

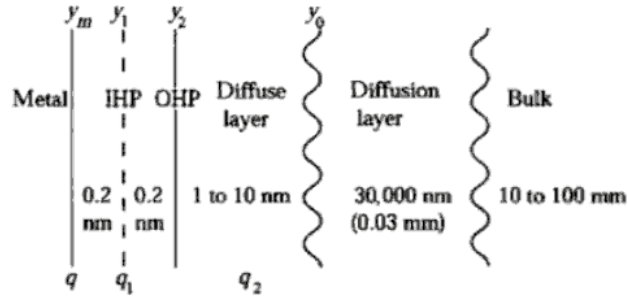
Compact Part of the Double Layer

1 Double-layer Capacitance

1.1 Stern Layer

As was discussed in the previous lecture, the Gouy-Chapman model predicts unphysically large counter-ion concentrations at large potentials. As an example, at 2.5 V, which is a typical battery electrode potential, counter-ion concentrations predicted by Gouy-Chapman would be on the order of $e^{100} \sim 10^{43}$, which is clearly impossible. The central problem is that the Boltzmann distribution upon which Gouy-Chapman is based only on the balance between electrostatic attraction of the counter-ions towards the charged surface and diffusion of them away from it. This approach does not take into account near range effects due to close packing of ions. For zeta potentials much larger than the thermal voltage, the electrostatic attraction becomes the dominant force in this model, and the infinitesimally small ions pile up infinitesimally close to the surface. In 1924, Stern came up with a model that addressed this problem. He proposed that a finite molecular size could be introduced into the model by requiring that there was some distance of closest approach to the surface. This distance was defined as h_s , and the region contained in that distance is commonly called the compact layer. The physical meaning of this model is not precisely defined, but it has been suggested that it is caused by a sphere of solvated water molecules attached to the ions. At sufficiently high voltages, this solvation layer has been shown to break down, leading to ions adsorbing onto the surface at an “inner Helmholtz” plane. This structure is illustrated in figure 1.

As was discussed in lecture 25, the dielectric constant is known to decrease for aqueous solutions at high electric fields due to the alignment of the



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Figure 1: Figure from Newman and Thomas-Alyea. *Electrochemical Systems, 3rd Edition*. 2004. The structure of a Stern Model double layer. The inner and outer Helmholtz plane act as planar capacitors in series with the diffuse layer.

water molecule dipoles. Rather than implementing a non-uniform dielectric constant, this model assumes that within the compact layer, the dielectric constant is some constant $\varepsilon \ll \varepsilon_{bulk}$. This approximation is quite reasonable since the compact layer is generally only one or two molecules thick, so making a more detailed continuum analysis of the dielectric constant would be taking the mean field approximation beyond its valid domain.

With these two assumptions in place, the compact layer takes the form of a parallel plate capacitor, with opposite charge lining up on the surface and on the Stern plane. The capacitance (per unit area) of such a system is well known, and can be written $C_s = \varepsilon_s/h_s$. This capacitance lies in series with the diffuse double layer capacitance C_D . Together, these two capacitances form the canonical model for modeling double layers, and describe a wide variety of conditions reasonably well. For convenience, we define the following dimensionless group:

$$\delta = \frac{c_D^0}{c_s} = \frac{\varepsilon/\lambda_D}{\varepsilon_s/h_s} = \frac{\lambda_s}{\lambda_D}. \quad (1)$$

Where $\lambda_S = \frac{\varepsilon}{\varepsilon_s} h_s$ is the effective stern layer thickness, taking into account the variation in dielectric constant, and $c_D^0 = \varepsilon/\lambda_D$ is the Debye-Hückel capacitance of the diffuse layer, which is equivalent to the Gouy-Chapman capacitance for low potentials. This parameter is extremely important in the model, as it describes the relative importance of the diffuse layer and the Stern layer.

1.2 Gouy-Chapman-Stern Model

To describe the total capacitance of this model, we simply model the system as the two capacitances in series, ignoring for the moment any effects due to the inner Helmholtz plane. Then the total capacitance can be written:

$$\frac{1}{c} = \frac{1}{c_s} + \frac{1}{c_D}. \quad (2)$$

We will also split up the potential drop $\Delta \phi$ into two separate components, describing the drop across the stern layer and the diffuse layer, respectively, so that:

$$\Delta \phi = \Delta \phi_s + \Delta \phi_D. \quad (3)$$

We have previously derived expressions for c_s and c_D , assuming a Gouy-Chapman diffuse layer:

$$c_s = \frac{\varepsilon_s}{h_s} \quad (4)$$

$$c_D = c_D^0 \cosh\left(\frac{ze\zeta}{2k_B T}\right). \quad (5)$$

We can now solve for the total capacitance of the system, and then simplify in terms of our dimensionless parameter δ :

$$c = \frac{c_D}{c_D/c_s + \operatorname{sech}\left(\frac{ze\zeta}{2k_B T}\right)}$$

$$c = \frac{c_D^0}{\delta + \operatorname{sech}\left(\frac{ze\zeta}{2k_B T}\right)}. \quad (6)$$

This expression closely matches the Gouy-Chapman result for low potentials, but the Stern layer provides a hard limit on the overall capacitance: it cannot exceed the Stern-Layer capacitance under any circumstance. This avoids the non-physical behaviors predicted by the Gouy-Chapman model.

