Lecture #18 of 20+

The Double Layer

Chapter 13

Q: What's in this set of lectures?

A: B&F Chapter 13 main concepts:

- Section 1.2.3: Double layer structure

- Sections 13.1 & 13.2: Gibbs adsorption isotherm, Electrocapillar(it)y, Surface excess, Lippmann's equation, Point of Zero Charge

- Section 13.3: Models: Helmholtz, Gouy–Chapman (Poisson–Boltzmann), Gouy–Chapman–Stern

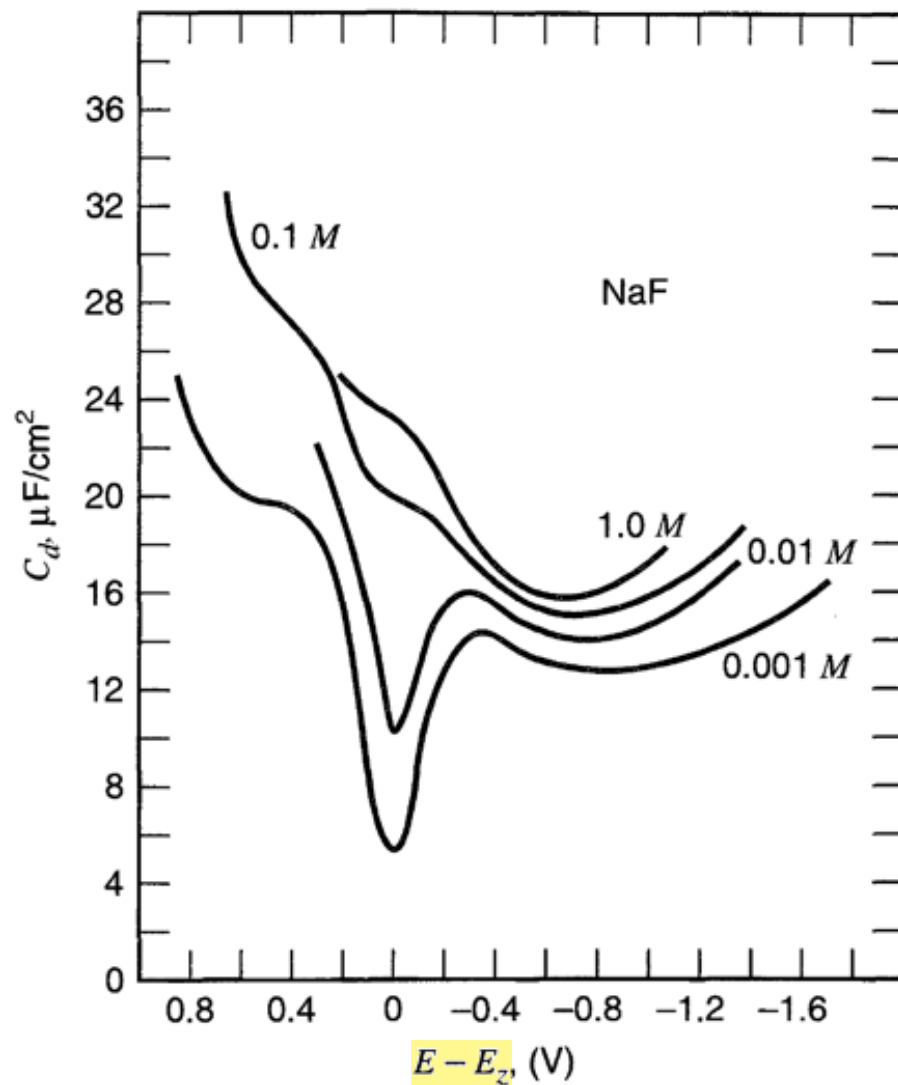- Section 13.5: Specific adsorption

RECALL:

Flat? … Eh; not really.

Why were both of these measured using fluoride salts?

In order to minimize specific adsorption!

Figure 13.3.1 Differential capacitance *vs.* potential for NaF solutions in contact with mercury at 25°C. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Grahame, *Chem. Rev.*, 1947, *41*, 441

For the purposes of this class, we want to understand the microscopic origin of the *most prominent features* of these C_d *vs. E* data:

a) A minimum in C_d exists at the pzc.

b) C_d is quasi-constant at potentials well positive and well negative of the pzc.

c) This quasi-constant C_d is larger when E is (+) of pzc than when it is (−) of pzc.

d) C_d increases with salt concentration at all potentials, and the "dip" near the pzc disappears.

Three traditional models for double layer structure:

1) Helmholtz

2) Gouy–Chapman (GC)

3) Gouy–Chapman–Stern (GCS)

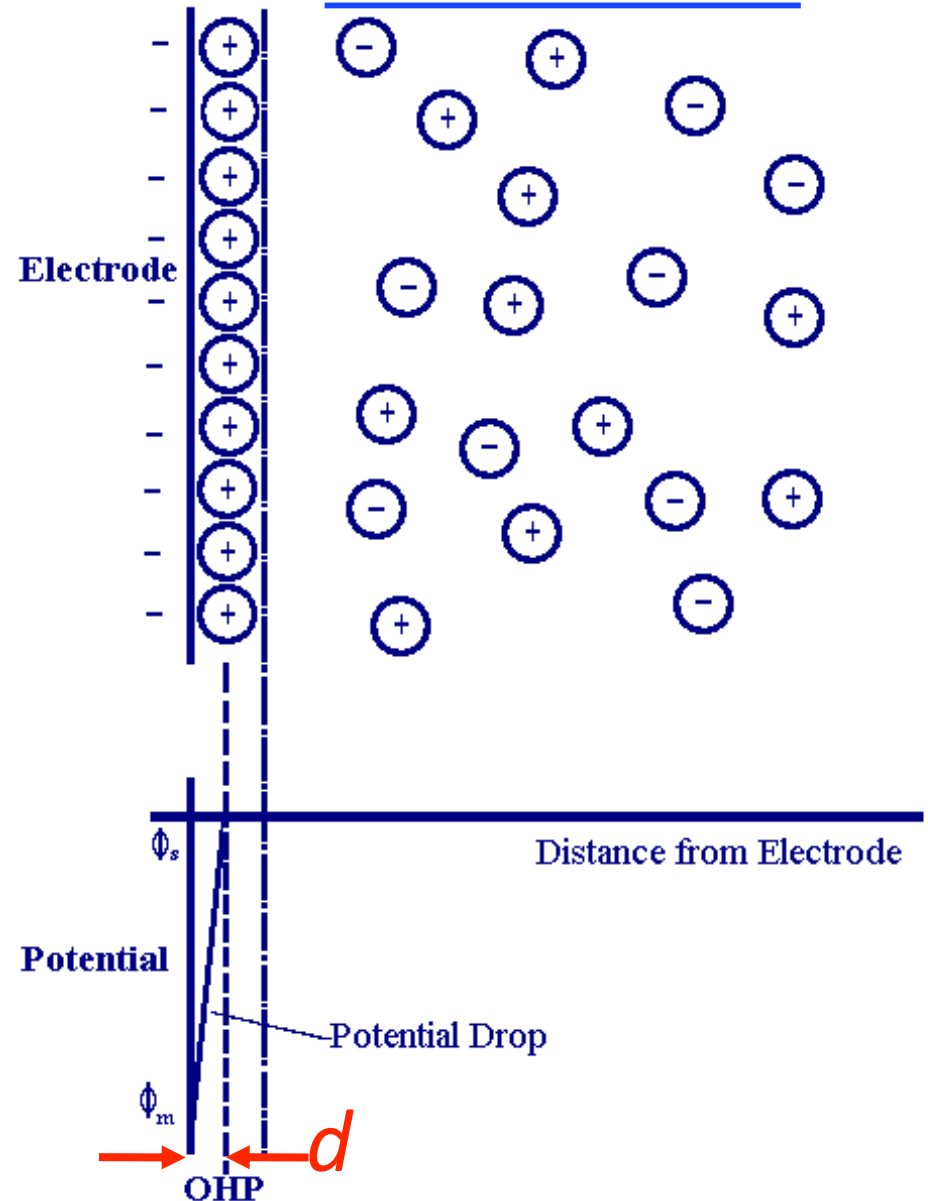… let's take a look at each of these…

Models of Electrical Double Layer:

1) **The Helmholtz Model**: this is the simplest possible model. It postulates that ions (anions *and* cations) occupy a plane located a distance, *d*, from the electrode surface, and that the effective "dielectric constant" operating in the double layer is potential independent:

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

... for a parallel plate capacitor, *C* is independent of *E* because the permittivity of the capacitor, $\varepsilon \varepsilon_0$, and its spacing, *d*, are both independent of applied potential...

Electrode

Distance from Electrode

Potential

Φ_s

Potential Drop

Φ_m

d

OHP

http://www.cartage.org.lb/

… the Helmholtz model says that the electrical double layer acts like, and looks like *(rare in EChem)*, a parallel plate capacitor…

RECALL:
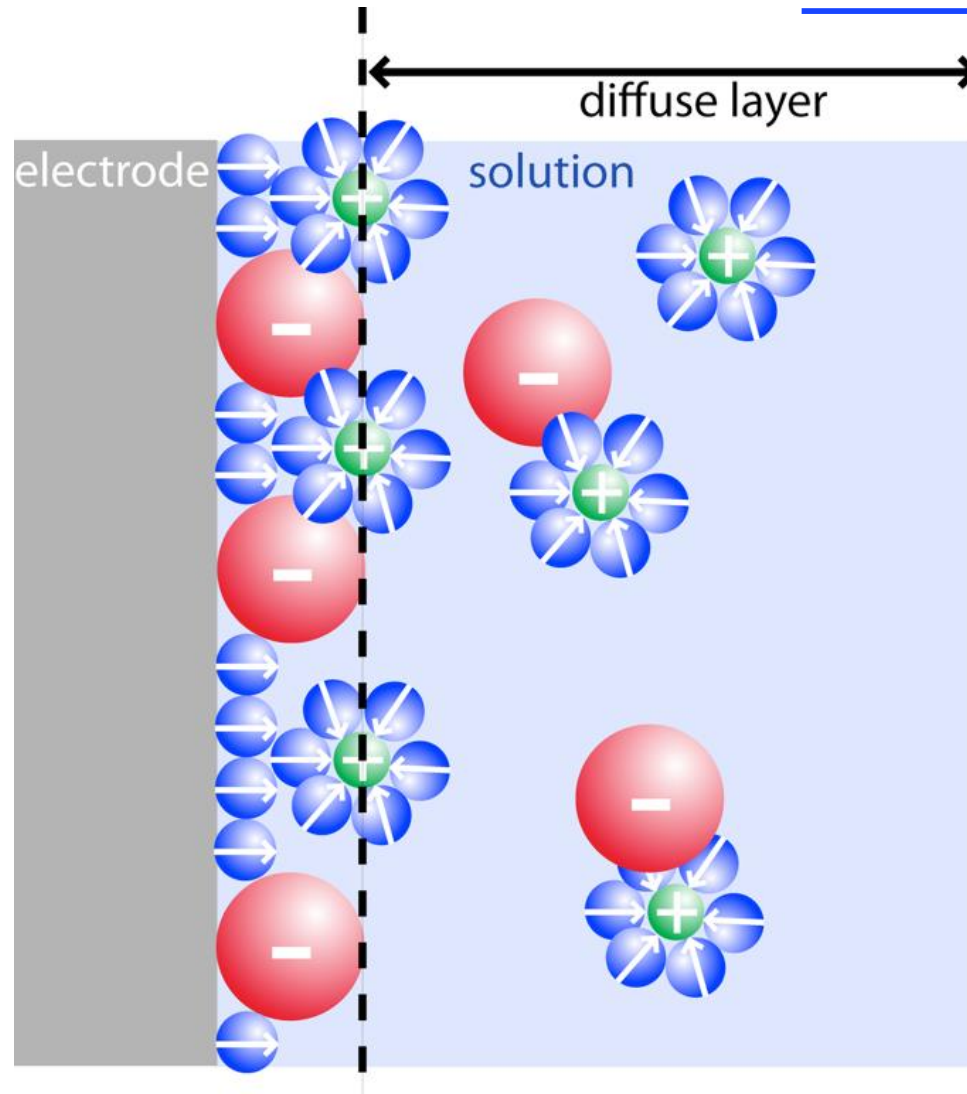
$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

… C_d is therefore independent of E because the permittivity of the capacitor, $\varepsilon \varepsilon_0$, and its spacing, d, are both independent of applied potential…

… Question: *What value for C_d do we calculate by plugging in to this model the known "dielectric constant" (permittivity = IUPAC) of water?*
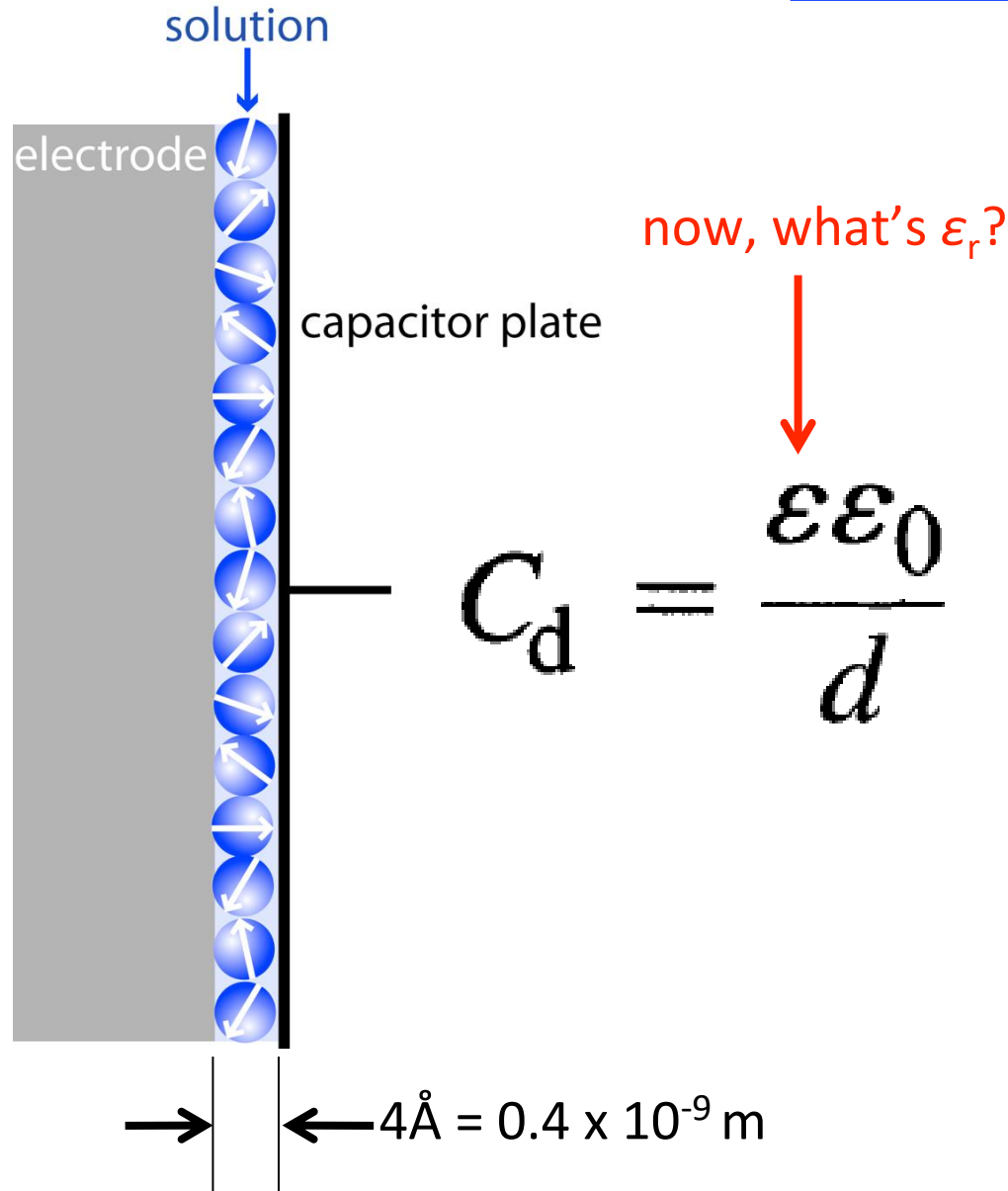
... recall, here's what the double layer really looks like...

