The predicted V-shaped capacitance function does resemble the observed behavior in NaF at low concentrations and at potentials not too far from the PZC (see Figure 13.3.1). However, the actual system shows a flattening in capacitance at more extreme potentials, and the valley at the PZC disappears altogether at high electrolyte concentrations. Moreover, the actual capacitance is usually much lower than the predicted value. The partial success of the Gouy–Chapman theory suggests that it has elements of truth, but its failures are significant and indicate major defects. We will see in the next section that one of those defects is related to the finite size of the ions in the electrolyte.

13.3.3 Stern's Modification

The reason for the unlimited rise in differential capacitance with ϕ_0 in the Gouy–Chapman model is that the ions are not restricted with respect to location in the solution phase. They are considered as point charges that can approach the surface arbitrarily closely. Therefore, at high polarization, the effective separation distance between the metallic and solution-phase charge zones decreases continuously toward zero.

This view is not realistic. The ions have a finite size and cannot approach the surface any closer than the ionic radius. If they remain solvated, the thickness of the primary solution sheath would have to be added to that radius. Still another increment might be necessary to account for a layer of solvent on the electrode surface. For example, see Figure 1.2.3. In other words, we can envision a *plane of closest approach* for the centers of the ions at some distance x_2.

In systems with low electrolyte concentration, this restriction would have little impact on the predicted capacitance for potentials near the PZC, because the thickness of the diffuse layer is large compared to x_2. However, at larger polarizations or with more concentrated electrolytes, the charge in solution becomes more tightly compressed against the boundary at x_2, and the whole system begins to resemble the Helmholtz model. Then we can expect a corresponding leveling of the differential capacitance. The plane at x_2 is an important concept and is called the *outer Helmholtz plane* (OHP).

This interfacial model (2–4, 6–8, 15, 16), first suggested by Stern (29), can be treated by extending the considerations of the last section. The Poisson–Boltzmann equation, (13.3.6), and its solutions, (13.3.10) and (13.3.11), still apply at distance $x \geq x_2$. Now the potential profile in the diffuse layer of a $z:z$ electrolyte is given by

$$\int_{\phi_2}^{\phi} \frac{d\phi}{\sinh(ze\phi/2\mathscr{k}T)} = -\left(\frac{8\mathscr{k}Tn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \int_{x_2}^{x} dx \qquad (13.3.22)$$

or

$$\boxed{\frac{\tanh(ze\phi/4\mathscr{k}T)}{\tanh(ze\phi_2/4\mathscr{k}T)} = e^{-\kappa(x-x_2)}} \qquad (13.3.23)$$

where ϕ_2 is the potential at x_2 with respect to the bulk solution, and κ is defined by (13.3.15).

The field strength at x_2 is given from (13.3.11):

$$\left(\frac{d\phi}{dx}\right)_{x=x_2} = -\left(\frac{8\mathscr{k}Tn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi_2}{2\mathscr{k}T}\right) \qquad (13.3.24)$$

Since the charge density at any point from the electrode surface to the OHP is zero, we know from (13.3.5) that this same field strength applies throughout that interval. Thus the

potential profile in the compact layer is linear. Figure 13.3.6b is a summary of the situation. Now we find the total potential drop across the double layer to be

$$\phi_0 = \phi_2 - \left(\frac{d\phi}{dx}\right)_{x=x_2} x_2 \qquad (13.3.25)$$

Note also that all of the charge on the solution side resides in the diffuse layer, and its magnitude can be related to ϕ_2 by considering a Gaussian box exactly as we did above.[4]

$$\boxed{\sigma^M = -\sigma^S = -\varepsilon\varepsilon_0\left(\frac{d\phi}{dx}\right)_{x=x_2} = (8kT\varepsilon\varepsilon_0 n^0)^{1/2} \sinh\left(\frac{ze\phi_2}{2kT}\right)} \qquad (13.3.26)$$

To find the differential capacitance, we substitute for ϕ_2 by (13.3.25):

$$\sigma^M = (8kT\varepsilon\varepsilon_0 n^0)^{1/2} \sinh\left[\frac{ze}{2kT}\left(\phi_0 - \frac{\sigma^M x_2}{\varepsilon\varepsilon_0}\right)\right] \qquad (13.3.27)$$