1.3 Grahame Model

In 1948, Grahame performed a series of experiments on liquid mercury drop electrodes submerged in an electrolyte. Grahame used employed electrowetting, or the impact of applied potential on surface tension, to back out the capacitance of the double layer as function of potential. Figure 3 shows a

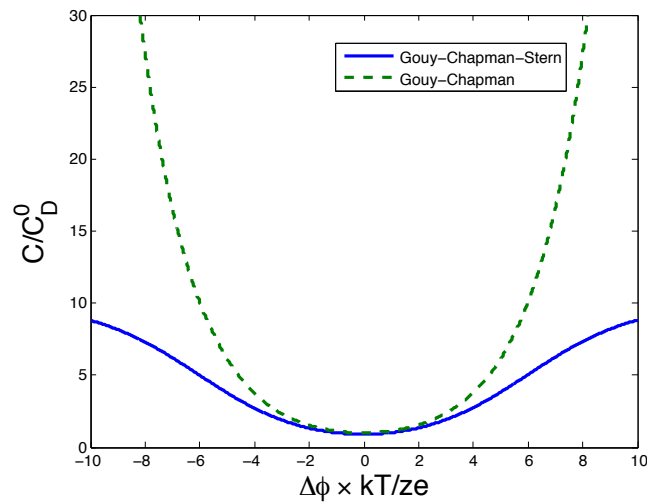
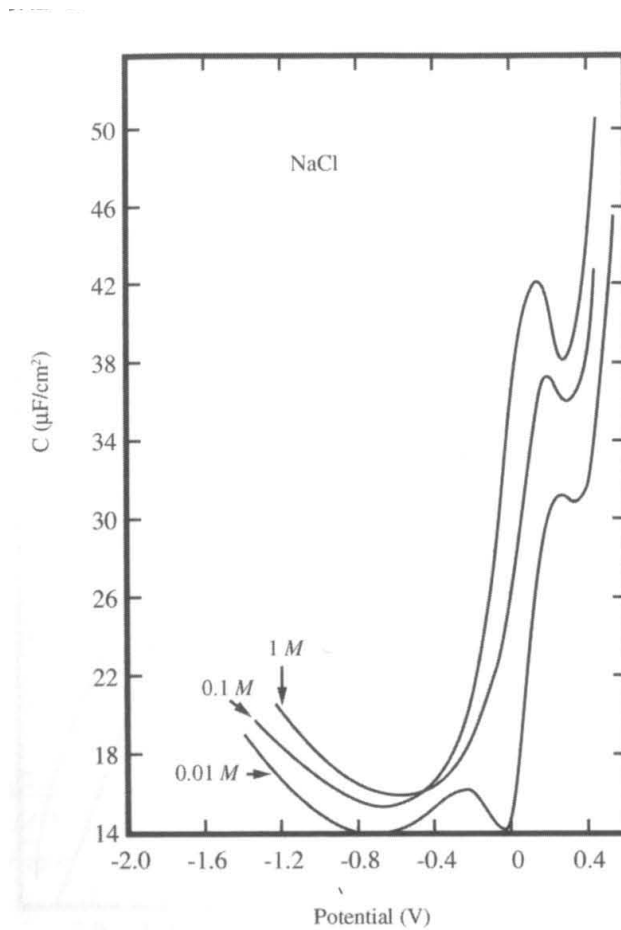


Figure 2: Double layer capacitance of a Gouy-Chapman-Stern (GCS) double layer and a Gouy-Chapman (GC) double layer as a function of potential drop across the double layer. At low potentials, the GCS model agrees with the GC model, but at high potentials, the Stern capacitance limits the overall capacitance (in this case, $\delta = .1$, and $c_s = 10c_D^0$.)



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Figure 3: Figure from Newman and Thomas-Alyea. *Electrochemical Systems, 3rd Edition*. 2004. Results from Grahame's 1948 mercury drop capacitance measurements. At low ionic strength, the hyperbolic cosine functional behavior is observed. At higher ionic strength, other more complicated effects, such as ion adsorption and finite size effects dominate.

summary of his results. Of particular interest in these results is that for sufficiently low ionic strength, the Gouy-Chapman relation between capacitance and potential is clearly visible at sufficiently small potentials, and was fitted well with a charge or voltage dependent Stern-layer capacitance in series with the Gouy-Chapman diffuse layer capacitance.