… and here's what the double layer looks like in the Helmholtz approximation…

RECALL:

solution

electrode

capacitor plate

now, what's ε_r?

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

4Å = 0.4 x 10^{-9} m

... first, what's ε_r for water? Well, that depends... *can it rotate?*   **(BRIEFLY)** 768
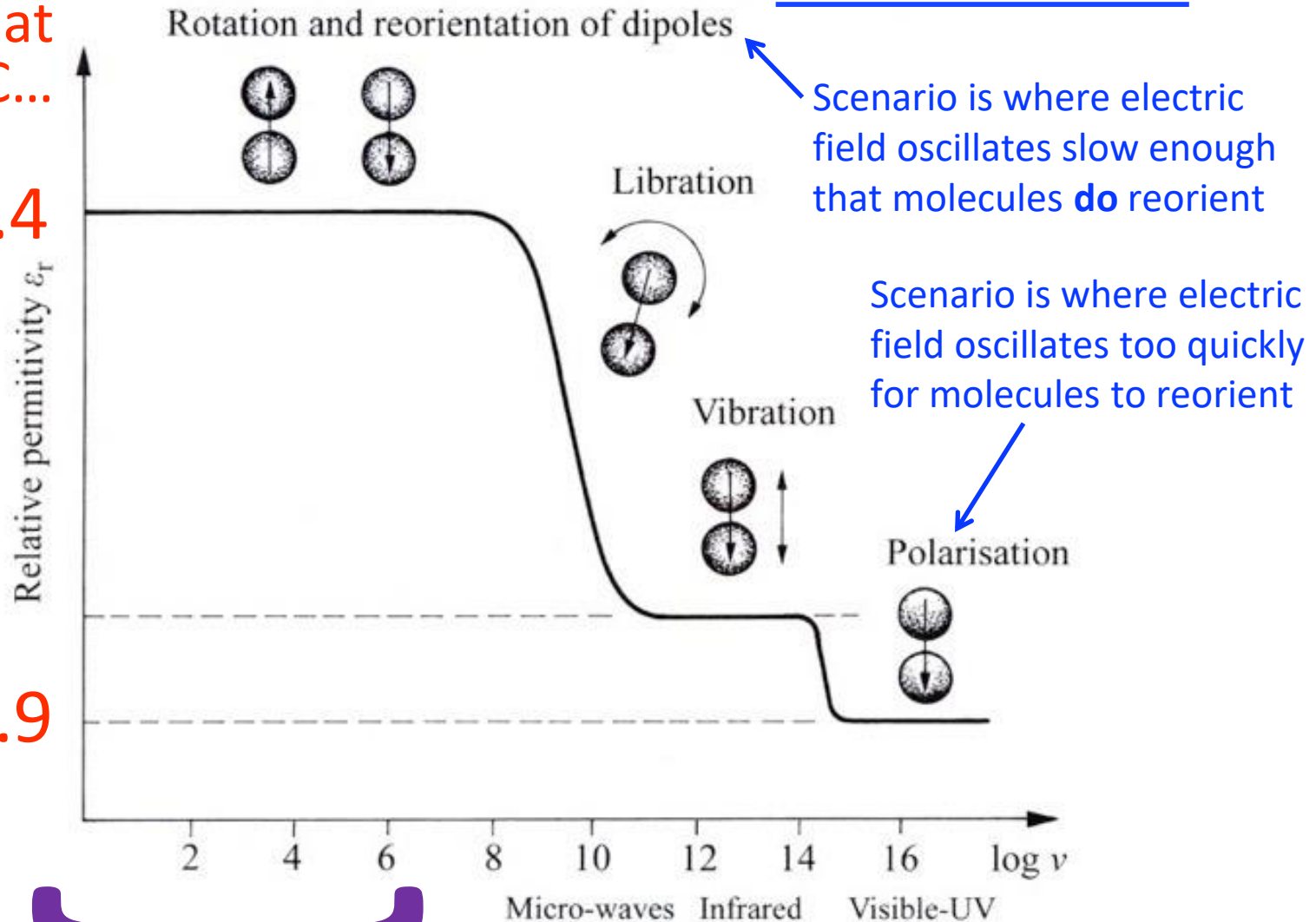
RECALL:

for water at 20 °C...

78.4

5.9

Rotation and reorientation of dipoles

Scenario is where electric field oscillates slow enough that molecules **do** reorient

Libration

Scenario is where electric field oscillates too quickly for molecules to reorient

Vibration

Polarisation

Relative permittivity ε_r

2   4   6   8   10   12   14   16 $\log \nu$
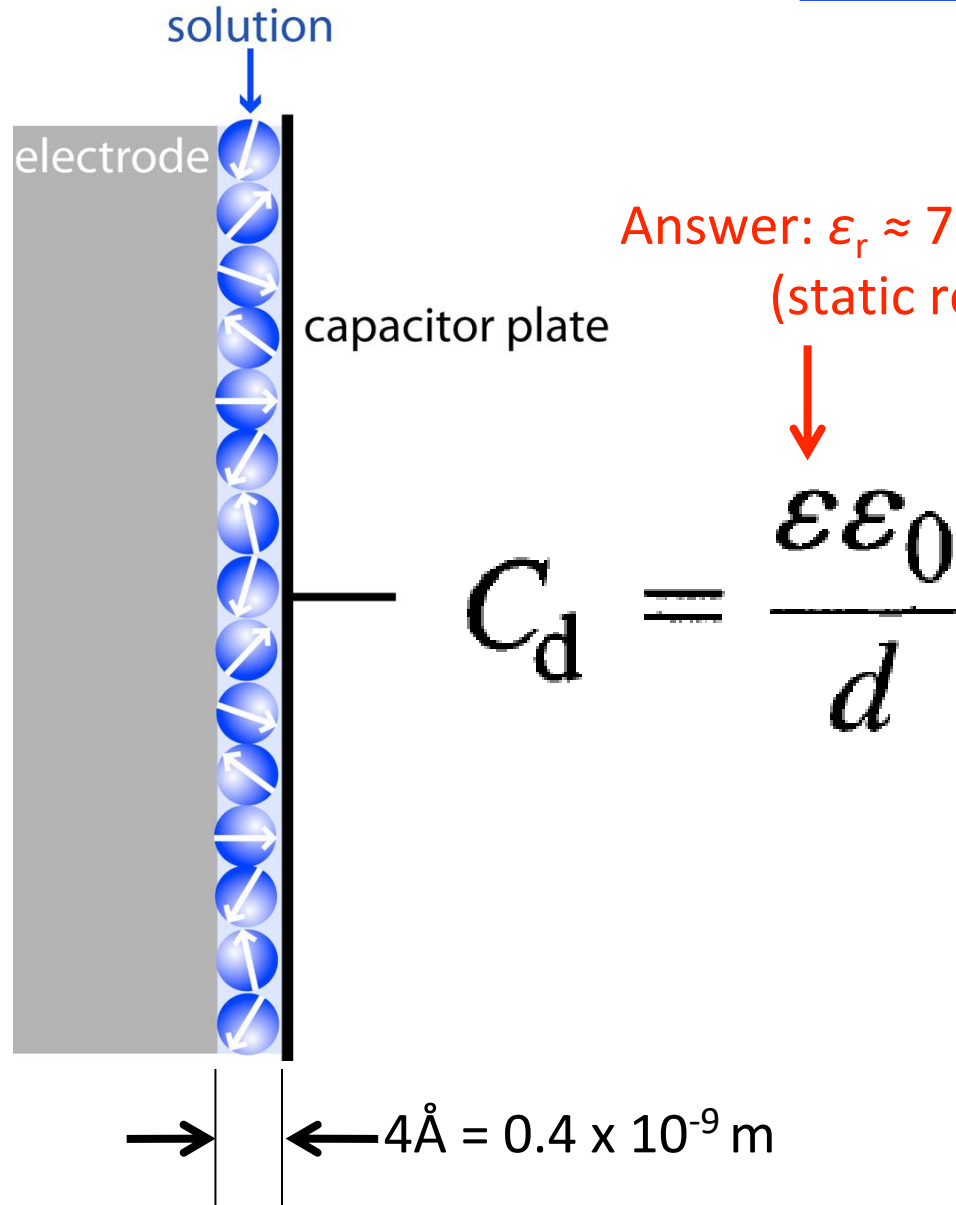
Micro-waves Infrared   Visible-UV

Fig. 1.7 Variation of the relative permittivity of water as a function of the frequency of the applied electric field.

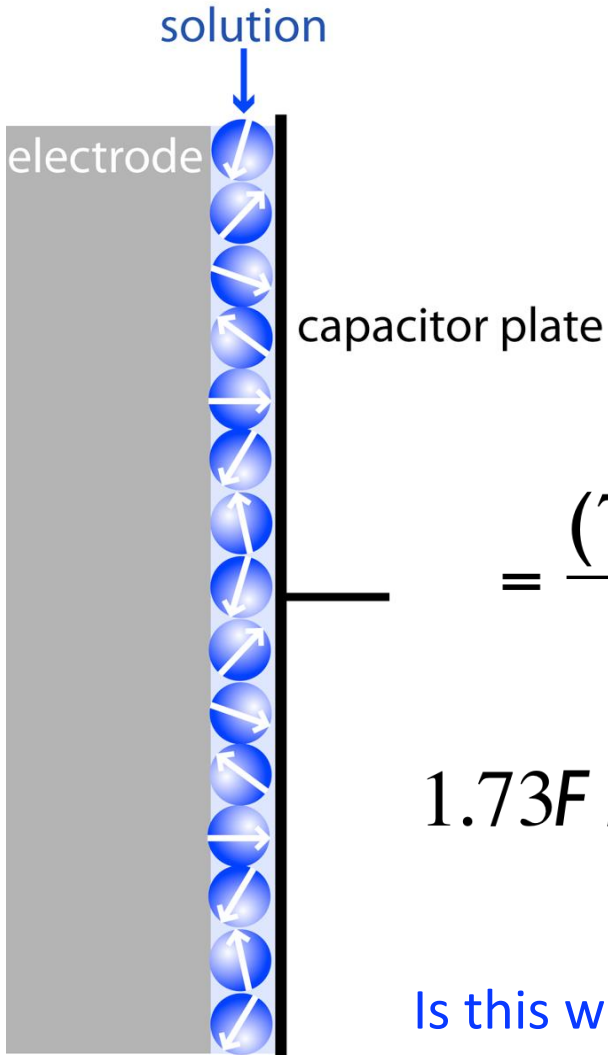*Electrochemical impedance spectroscopy range*

… and here's what the double layer looks like in the Helmholtz approximation…

RECALL:

solution

electrode

capacitor plate

Answer: $\varepsilon_r \approx 78$
(static relative permittivity)

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

4Å = 0.4 x 10^{-9} m

... and here's what the double layer looks like in the Helmholtz approximation...

RECALL:

solution

electrode

capacitor plate

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

$$= \frac{(78)(8.854 \, x10^{-12} F/m)}{0.4 \, x10^{-9} m} = 1.73 F/m^2$$

$$1.73F/m \frac{10^6 \mu F}{F} \frac{m^2}{100^2 cm} = 172.6 \mu F/cm^2$$

Is this what is observed? **Nope!**... OK, now what?

$\longrightarrow$ $\longleftarrow$ 4Å = 0.4 x 10^{-9} m

… now, what if the water dielectric is saturated, and thus fixed?

… so that water cannot rotate…

$\varepsilon_r \approx 6$ **RECALL:**

solution

electrode

capacitor plate

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

$$C = \frac{(6)(8.854\,x10^{-12}F/m)}{0.4\,x10^{-9}m} = 0.133F/m^2$$

$$0.133F/m\,\frac{10^6\mu F}{F}\,\frac{m^2}{100^2\,cm} = 13.3\mu F/cm^2$$

… much more reasonable!

4Å = 0.4 x 10⁻⁹ m
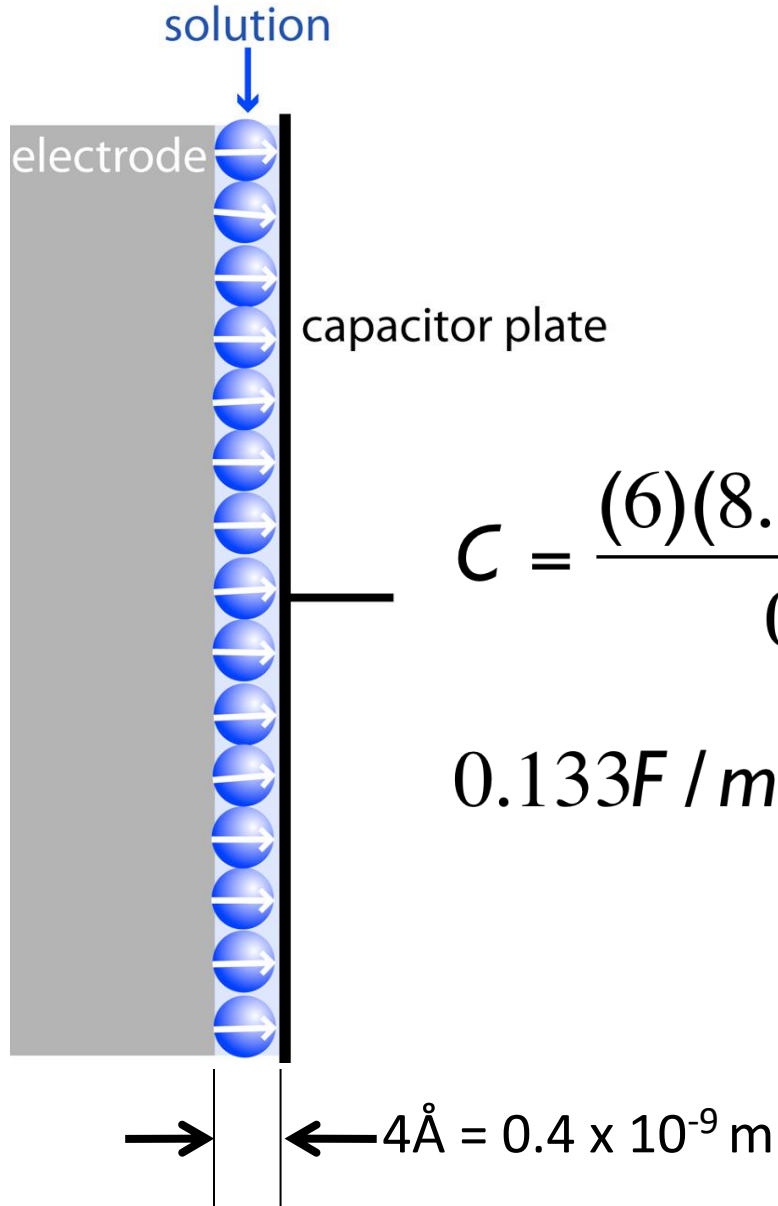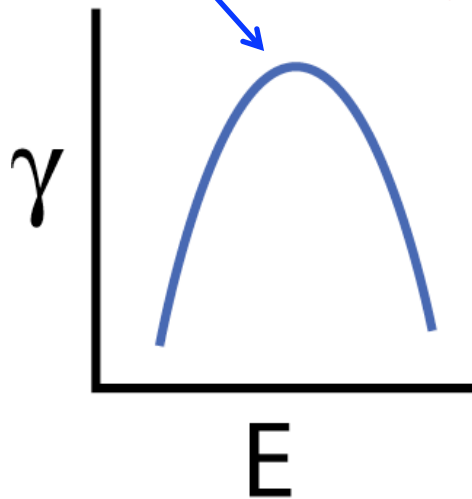
… if we can measure γ, we can determine σ_M…
… and if we can determine σ_M, we can determine C…
… and all of this only works for *liquid electrodes whose surface areas change over time*… Crazy!

