^{3/2}\right] \tag{19}$$

during the charging period $\tau < T$ and is

$$\Phi_1 = \int_0^\infty EdX = \frac{2}{3t_+^2}\left\{(1+t_+\tau')3t_+t_-T + (1+t_+\tau')^3 - \left[(1+t_+\tau')^2 + 2t_+t_-T\right]^{3/2}\right\} \tag{20}$$

during the decay period $\tau > T$. This will represent an important contribution to the observed potential but will be modified by other considerations in the subsequent section.

The dimensionless surface charge density is composed of a part σ_2 comprising the extended charge and a part σ comprising the diffuse layer near the electrode surface as follows:

$$\sigma_2 = \tau - \sigma = \left[(1+2t_+t_-\tau)^{1/2} - 1\right]/t_+ \quad \text{for } \tau < T\text{ ,} \tag{21}$$

$$\sigma_2 = T - \sigma = \left\{\left[(1+t_+\tau')^2 + 2t_+t_-T\right]^{1/2} - 1 - t_+\tau'\right\}/t_+ \quad \text{for } \tau > T. \tag{22}$$

The Diffuse Part of the Double Layer

In the absence of diffusion, cations pile up at $X = 0$ forming the surface charge density σ. In reality these cations will form a diffuse layer, but one which is thin compared to the region of extended charge. Since anions are excluded from this region, $Q = C$, and equations 7 and 8 become

$$\frac{1}{2t_+}\frac{\partial Q}{\partial \tau} = A\frac{\partial^2 Q}{\partial X^2} - \frac{\partial EQ}{\partial X} . \tag{23}$$

In this region it is appropriate to use the variables

$$e = E/\sigma(\tau), \quad q = 2AQ/\sigma^2, \quad y = X\sigma/2A , \tag{24}$$

since these variables are now of order unity in the diffuse layer. Equations 23 and 9 and conditions 12 then become

$$\frac{1}{2}\frac{\partial^2 q}{\partial y^2} - \frac{\partial eq}{\partial y} = \frac{A}{t_+\sigma^3}\left[2q\frac{d\sigma}{d\tau} + \sigma\frac{\partial q}{\partial \tau} + y\frac{\partial q}{\partial y}\frac{d\sigma}{d\tau}\right] , \tag{25}$$

$$\partial e/\partial y = q \tag{26}$$

$$\partial q/\partial y = 2qe \text{ at } y = 0. \tag{27}$$

For small values of A/σ^3, the right side of equation 25 can be dropped. The solution of the problem posed here then constitutes the basis of the inner expansion of a singular-perturbation series, where the results of the preceding section are the basis of the outer expansion.

With this approximation, integration of equation 25 subject to condition 27 gives

$$2eq = \partial q/\partial y = (\partial q/\partial e)(\partial e/\partial y) = q\ \partial q/\partial e. \tag{28}$$

A second integration gives

$$q = \partial e/\partial y = e^2 - e_\infty^2 . \tag{29}$$

The constant of integration is evaluated by matching with the outer solution; q is of order A/σ^2 and e is of order unity in the outer solution. Thus $q \to 0$ and $e \to e_\infty$ as $y \to \infty$, where e_∞ is the value of e in the outer solution as $X \to 0$. A third integration gives

$$y = \frac{1}{2e_\infty} \ln\left(\frac{1}{F}\frac{e-e_\infty}{e+e_\infty}\right), \tag{30}$$

where $F = (e_o-e_\infty)/(e_o+e_\infty)$. After rearrangement, the solution for e and q is

$$e = e_\infty \frac{1+F\ e^{2e_\infty y}}{1-F\ e^{2e_\infty y}} \quad \text{and} \quad q = \frac{4F\ e_\infty^2 e^{2e_\infty y}}{(1-F\ e^{2e_\infty y})^2}\ . \tag{31}$$

The charge σ has a greater spatial distribution than was assumed in the last section. Hence it makes an additional contribution to the potential:

$$\Phi_2 = 2A \int_0^\infty (e-e_\infty)\, dy = 2A \ln(1-F)\ , \tag{32}$$

where

$$\left.\begin{aligned} 1-F &= \frac{1+\tau-\sigma}{1+\tau-\frac{1}{2}\sigma} \quad \text{for } \tau < T\ . \\ 1-F &= \frac{T-\sigma}{T-\frac{1}{2}\sigma} \quad \text{for } \tau > T\ . \end{aligned}\right\} \tag{33}$$

Back Diffusion of Excluded Salt

The potential should decay to the value corresponding to the equilibrium diffuse double layer at the given charge density. However, $\sigma \to T$ as $\tau \to \infty$ and consequently Φ_2 becomes infinitely large. As the extended charge decays to zero, the contribution of the diffuse layer is no longer small compared to that of the extended charge, and the above analysis is no longer valid. Instead the diffuse layer begins to interact with the salt solution of anions which had been driven away from the electrode. When the extended charge has decayed, the salt solution from $X > 2t_-T$ begins to diffuse back into the essentially pure water left behind.