2 Non-equilibrium Effects of the Compact Layer

See Refs. 1-4 for more details.

2.1 Stern Boundary Condition

By splitting the potential drop across the double layer into two components, we have introduced an additional degree of freedom into the problem, and therefore need an additional boundary condition in order to fully specify the problem. One possibility is to employ Gauss' Law at the Stern plane to obtain a relationship between the field just outside the Stern plane and the field just inside the Stern plane. To a reasonable approximation, the field within the compact layer is constant, so if we define $x = 0$ to be the Stern plane, our boundary condition can be written in terms of our effective compact layer thickness λ_s as:

$$\Delta\phi_s = \phi(x=0) - \phi_e = -\lambda_s \hat{n} \cdot \nabla\phi|_{x=0}. \quad (7)$$

This is a Robin-type or mixed boundary condition on the potential at the electrode is known as the Stern boundary condition, and is exactly what is needed to complete the problem description. If we scale this equation to λ_D and the thermal voltage $k_B T/e$, we obtain the dimensionless form:

$$\tilde{\phi} + \delta \hat{n} \cdot \tilde{\nabla}\tilde{\phi}|_{\tilde{x}=0} = \tilde{\phi}_e. \quad (8)$$

In this form, it is easy to see that δ is the critical parameter for describing the nature of this boundary condition. For large δ , nearly all of the potential drop occurs in the compact layer, in which case the diffuse layer can be neglected. This is the Helmholtz limit. For small δ , the diffuse layer absorbs all of the potential drop, in which case the compact layer can be neglected. This is the Gouy-Chapman limit. When δ is neither small nor large, both parts of the double layer are important, and the analysis becomes considerably more complicated.

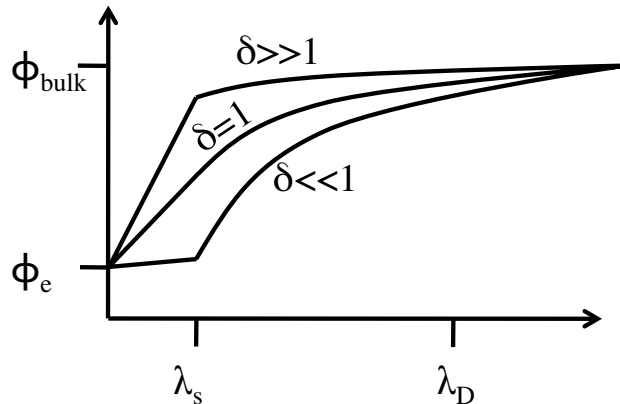


Figure 4: Potential drop across the double layer. Depending on the value of δ , the potential drop is distributed between the compact layer and the diffuse layer.

2.2 Faradaic Reactions

These results have far reaching implications for faradaic reactions. By definition, faradaic reactions must occur at the electrode electrolyte interface; in other words, within the double layer. It is customary to assume a neutral electrolyte, but we have just shown that this is inaccurate. As a result, although the distribution of voltage across the double layer is a nanoscale phenomenon, it has far reaching macroscopic consequences on reaction kinetics. A common way to address this problem is to assume that the reactions occur within the compact layer, and that the important potential is $\Delta\phi_s$ as opposed to $\Delta\phi$. This is known as the Frumkin correction to the Butler-Volmer equation, and will be discussed in more detail next lecture. It was first suggested in the 1930s, but the diffuse layer voltage ζ is still commonly left as a fitted constant, even though as shown in figure 4, $\zeta = \phi(\lambda_s)$ varies depending on applied voltage. A better approach would be to apply the Butler Volmer equation across the compact layer, using the Stern boundary condition to determine $\Delta\phi_s$. This procedure eliminates the need for fitting parameters, and allows for a complete mathematical understanding of the double layer.

REFERENCES

1. Analysis of diffuse-layer effects on time-dependent interfacial kinetics, A. Bonnefont, F. Argoul and M. Z. Bazant, *J. Electroanal. Chem.* 500, 52 (2001).
2. Current-voltage relations for electrochemical thin films, M. Z. Bazant, K. T. Chu, and B. J. Bayly, *SIAM J. Appl. Math* 65, 1463-1484 (2005).
3. Imposed currents in galvanic cells, P. M. Biesheuvel, M. van Soestbergen, and M. Z. Bazant, *Electrochimica Acta* 54, 4857-4871 (2009).
4. Diffuse-charge dynamics in electrochemical systems, M. Z. Bazant, K. Thornton, and A. Ajdari, *Phys. Rev. E* 70, 021506 (2004).

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