RECALL:

$$\sigma^{\mathrm{M}} = -\left(\frac{d\gamma}{dE}\right)_{\mu_i} \qquad C_{\mathrm{d}} = \left(\frac{\partial\sigma^{\mathrm{M}}}{\partial E}\right)$$
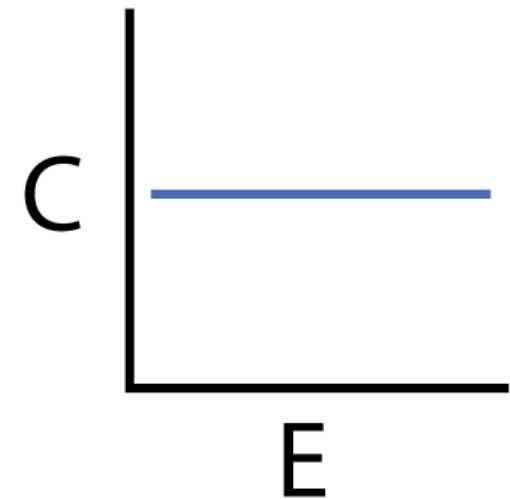

electrocapillary curve
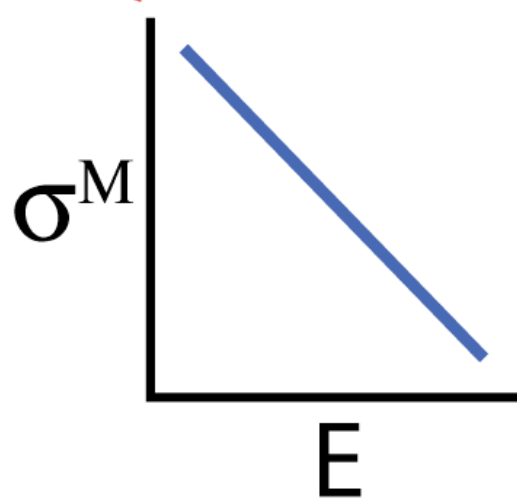
differentiate   differentiate

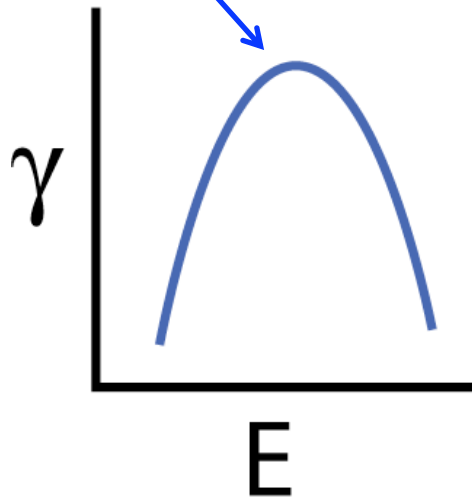… Aside: One can determine E_{pzc} of a solid electrode using its capacitance

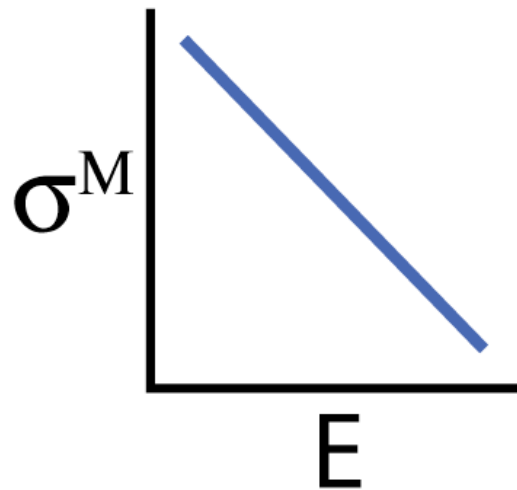… if the Helmholtz model is correct, we'd get this *exactly*:

RECALL:

$$\sigma^{\mathrm{M}} = -\left(\frac{d\gamma}{dE}\right)_{\mu_i} \qquad C_{\mathrm{d}} = \left(\frac{\partial\sigma^{\mathrm{M}}}{\partial E}\right)$$
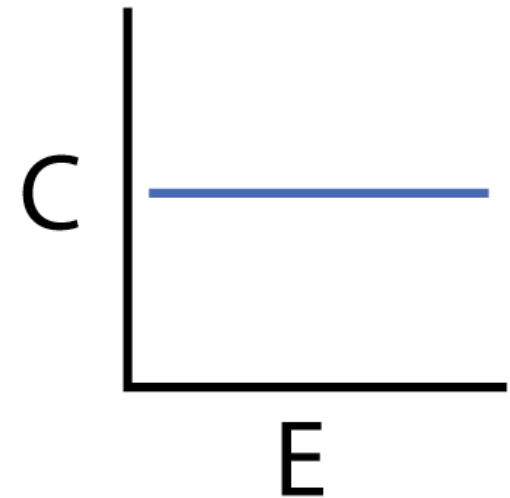
electrocapillary curve

differentiate   differentiate
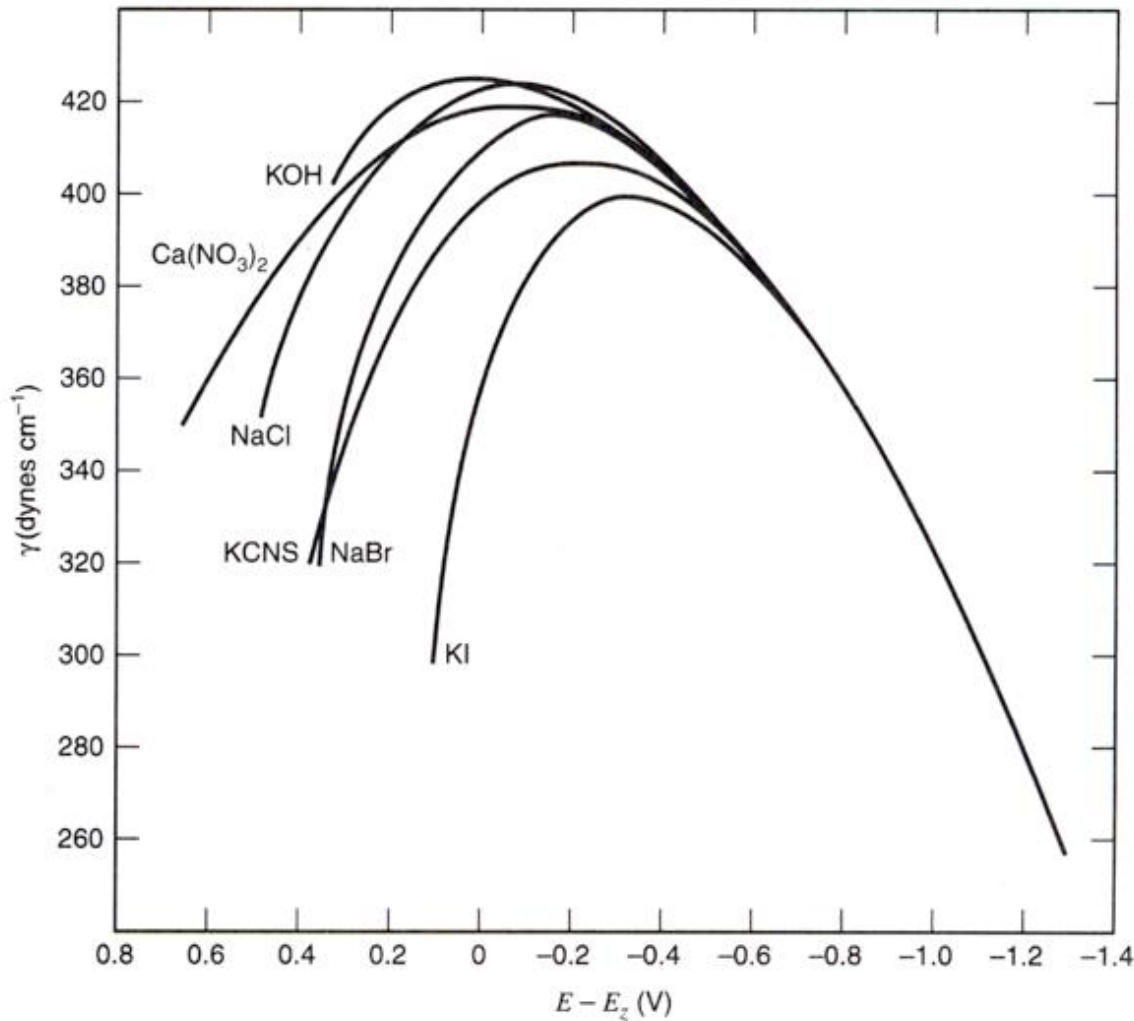
… here are electrocapillary data for various electrolytes…

… hey, you can already see that the Helmholtz Model fails a little…
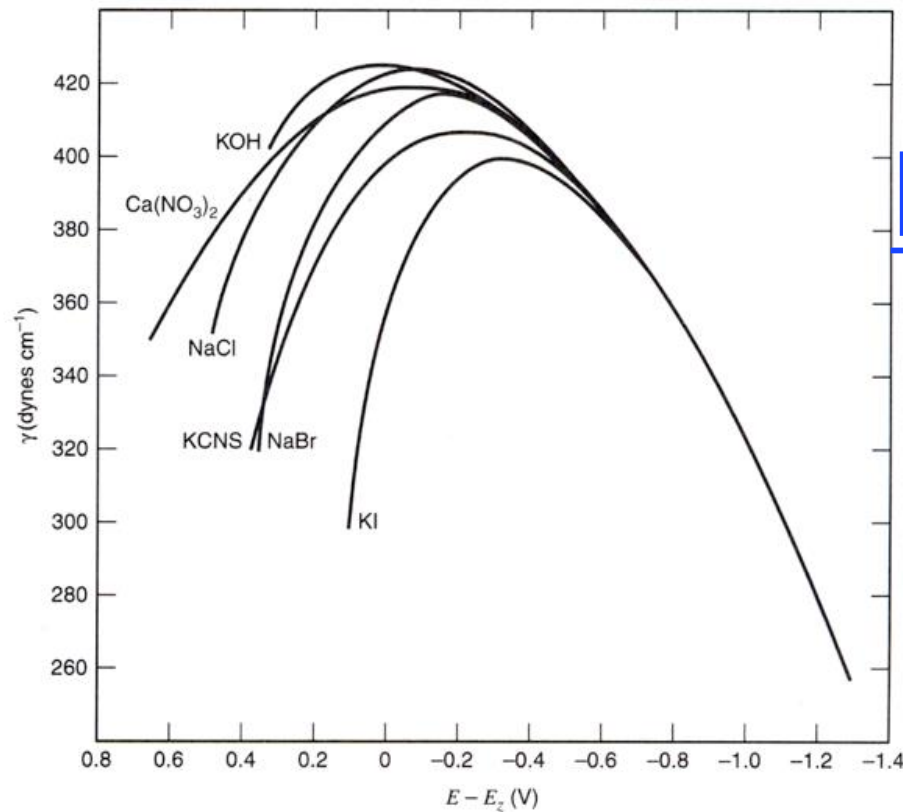
… mostly on the left…

RECALL:

Figure 13.2.2 Electrocapillary curves of surface tension *vs.* potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

RECALL:

Figure 13.2.2 Electrocapillary curves of surface tension *vs.* potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]
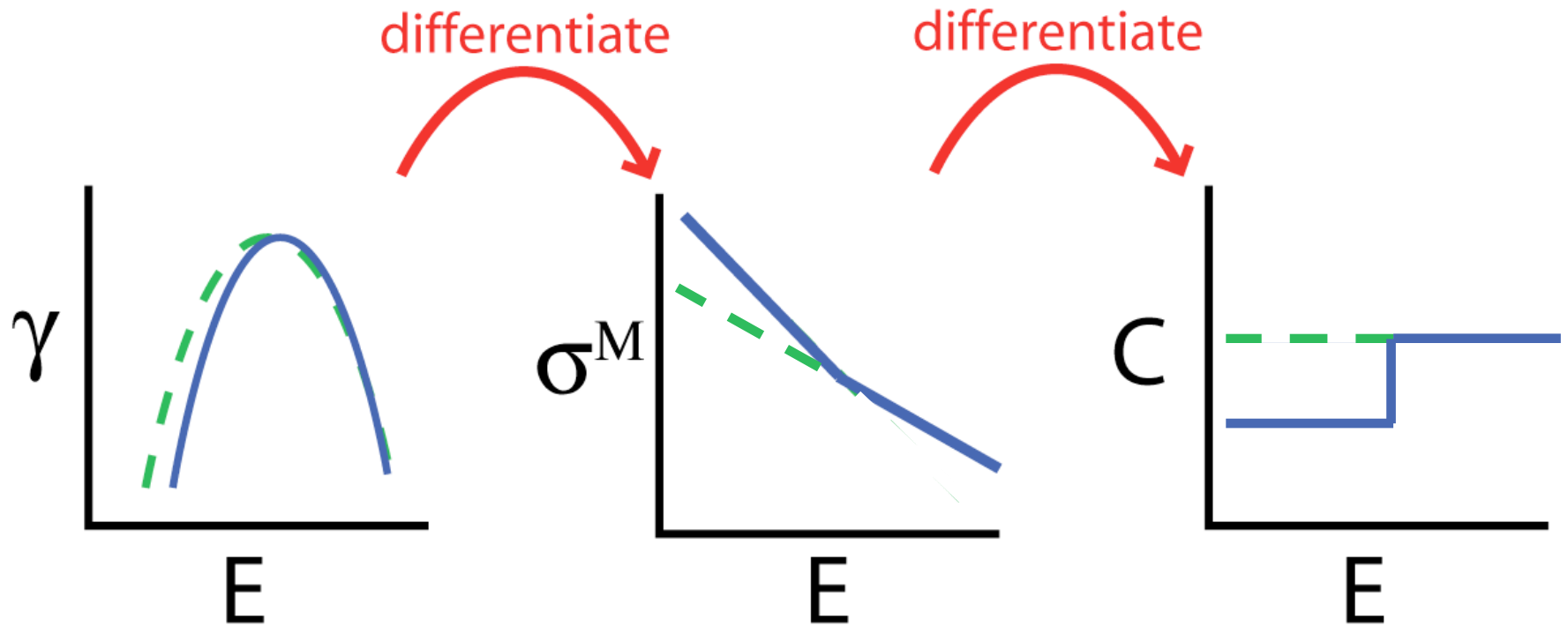
Notwithstanding, notice particularly the following:

a) the γ vs. E parabola is independent of salt…

 … at potentials negative of the pzc…

b) … but strongly dependent on salt positive of pzc…

c) … and pzc itself depends on the electrolyte…

 … we'll get to this shortly…

… if *C* is dependent on potential, then the γ vs. *E* parabola will be asymmetric…

… for example…

… and a flat C_d is in no way observed… *we need a more sophisticated model*…
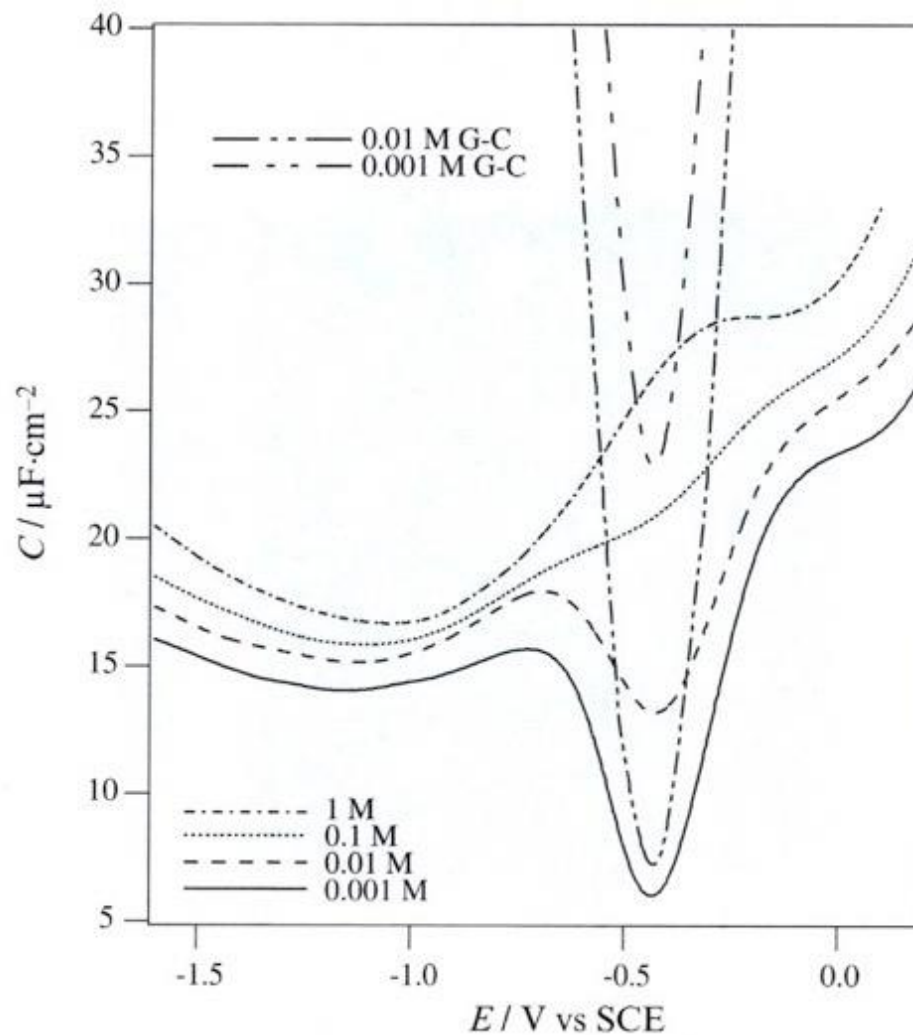
Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433V$) with the respective Gouy-Chapman capacity [Paolo Galleto, EPFL thesis].