Differentiation and rearrangement (Problem 13.4) gives

$$C_d = \frac{d\sigma^M}{d\phi_0} = \frac{(2\varepsilon\varepsilon_0 z^2 e^2 n^0/kT)^{1/2} \cosh(ze\phi_2/2kT)}{1 + (x_2/\varepsilon\varepsilon_0)(2\varepsilon\varepsilon_0 z^2 e^2 n^0/kT)^{1/2} \cosh(ze\phi_2/2kT)} \qquad (13.3.28)$$
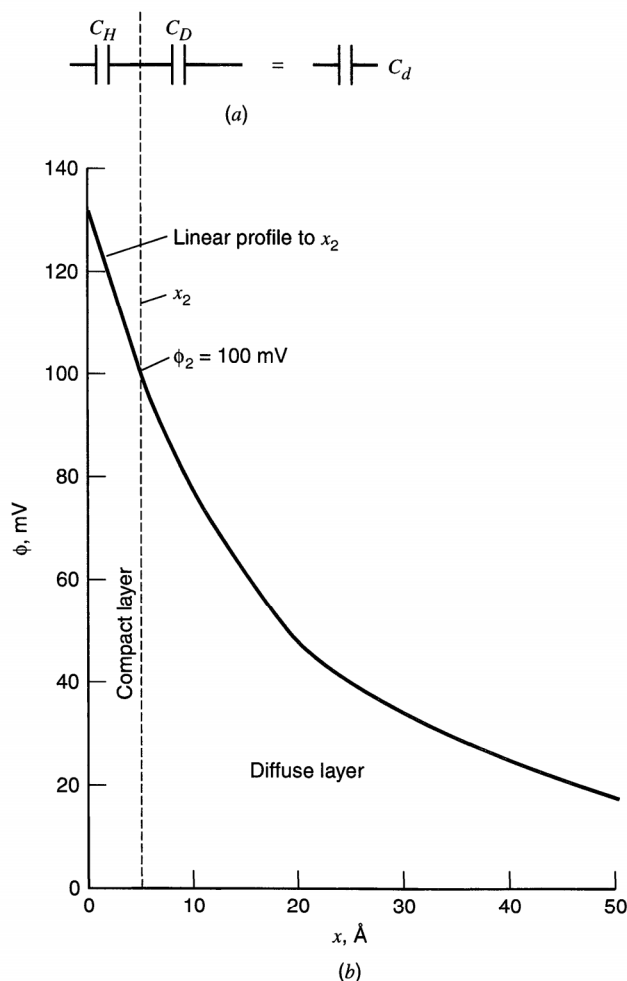

Figure 13.3.6 (a) A view of the differential capacitance in the Gouy–Chapman–Stern (GCS) model as a series network of Helmholtz-layer and diffuse-layer capacitances. (b) Potential profile through the solution side of the double layer, according to GCS theory. Calculated from (13.3.23) for $10^{-2}\,M$ 1:1 electrolyte in water at 25°C.

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[4]See (13.3.15b), (13.3.20b), and (13.3.21b) for evaluations of the constants for aqueous solutions at 25°C.

which is more simply stated as the inverse:

$$\frac{1}{C_d} = \frac{x_2}{\varepsilon\varepsilon_0} + \frac{1}{(2\varepsilon\varepsilon_0 z^2\, e^2 n^0/\ell T)^{1/2}\,\cosh(ze\phi_2/2\ell T)}$$

(13.3.29)

This expression says that the capacitance is made up of two components that can be separated in the reciprocal, exactly as one would find for two capacitors in series. Thus we can identify the terms in (13.3.29) as the reciprocals of component capacitances, C_H and C_D, which can be depicted as in Figure 13.3.6a:

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$$

(13.3.30)

By comparing the terms of (13.3.29) with (13.3.2) and (13.3.21), it is clear that C_H corresponds to the capacitance of the charges held at the OHP, whereas C_D is the capacitance of the truly diffuse charge.

The value of C_H is independent of potential, but C_D varies in the V-shaped fashion we found in the last section. The composite capacitance C_d shows a complex behavior and is governed by the *smaller* of the two components. Near the PZC in systems with low electrolyte concentration, we expect to see the V-shaped function characteristic of C_D. At larger electrolyte concentrations, or even at large polarizations in dilute media, C_D becomes so large that it no longer contributes to C_d and one sees only the constant capacitance of C_H. Figure 13.3.7 is a schematic picture of this behavior.

This model, known as the *Gouy–Chapman–Stern* (GCS) *model*, gives predictions that account for the gross features of behavior in real systems. There are still discrepancies, in that C_H is not truly independent of potential. Figure 13.3.1 is a plain illustration. This aspect must be handled by refinements to the GCS theory that take into account the structure of the dielectric in the compact layer, saturation (i.e., full polarization) of that dielectric in the strong interfacial field, differences in x_2 for anionic and cationic excesses, and other similar matters (2–4, 6–8, 13, 15–18, 30). The theory also neglects ion pairing (or ion–ion correlation) effects in the double layer and strong nonspecific interactions of the ions with the surface charge on the electrode. The latter effect can be described in terms of "ion condensation" in the electrical double layer and can be treated by a model in which the surface charge is considered as an "effective surface charge," smaller than the actual charge on the electrode because of the condensed ionic counter charge (30, 31). These types of effects are not easily probed by measurements of capacitance or surface tension, but may be addressed by alternative methods of studying the interface, as discussed in Chapters 16 and 17.
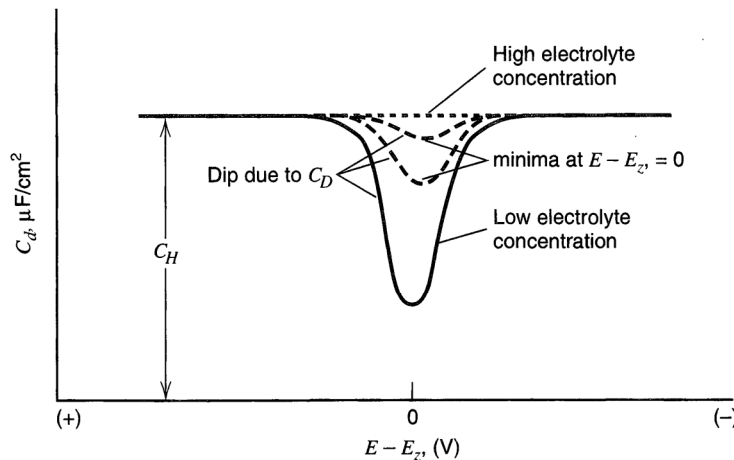

Figure 13.3.7 Expected behavior of C_d according to GCS theory as the electrolyte concentration changes.