If there is no charge density in the solution ($Q = 0$), equations 7 and 8 become

$$\partial EC/\partial X = (t_+ - t_-)\, A\partial^2 C/\partial X^2 \,, \tag{34}$$

$$\partial C/\partial \tau = 4t_+t_- A\partial^2 C/\partial X^2 \,. \tag{35}$$

If equation 35 is solved subject to the conditions

$$\left.\begin{array}{lll} C = 0 & \text{for} & X < 2t_-T \\ C = 1 & \text{for} & X > 2t_-T \end{array}\right\} \text{ for } \tau = T \,,$$

$$\partial C/\partial X = 0 \quad \text{at} \quad X = 0 \,,$$

$$C \rightarrow 1 \quad \text{as} \quad X \rightarrow \infty \,,$$

then the concentration C_0 at $X = 0$ approaches the equilibrium value as follows:

$$C_0(\tau') = \operatorname{erfc}\, [\tfrac{1}{2}\, T(t_-/t_+A\tau')^{\frac{1}{2}}] \,. \tag{36}$$

The time required for the back diffusion will be large compared to that for decay of extended charge if the solution is dilute and the charge is large. It will then at some time become appropriate to consider the diffuse layer of charge σ to interact with a solution having the concentration C_0. The value of C_0 will be changing so slowly with time that the diffuse layer is essentially in equilibrium, giving rise to a potential difference of

$$\Phi_3 = -2A \sinh^{-1}[\sigma/2(AC_0)^{\frac{1}{2}}] \,. \tag{37}$$

At the same time there will be a liquid-junction or diffusion potential in the bulk solution between the concentrations of C_0 and 1. This value calculated from equation 34, is

$$\Phi_4 = -(t_+ - t_-)A\, ln\, C_o\ . \qquad (38)$$

Potential Decay Curves

Figures 4 and 5 show how the potential decays after rapid charging in millimolar solutions of KOH, KCl, and HCl. Some of the parameters involved are given in table 1. The potential is calculated from $\Phi_1 + \Phi_2$ or from $\Phi_1 + \Phi_3 + \Phi_4$, whichever is less in magnitude. Figure 4 also shows part of the charging period, where the potential $\Phi_1 + \Phi_2$ has been corrected for ohmic drop as outlined earlier.

The potential due to the extended charge itself decreases fairly rapidly, a characteristic time for the process being ϵ/κ_∞. The potentials associated with back diffusion of excluded salt are characterized by a larger time constant, L^2/D, where L is the distance of anion exclusion and D is the diffusion coefficient of the salt. These characteristic times are given in table 1. At short decay times, the extended charge resulting from the exclusion of anions leads to a large, rapidly decaying potential. At long times the back diffusion of salt into the relatively pure solvent in the disturbance region determines the potential of the diffuse layer.

At intermediate times, a completely satisfactory mathematical description has not been possible, but these two concepts can be superimposed qualitatively to provide a reasonably complete and accurate picture of the decay process. One may expect that the presence of the extended charge tends to continue to exclude anions, while the back diffusion of salt increases the conductivity and speeds the decay of the extended charge.