H.H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, 2004, Figure 5.13

… and specifically, one where the model of the double layer captures these elements

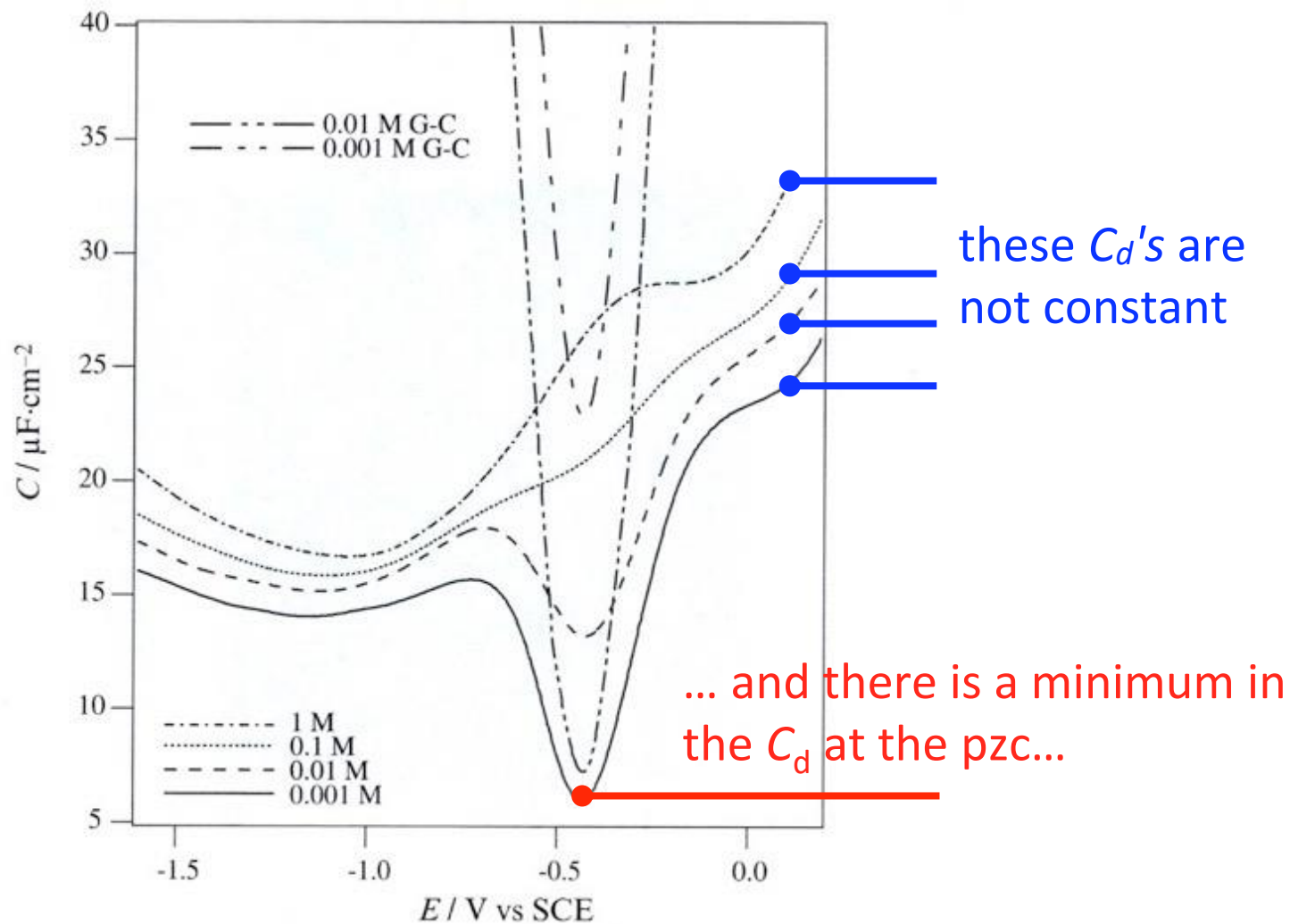these C_d's are not constant

… and there is a minimum in the C_d at the pzc…

Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433V$) with the respective Gouy-Chapman capacity [Paolo Galleto, EPFL thesis].

H.H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, 2004, Figure 5.13

Three traditional models for double layer structure:

1) Helmholtz

2) Gouy–Chapman (GC)

3) Gouy–Chapman–Stern (GCS)

… let's take a look at each of these…

Models of Electrical Double Layer:

2) **The Gouy–Chapman Model**: this model adopts all the same assumptions used in Debye–Hückel Theory, which are the following:

a) ions are considered to be point charges; their polarizability is neglected

b) interactions between ions, and between ions and the electrode are purely electrostatic (i.e. no specific (chemical) adsorption); thus, the IHP and OHP will **not** exist in this model since these planes explicitly require finite ion size = polarizability)

c) the metal is considered a planar surface with a surface charge density, σ^M

d) ions are distributed according to Maxwell–Boltzmann statistics…

RECALL: Debye–Hückel equation
(in water at 25 °C)

$$-\log \gamma_x = \frac{0.51 z_x^2 \sqrt{I}}{1 + 3.3 \alpha_x \sqrt{I}}$$

α = effective diameter of hydrated ion (nm)

… the derivation is long… but the main idea is that you balance thermal motion (Boltzmann) with electrostatics (Poisson/Gauss)…

Physicist & P-Chemist

Physicist & P-Chemist

Peter Joseph William Debye
(1884–1966)

Erich Armand Arthur Joseph Hückel
(1896–1980)
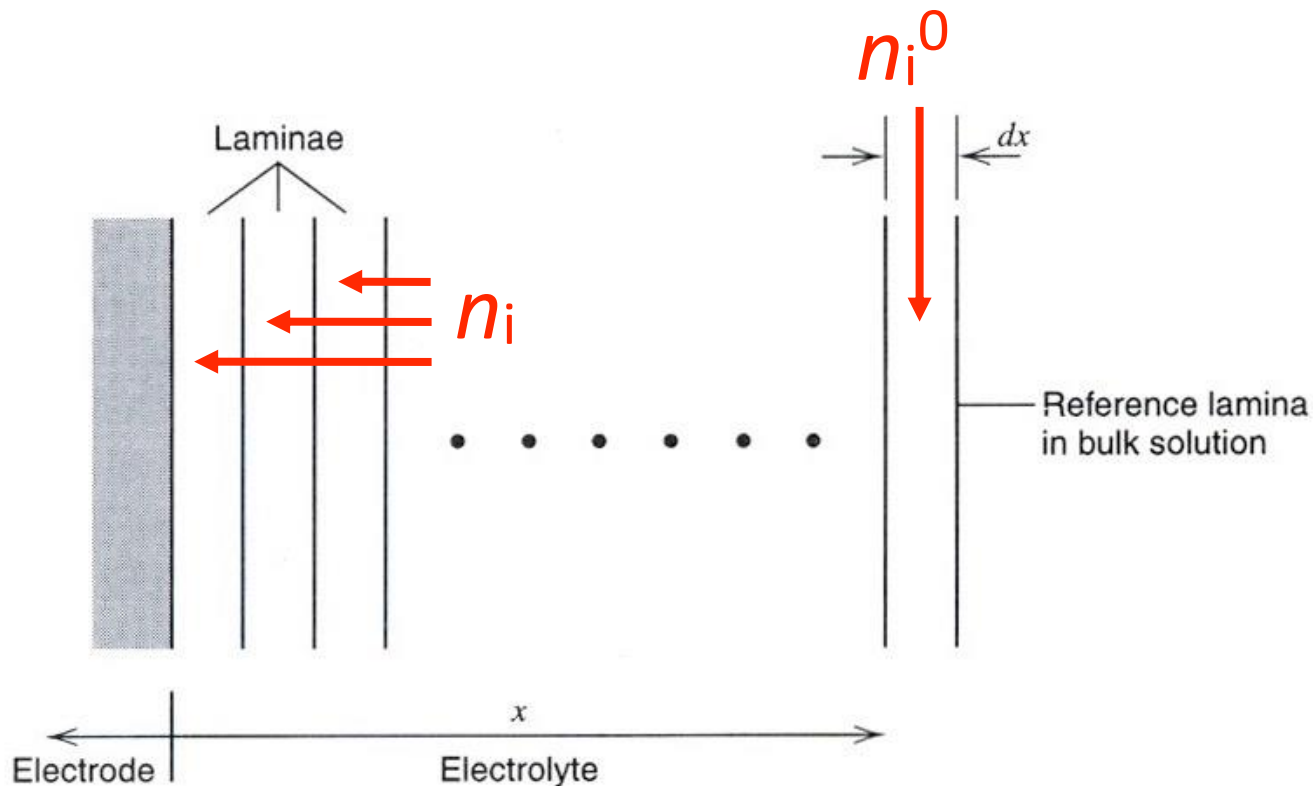
from Wiki

… d) ions are distributed according to Maxwell–Boltzmann statistics…

$$n_i = n_i^0 \exp\left(\frac{-z_i e\phi}{kT}\right)$$

where e is the elementary charge, and ϕ is the electric potential relative to the bulk solution

Figure 13.3.2   View of the solution near the electrode surface as a series of laminae.

the charge density, i.e. charge per unit volume, $\rho(x)$, is defined as:

$$\rho(x) = \sum_i n_i z_i e$$

… so substituting from the last slide…

$$\rho(x) = \sum_i z_i e\, n_i^0 \exp\left(\frac{-z_i e\phi}{kT}\right)$$

… and now the Poisson Equation gives us another expression for $\rho(x)$:

$$\rho(x) = -\varepsilon\varepsilon_0 \frac{d^2\phi}{dx^2}$$

… substituting, we get the Poisson–Boltzmann Equation *(no Maxwell)*…

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\varepsilon\varepsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e\phi}{kT}\right)$$

… if we apply the Poisson–Boltzmann Equation to a 1:1 electrolyte, we obtain the following (see B&F, pp. 547–548):

$$\frac{d\phi}{dx} = -\left(\frac{8\boldsymbol{k}Tn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi}{2\boldsymbol{k}T}\right)$$

… and if we further assume that ϕ^0 is small, we get…
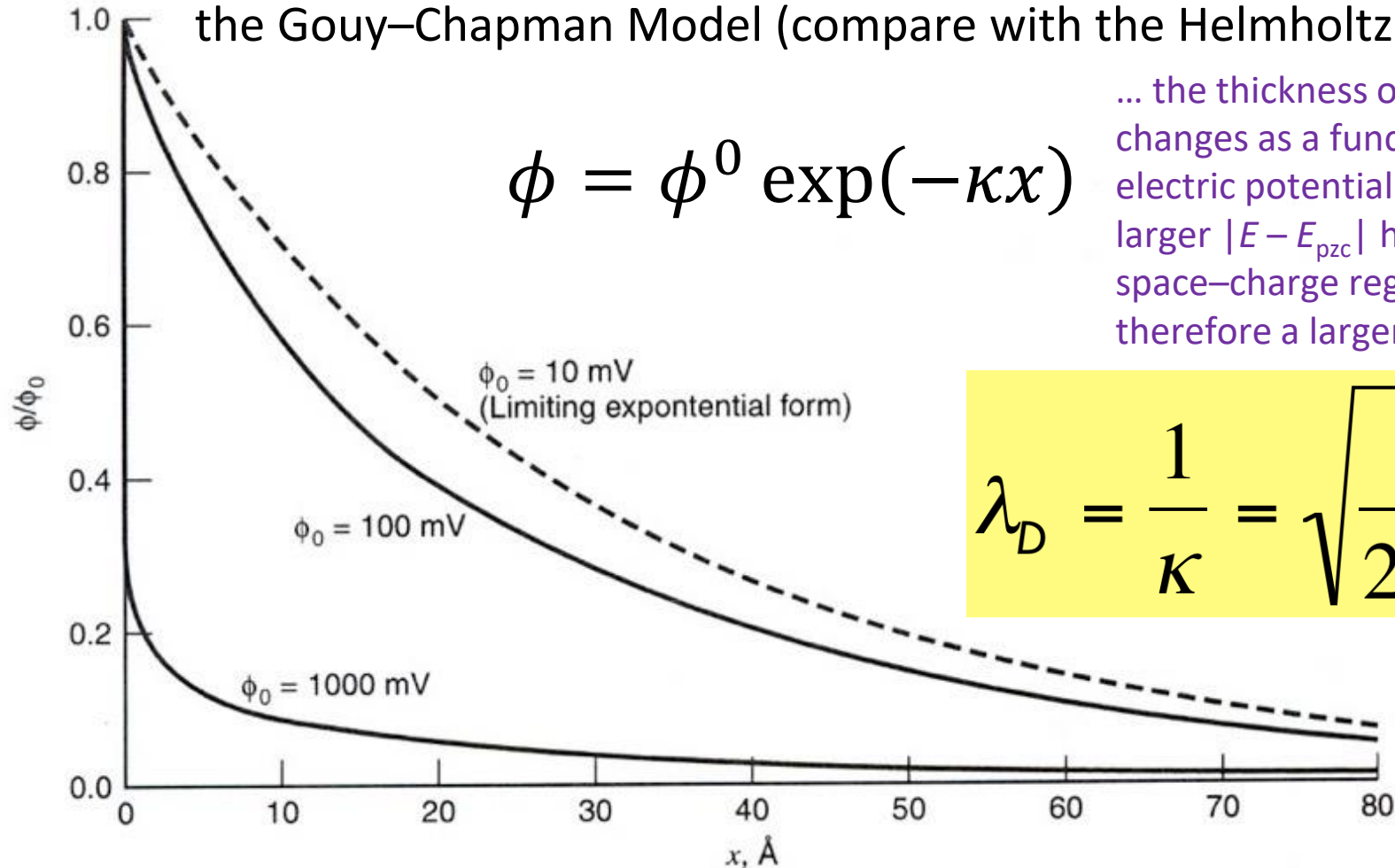
$$\phi = \phi^0 \exp(-\kappa x)$$

… where

$$\kappa = \left(\frac{2n^0 z^2 e^2}{\varepsilon\varepsilon_0 \boldsymbol{k}T}\right)^{1/2}$$

… here, κ has units of 1/distance… we commonly refer to κ^{-1} as λ_D, the "Debye (screening) length" characterizing the solution

… Does a more sophisticated model of the double layer better capture features observed experimentally?

… the electric potential variation near the electrode under the Gouy–Chapman Model (compare with the Helmholtz Model…)

$$\phi = \phi^0 \exp(-\kappa x)$$

… the thickness of the capacitor changes as a function of electric potential… such that a larger $|E - E_{pzc}|$ has a thinner space–charge region… and therefore a larger capacitance

$$\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{2n^0 z^2 e^2}}$$

$\phi_0 = 10$ mV (Limiting expontential form)

$\phi_0 = 100$ mV

$\phi_0 = 1000$ mV

Figure 13.3.3 Potential profiles through the diffuse layer in the Gouy–Chapman model.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.3

… how does the Gouy–Chapman Model do in terms of predicting the correct value of C_d?

$$C_d = \frac{d\sigma^M}{d\phi_0} = \left(\frac{2z^2 e^2 \varepsilon\varepsilon_0 n^0}{kT}\right)^{1/2} \cosh\left(\frac{ze\phi_0}{2kT}\right)$$
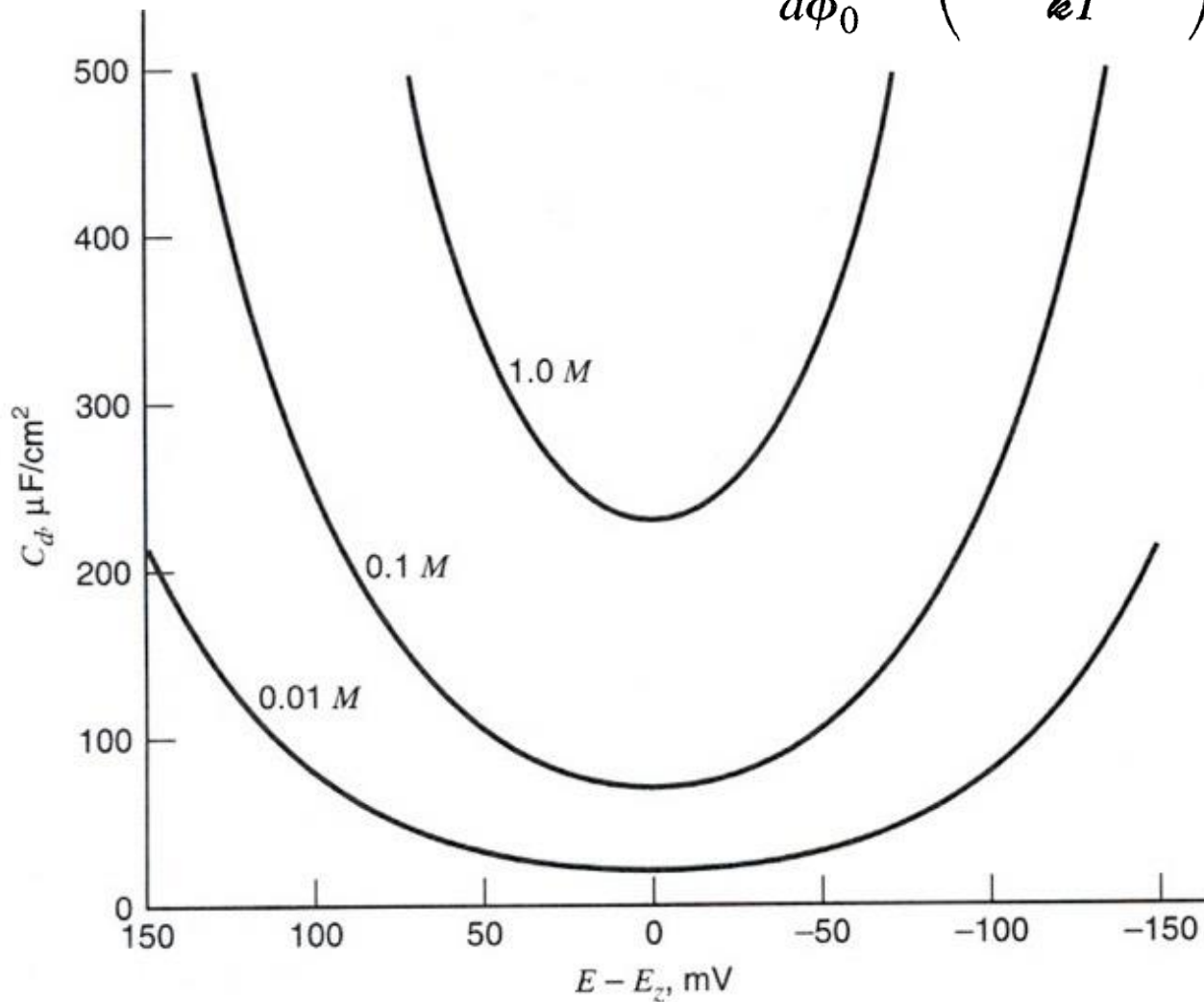
Figure 13.3.5 Predicted differential capacitances from the Gouy–Chapman theory. Calculated from (13.3.21) for the indicated concentrations of a 1:1 electrolyte in water at 25°C. Note the very restricted potential scale. The predicted capacitance rises very rapidly at more extreme potentials relative to E_z.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.5
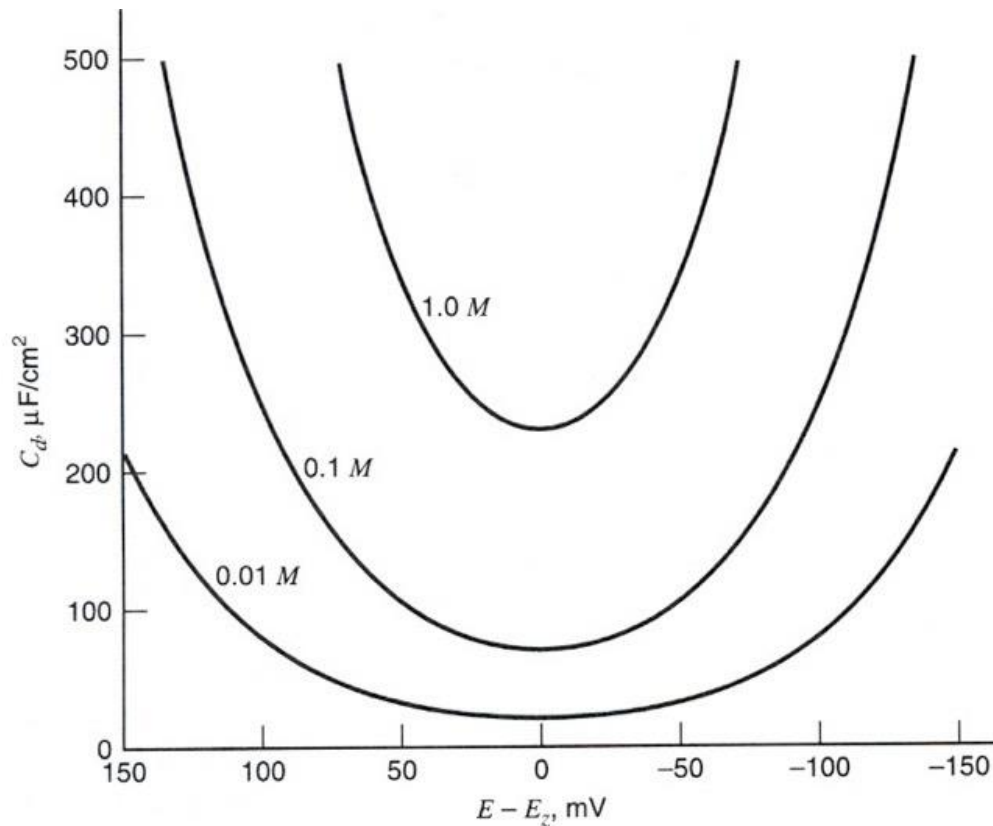
Figure 13.3.5 Predicted differential capacitances from the Gouy–Chapman theory. Calculated from (13.3.21) for the indicated concentrations of a 1:1 electrolyte in water at 25°C. Note the very restricted potential scale. The predicted capacitance rises very rapidly at more extreme potentials relative to E_z.

About Gouy–Chapman Theory we can say the following:

a) it predicts a "dip" in C_d, that becomes more capacitive with increased ionic strength = ***Good!***

b) but it predicts a C_d that is WAY too high as the potential becomes far from the pzc = ***Bad!***...

c) and the C_d is symmetrical about the pzc (why?); this is not what is observed experimentally...

Getting close?

… Notably, near the pzc?
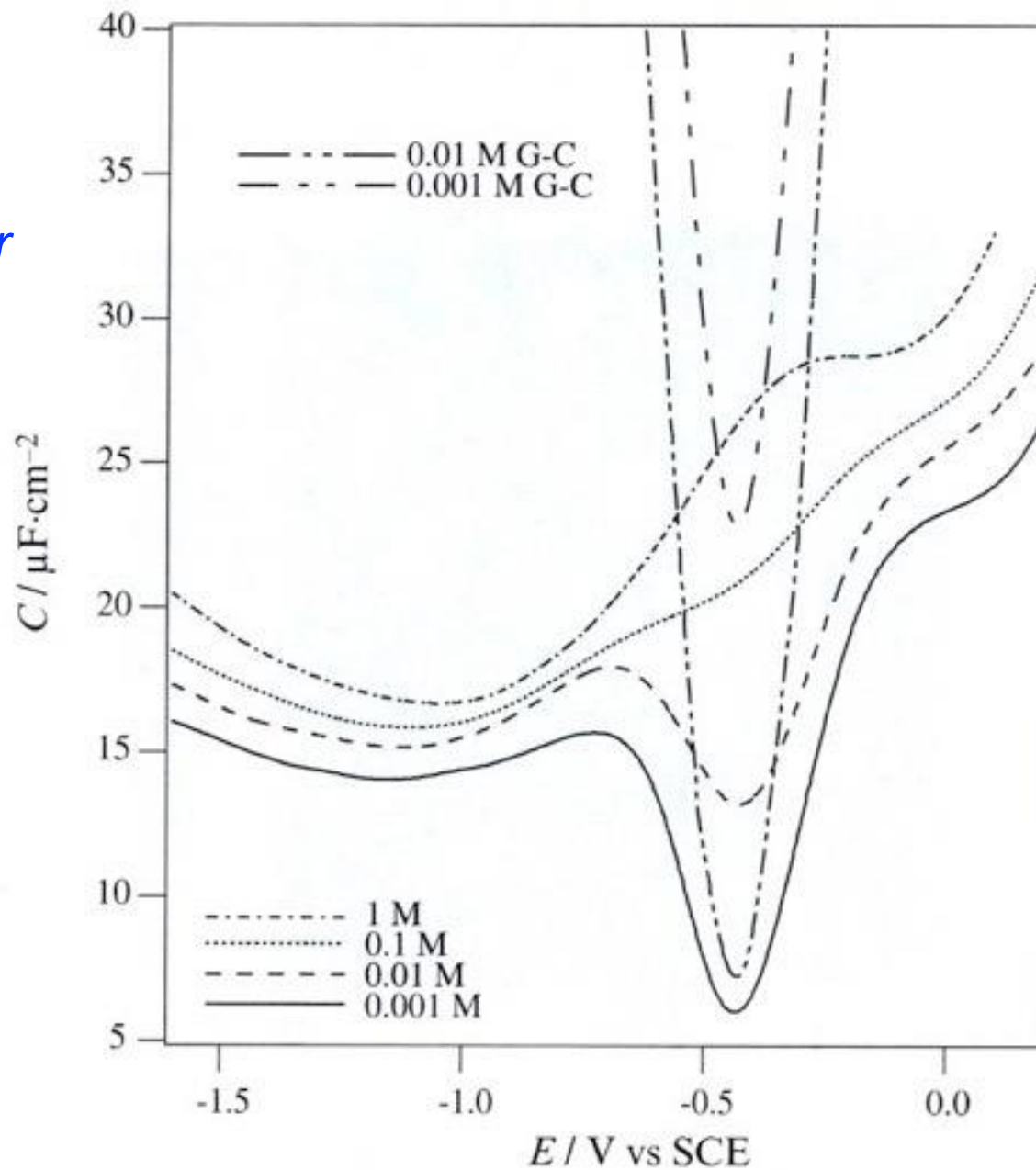
Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433\,V$) with the respective Gouy-Chapman capacity [Paolo Galleto, EPFL thesis].

… example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M $NaClO_4$ solution?

Answer: The diffuse layer thickness is approximated by λ_D. Let's calculate it.

$$\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{2n^0 z^2 e^2}}$$

$$= \sqrt{\frac{(78)(8.854 \, x10^{-12} C^2 / Jm)(1.381 x10^{-23} J/K)(298K)}{2(100(6.022 x10^{23})/m^3)(1)^2(1.602 x10^{-19} C)^2}}$$

$$n^0 = \frac{0.1 moles}{dm^3} \frac{10^3 dm^3}{m^3} \frac{6.022 x10^{23} \, ions}{mole} = 6.022 x10^{25} ions / m^3$$

... *example*: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M $NaClO_4$ solution?

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$$\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{2n^0 z^2 e^2}}$$

$$= \sqrt{\frac{(78)(8.854 \times 10^{-12} C^2 / Jm)(1.381 \times 10^{-23} J/K)(298K)}{2(100(6.022 \times 10^{23})/m^3)(1)^2(1.602 \times 10^{-19} C)^2}}$$

$$= 9.589 \times 10^{-10} m = 9.6 \text{Å}$$

≈ 1 nm... about the same thickness as the compact layer...

Wow!

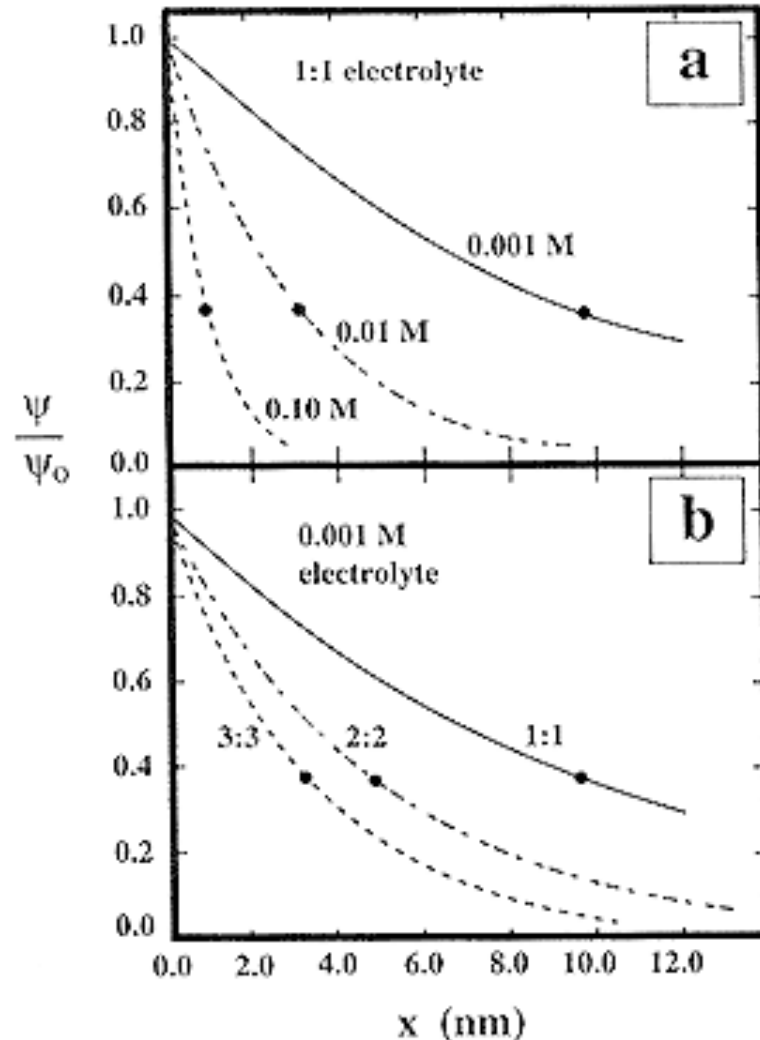*... example*: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M $NaClO_4$ solution?

TABLE 13.3.1   Characteristic Thickness of the Diffuse Layer[a]

$C*(M)^b$	$1/\kappa(\mathring{A})$
1	3.0
10^{-1}	9.6
10^{-2}	30.4
10^{-3}	96.2
10^{-4}	304

[a]For a $1:1$ electrolyte at 25°C in water.
[b]$C* = n^0/N_A$ where N_A is Avogadro's number.

... and related, this means that the electrostatic repulsion between charged colloid particles, for example, is *very short range* at high electrolyte concentrations... suspensions of these particles frequently precipitate

Paul Hiemenz, Raj Rajagopalan. *Principles of Colloid and Surface Chemistry, Third Edition.* Dekker, New York: 1997, p. 514

Three traditional models for double layer structure:
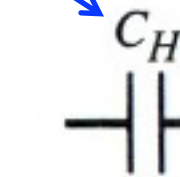
1) Helmholtz

2) Gouy–Chapman (GC)

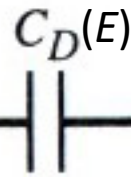3) Gouy–Chapman–Stern (GCS)

… let's take a look at each of these…

Models of Electrical Double Layer:

3) **The Gouy–Chapman–Stern Model**: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

Parallel plate capacitance of the compact layer from the (H)elmholtz model

Potential-dependent non-parallel-plate capacitance of the (D)iffuse layer from the GC model

C_H $C_D(E)$ = $C_d(E)$

Potential-dependent non-parallel-plate capacitance of the (d)ouble layer from the GCS model

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

Models of Electrical Double Layer:

3) **The Gouy–Chapman–Stern Model**: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

Parallel plate capacitance of the compact layer from the (H)elmholtz model

Potential-dependent non-parallel-plate capacitance of the (D)iffuse layer from the GC model

$$C_H \qquad C_D(E) \qquad = \qquad C_d(E)$$
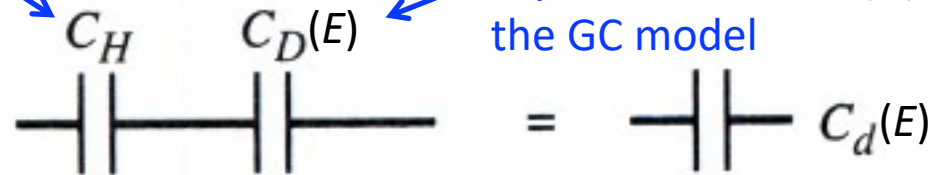
But, wait a minute! This is modeling just one interface with two sides, but there are two capacitors (and thus in total seemingly four sides)… what gives?