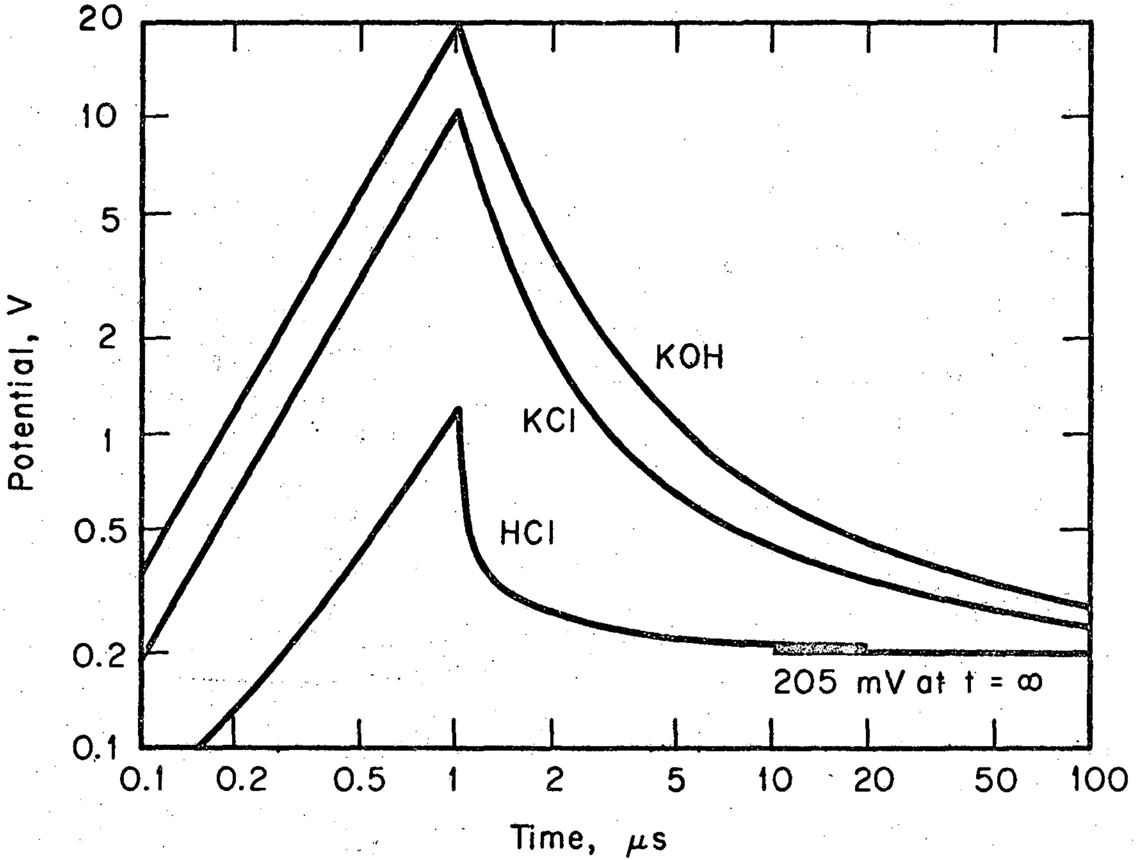

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Figure 4. Potential at inner limit of diffuse double layer. Charge produced in 1 millimolar solutions at 25°C by passing 10 A/cm^2 for 1 μs. During the charging period, the potential is corrected for ohmic drop.

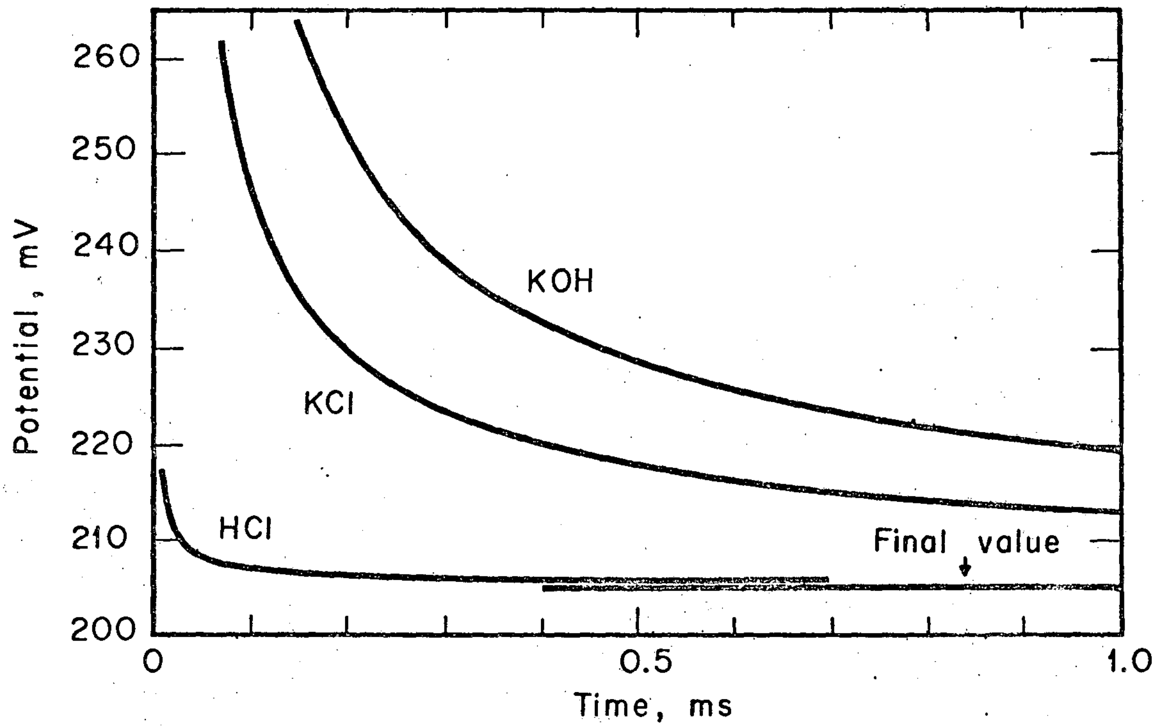

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Figure 5. Decay of potential to 1 millisecond.