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

If it barks like a dog, and it smells like a dog, then maybe we should model it as being a dog…
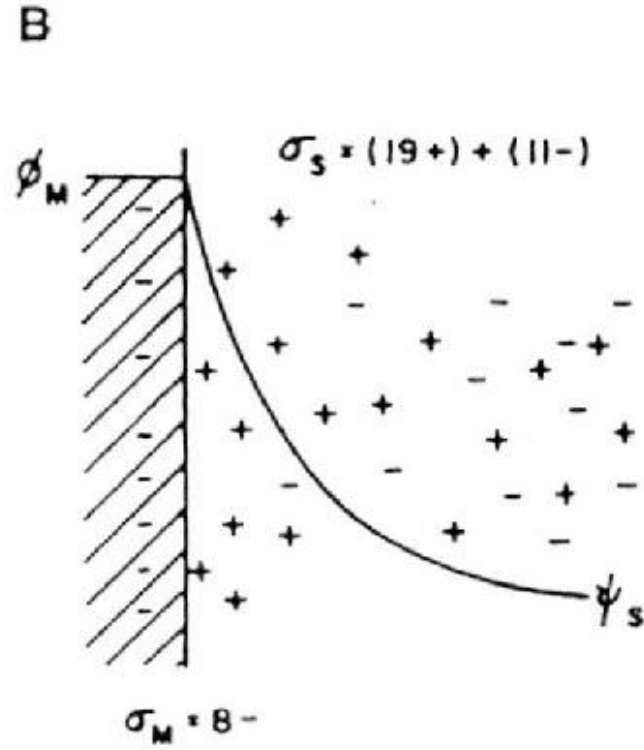
… **What are the units?**

This means that the electric potential drop across the Helmholtz Layer (inside of the OHP) will be linear, and a quasi-exponential potential drop will extend from this point and into the bulk solution…
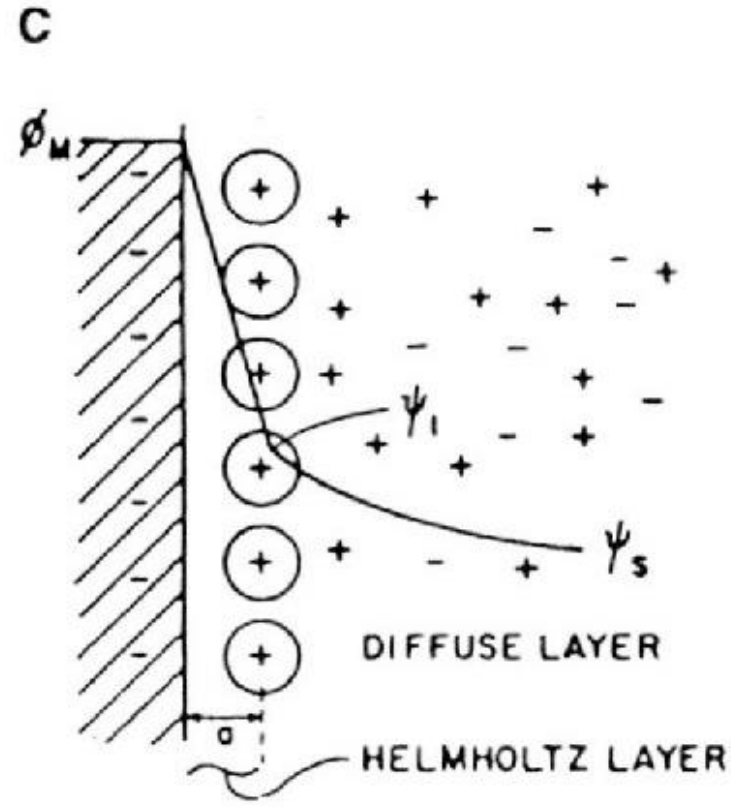
... our three models for the potential distribution near a charged electrode immersed in an electrolyte solution...
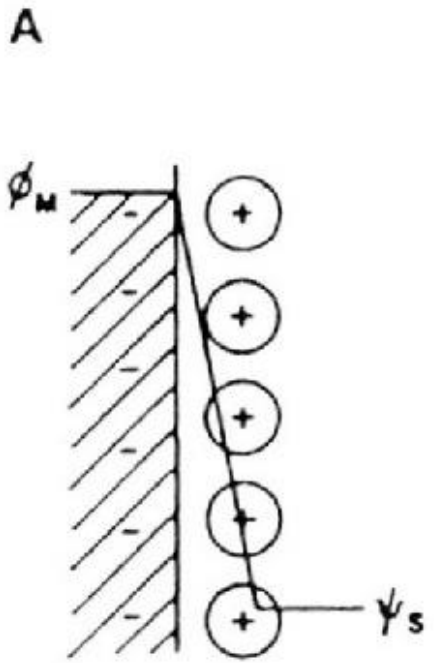
Helmholtz (H)   Gouy–Chapman (GC)   Gouy–Chapman–Stern (GCS)

http://electrochem.cwru.edu/

Physician & Physicist

Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)

Physicist

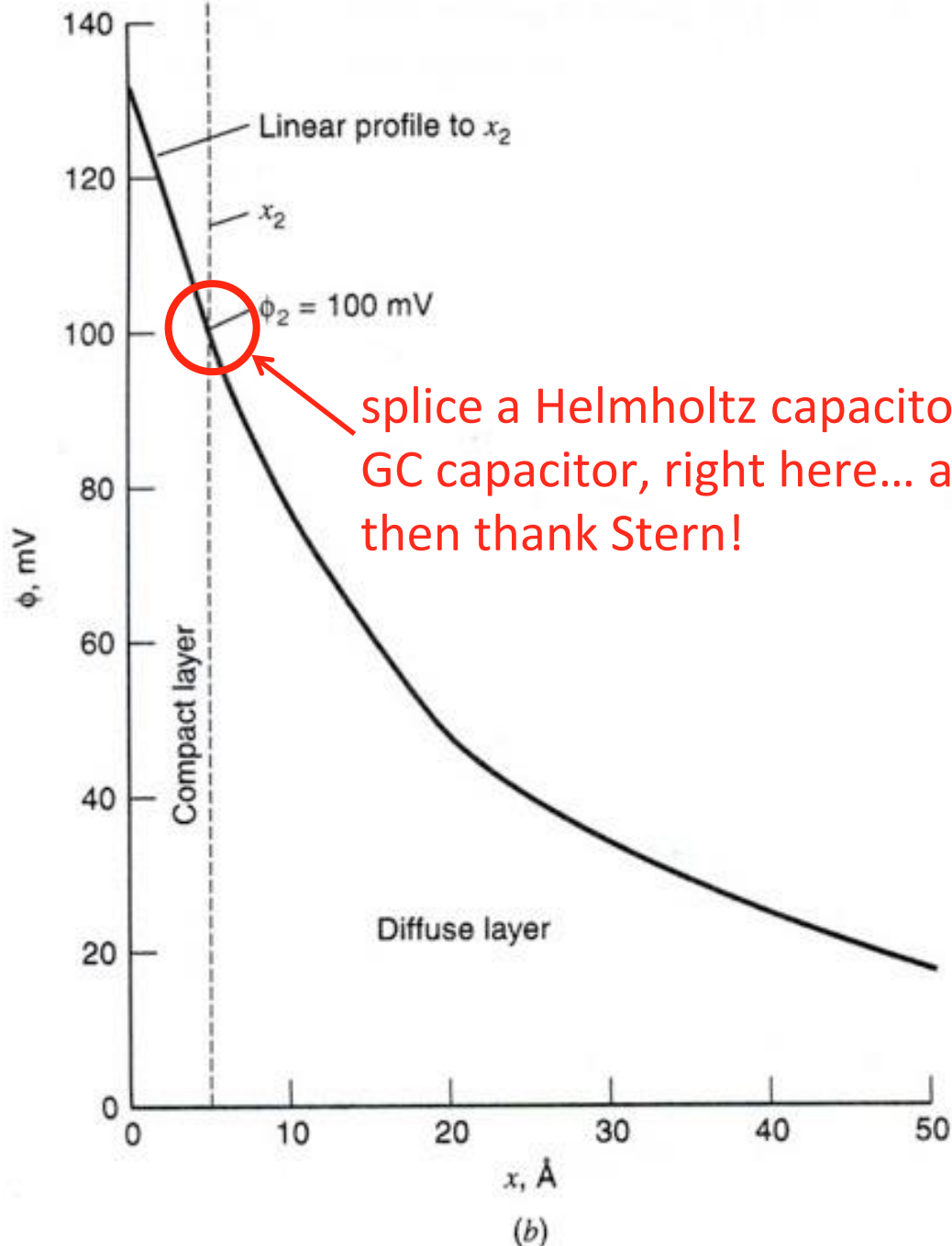Otto Stern
(1888–1926)
Nobel Prize (Physics, 1943)

Physicist

Louis Georges Gouy
(1854–1926)

P-Chemist

David Leonard Chapman
(1869–1958)

from Wiki

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.

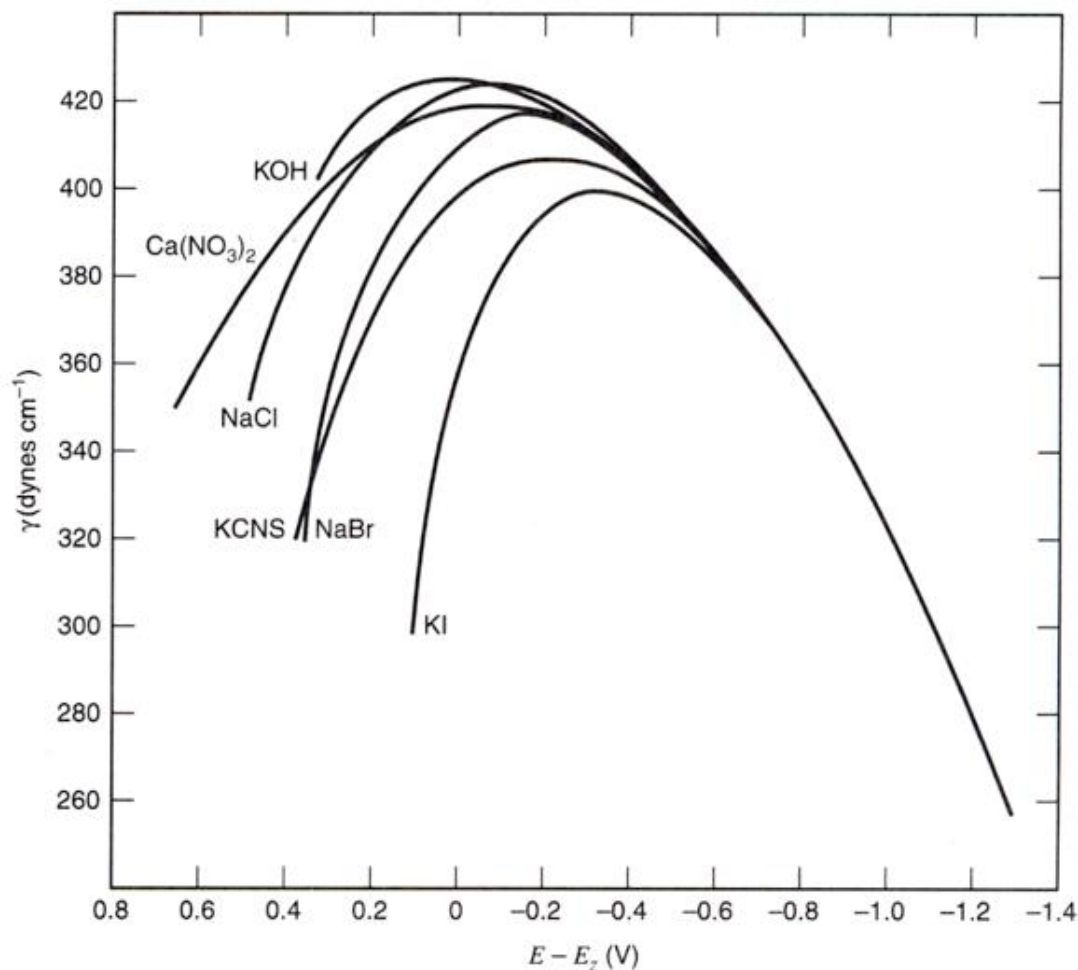Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.6

... the mathematical details are in B&F, pp. 551 − 552, but qualitatively, what GCS does is it uses the smaller capacitance of either C_H or $C_{D(GC)}$...

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

$C_H \ll C_{D(GC)}$

$C_d \approx C_H$

$C_{D(GC)} \ll C_H$

$C_d \approx C_{D(GC)}$
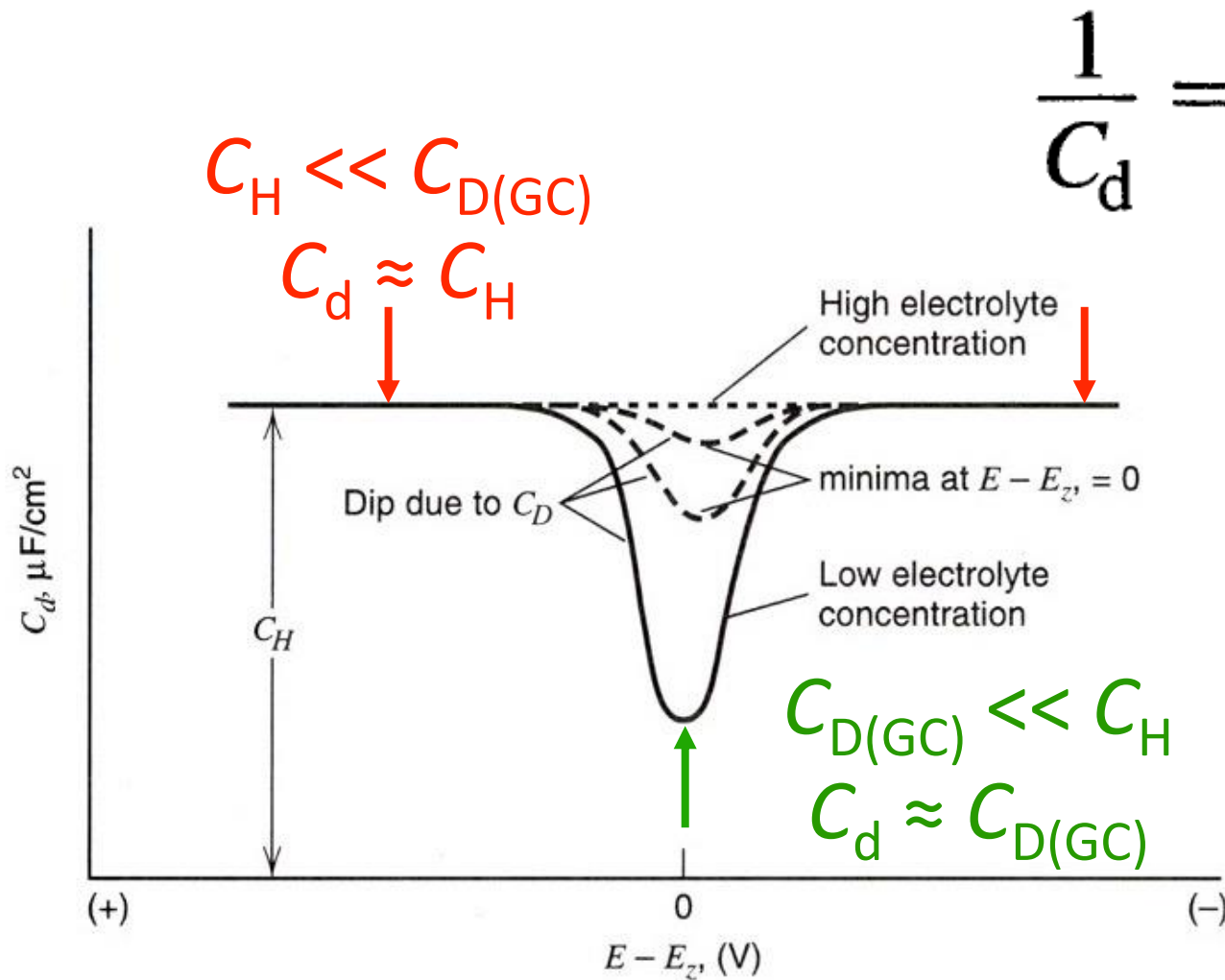
Figure 13.3.7 Expected behavior of C_d according to GCS theory as the electrolyte concentration changes.

And lastly, what effect does *specific adsorption* have on the pzc?
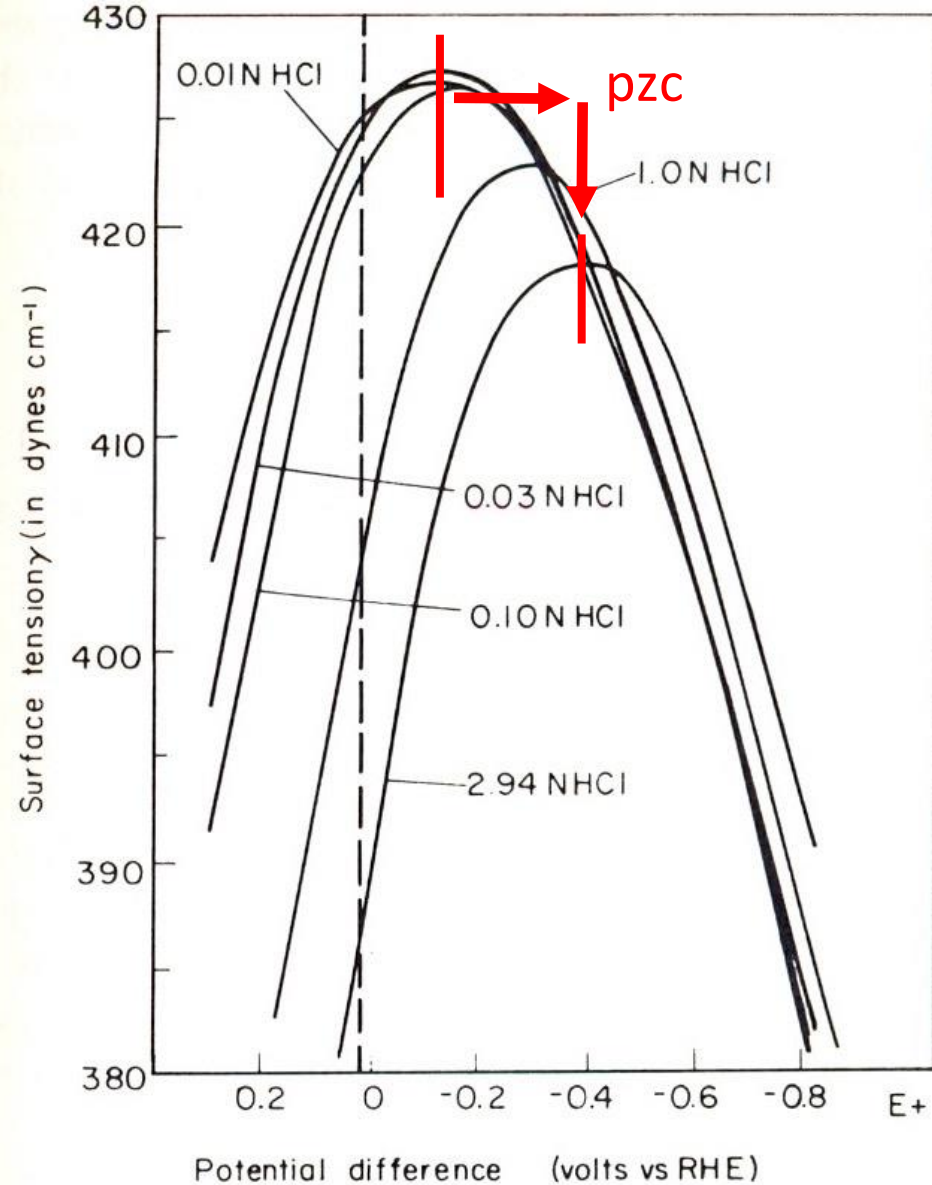The answer is hinted at in the data that we saw earlier…

Figure 13.2.2 Electrocapillary curves of surface tension *vs.* potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.2.2

… but to really reveal specific adsorption, one must look carefully at the concentration (activity) dependence of the pzc. *If there is one, then specific adsorption is occurring…*
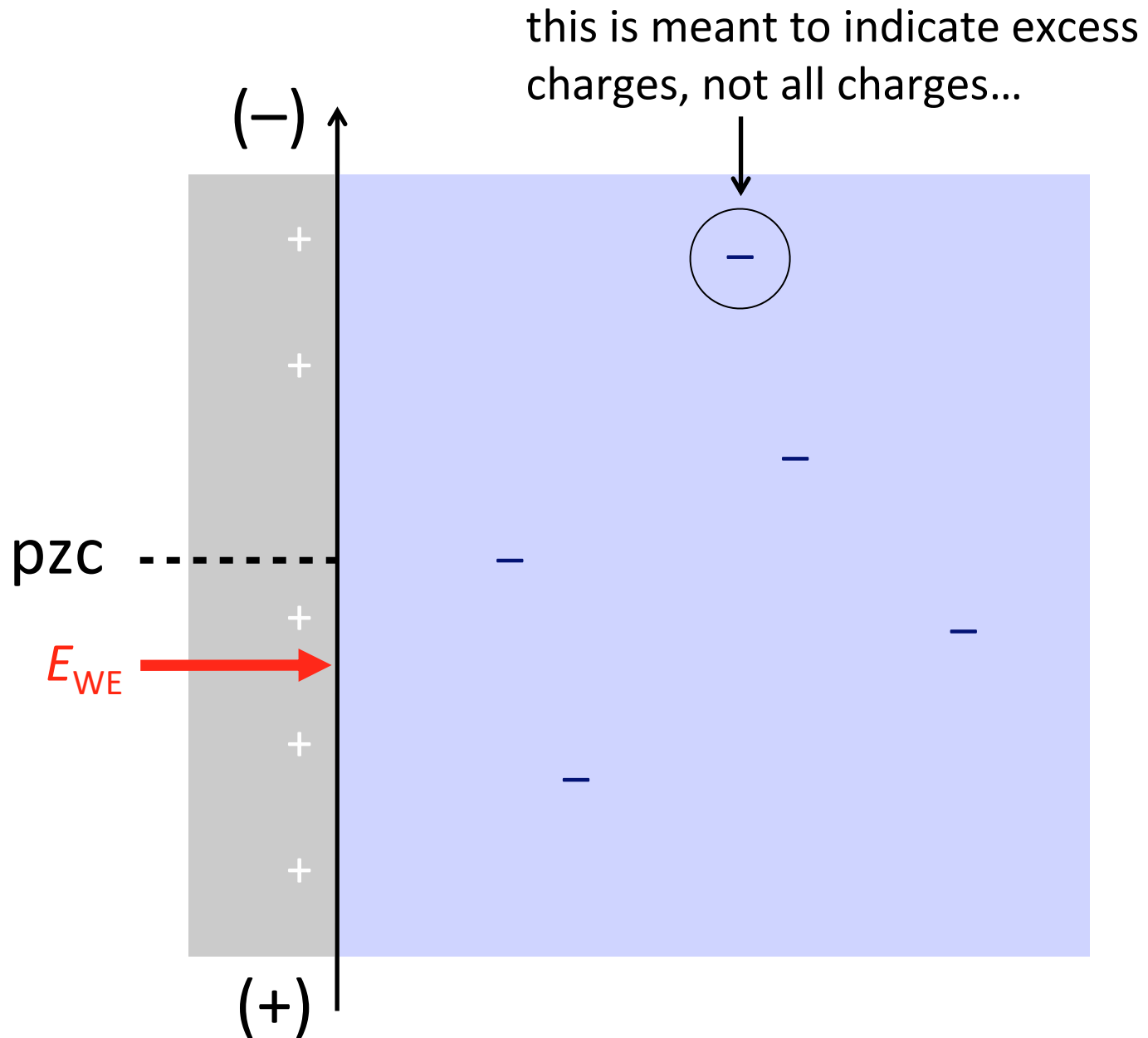
The *sign* of the shift in pzc is the sign of the ion that is adsorbing…

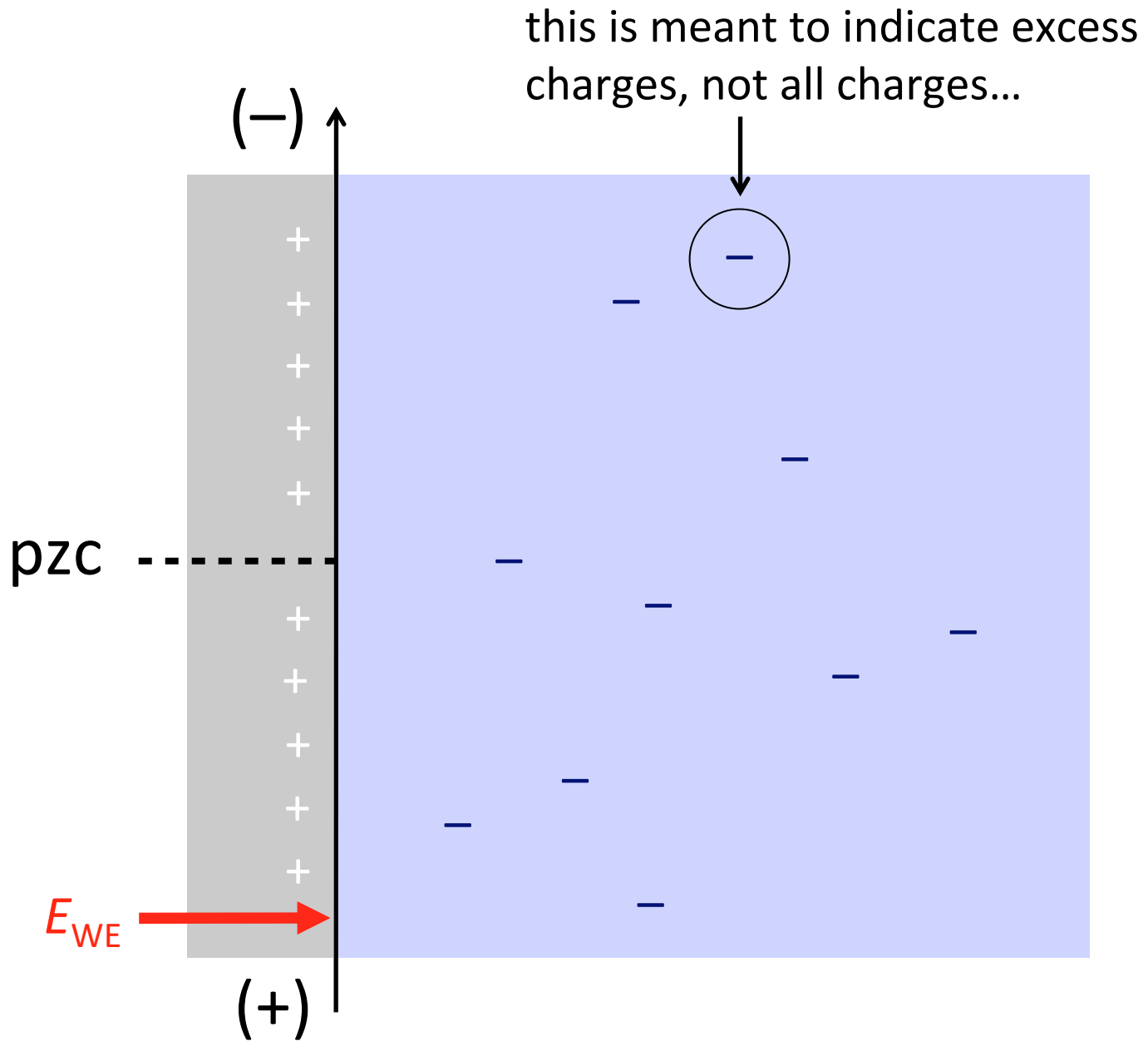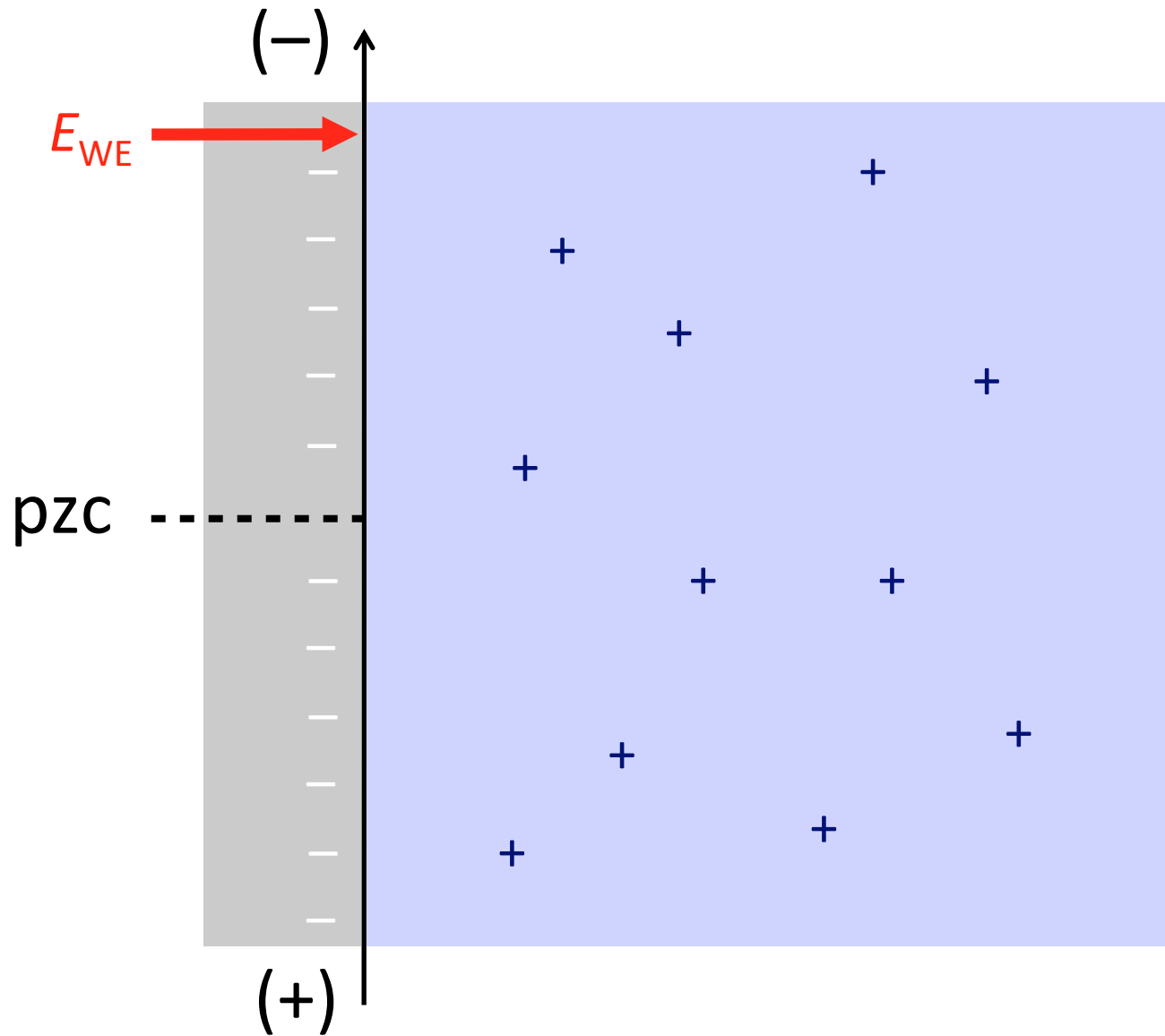… for this we define the *Esin–Markov coefficient* for a given σ^M (= 0), as the following slope:

$$\frac{1}{RT}\left(\frac{\partial E_{\pm}}{\partial \ln a_{salt}}\right)_{\sigma^M} = \left(\frac{\partial E_{\pm}}{\partial \mu_{salt}}\right)_{\sigma^M}$$