Table 1. Parameters for charging at 10A/cm^2 for 1 μs in various millimolar solutions at 25°C.

	KOH	KCl	HCl
t_+	0.2695	0.4905	0.8208
A	0.5317	0.1606	1.299
L, disturbance distance, Å	7570	5280	1857
Debye length, Å	96.1	96.1	96.1
T for 1 μs	39.33	21.61	61.47
ϵ/κ_∞, μs	0.0254	0.0463	0.0163
L^2/D, μs	201	140	10.3

Discussion

This analysis of rapid charging of double layers in dilute solutions treats the limited rates of ion movement and the departures from equilibrium in the charge region. In Anson's[1] treatment of such problems, the diffuse charge layer was assumed to be in equilibrium with an electrically neutral solution whose concentration at the surface varied with time as a consequence of the charge injection. A similar model is used here for large decay times, but the establishment of conditions in the bulk solution at early times is different when one considers the formation and decay of the extended charge.

Anson and Martin[2] present potential decay curves for hanging mercury drops following charge injection and discuss the pertinent literature. They point out that the usual assumption of an equilibrium double layer in a transient or alternating-current experiment remains valid except under extreme conditions of dilute solutions, large charge changes, and short response times. In the curves of Anson and Martin, the potential decays more slowly than can be explained by the analysis of the present paper.

We should mention here the expected consequences of making experiments under conditions different from those treated in this paper. If the initial charge is +5 $\mu C/cm^2$ and the final charge is -10 $\mu C/cm^2$, then the extended charge region will not form until the stored anions have been driven away from the surface, and by that time $5t_+/t_-$ $\mu C/cm^2$ of cations will already have been driven to the surface. Thus if

$$-\sigma_{final} < t_+\sigma_{initial}/t_- ,$$

no region of extended charge will be formed, and departures from the final, equilibrium potential should be small. The region of extended charge, if it exists, can be treated by methods not essentially different from those used in the present paper.

In the experiments of Anson and Martin, the current varies with time, decreasing exponentially with time throughout the experiment. This difference probably has little practical consequence because the experimental observation times are much larger than the time constant for the decay of current and are so large that the extended charge has decayed and the ohmic potential drop is negligible. The primary differences would occur in the early charging period and are not subject to observation.

In this paper it has been assumed that specific adsorption is absent, a good assumption for cations. Specific adsorption would modify the behavior of the diffuse layer and the observed potential, particularly at large times, but it would have little effect on the extended charge since the ions must reach the surface before specific adsorption is possible.

We should also like to mention in passing that is is possible to give a more accurate account of the diffuse nature of the boundary between the extended charge and the bulk solution during the charging period. This has not been included here since the potential at the surface would not be changed significantly.

Conclusions

Large, non-equilibrium potentials should be produced by large, fast changes in the charge of an ideally polarizable electrode in a dilute solution. This phenomenon, which can be analyzed by neglecting diffusion, is associated with a charged region much thicker than the equilibrium diffuse charge layer. Such potentials should decay faster than can be observed in most experiments. Non-equilibrium potentials associated with the back diffusion of salt into the space vacated by the extended charge should be smaller in magnitude but persist for longer times.

Acknowledgment

The problem treated here was posed to the author by Fred C. Anson.

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Nomenclature

A - dimensionless parameter, see equation 6.

B - magnitude of electric field far from electrode (V/cm).

c_i - concentration of species i (mole/cm^3).

C - dimensionless average concentration of cations and anions.

D_i - diffusion coefficient of species i (cm^2/sec).

e - dimensionless electric field.

E - dimensionless electric field.

$\mathcal{E}$ - electric field (V/cm).

F - Faraday's constant (C/equiv).

F - see equation 33.

L - disturbance distance, cm.

N_i - flux of species i ($mole/cm^2$-sec).

q - dimensionless charge density.

Q - dimensionless charge density.

R - universal gas constant (joule/mole-deg).

t - time (sec).

t_i - transference number of species i.

T - absolute temperature (deg).

T - dimensionless time of charging.

x - distance from inner limit of diffuse layer (cm).

X - dimensionless distance.

y - dimensionless distance.

z_i - charge number of species i.

ϵ - dielectric constant (farad/cm).

κ_∞ - conductivity of bulk solution (mho/cm).

σ - dimensionless surface charge density in diffuse layer.

σ_2 - dimensionless surface charge density in extended charge.

τ - dimensionless time.

Φ - dimensionless potential at $x = 0$.

References

1. Fred C. Anson. "The Transient Potentials Produced by the Creation or Annihilation of the Diffuse Double Layer in Dilute Solutions." _Journal of Physical Chemistry_, _71_, 3605-3610 (1967).

2. Fred C. Anson and Robert F. Martin. "Creation of Non-equilibrium Diffuse Double Layers and Studies of Their Relaxation." To be published.