Bockris and Reddy, Plenum Press, 1973, Figure 7.57
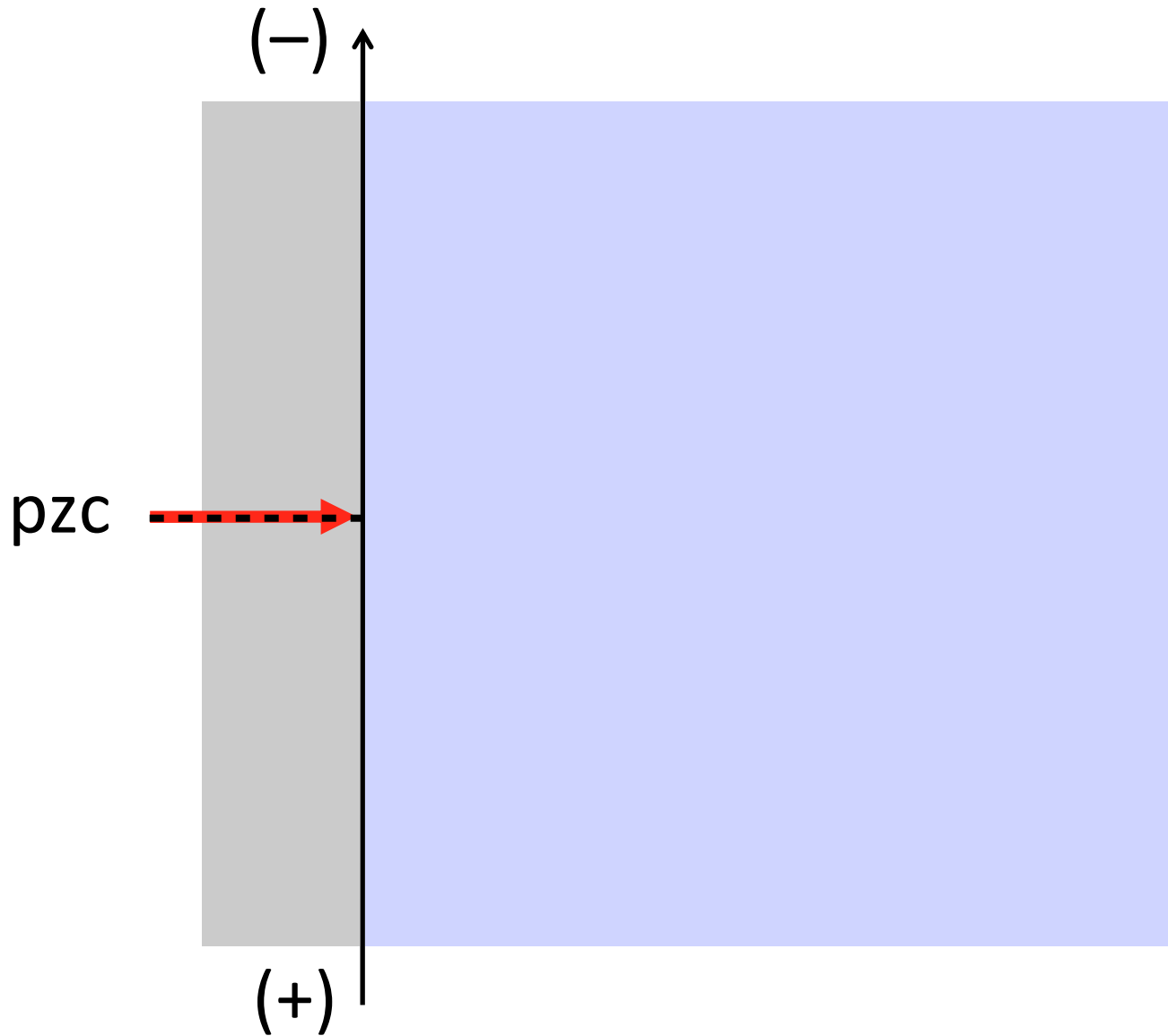

Fig. 7.57. Electrocapillary curves from solutions of different electrolyte (HCl) concentration. The symbol RHE stands for a reversible hydrogen electrode immersed, not in a standard solution, but in the same electrolyte as the electrode under study.

… why a negative shift with anion adsorption?

this is meant to indicate excess charges, not all charges…

(−)

pzc

E_{WE}

(+)

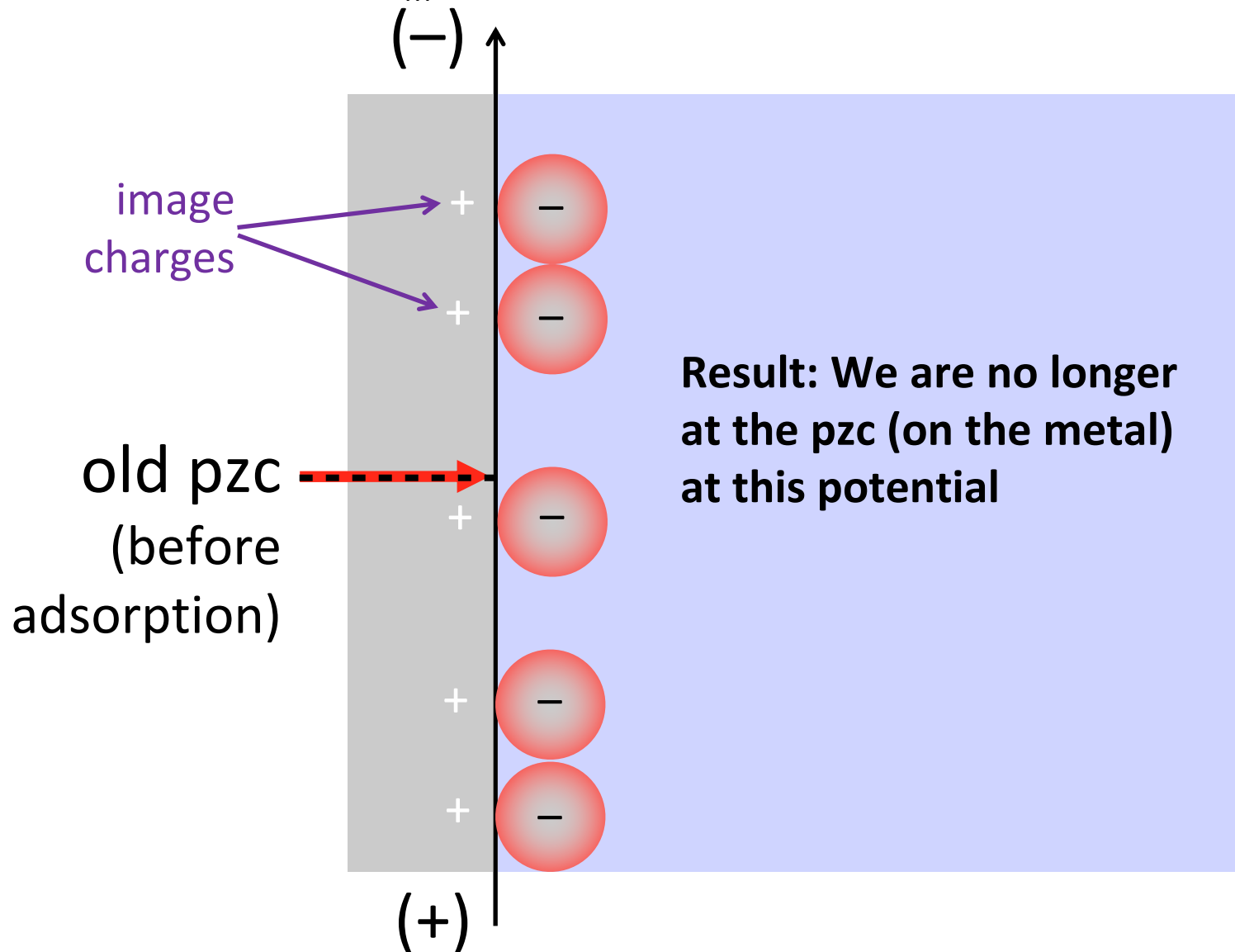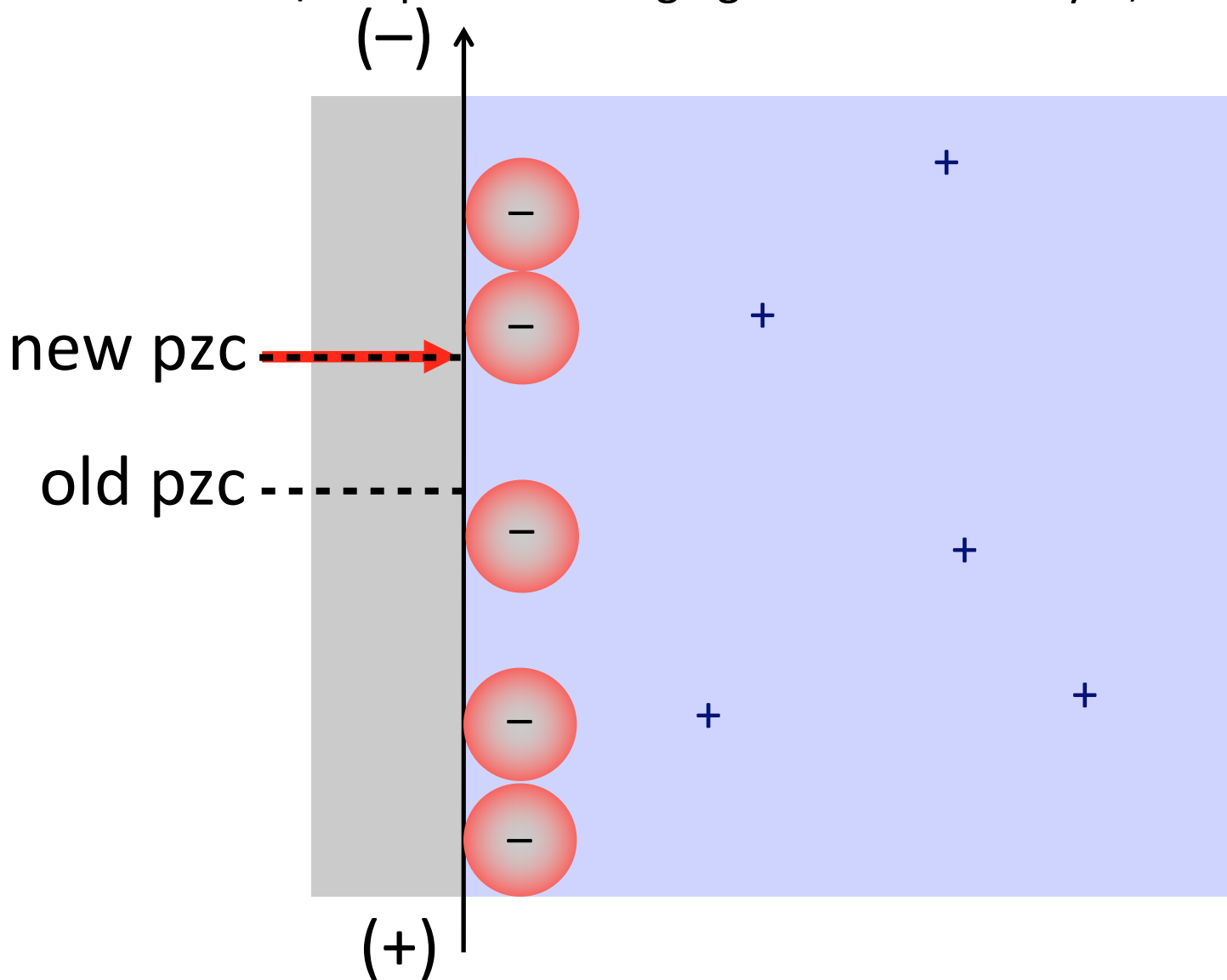… at the pzc, $q_M = 0$ and there is no excess positive or negative charge in the solution…

… now, an adsorbing anion is added and thus fixed negative charge is added to the solution side of the interface… this new q_S is matched by an equal **and opposite** q_M on the electrode side…

image charges

old pzc (before adsorption)

Result: We are no longer at the pzc (on the metal) at this potential

(−)

(+)

… a new pzc exists, which is the potential required to neutralize charges in the metal, but due to charges *on both sides of the interface*… notice the location of the +/− capacitive charging in the diffuse layer, in this case
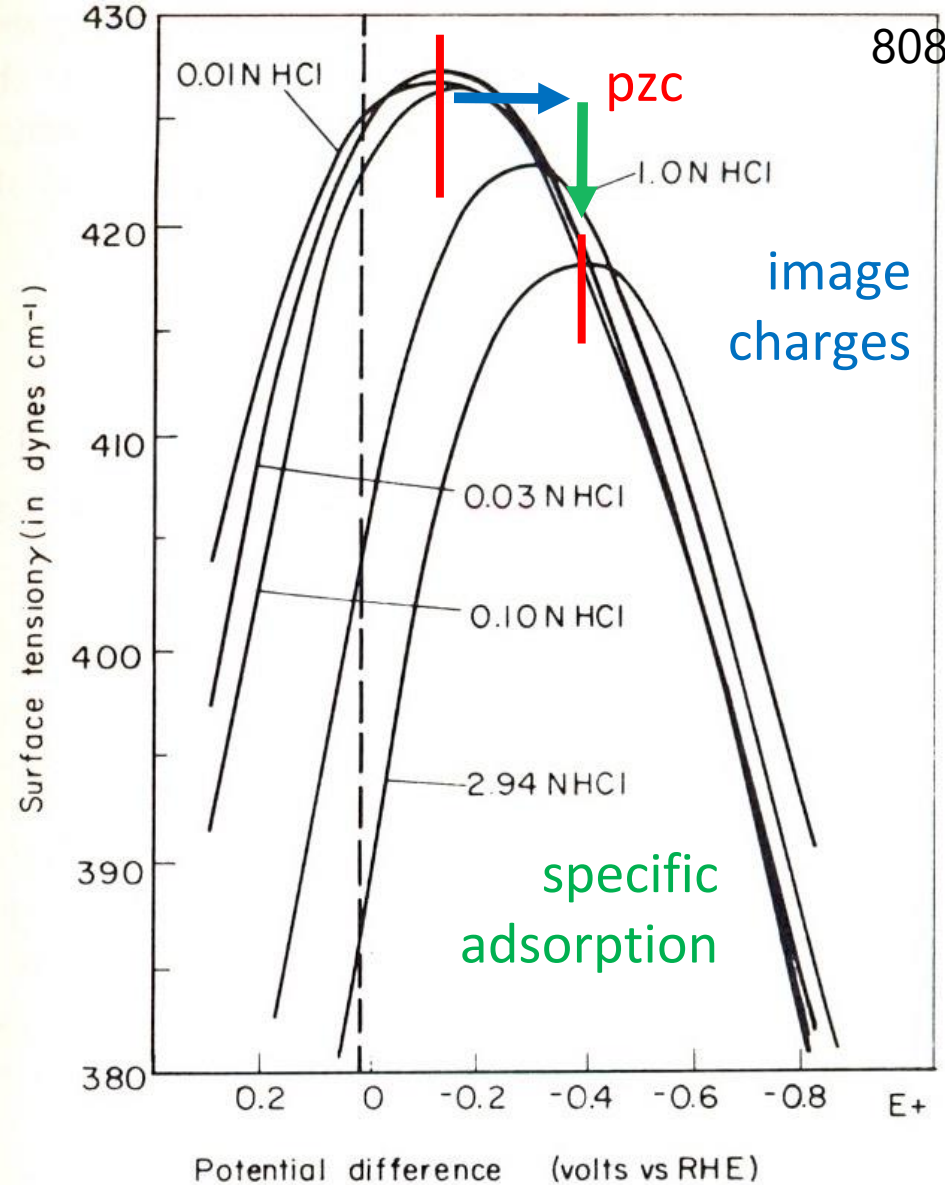
… but to really reveal specific adsorption, one must look carefully at the concentration (activity) dependence of the pzc. *If there is one, then specific adsorption is occurring…*

The *sign* of the shift in pzc is the sign of the ion that is adsorbing…

… for this we define the *Esin–Markov coefficient* for a given σ^M (= 0), as the following slope:

$$\frac{1}{RT}\left(\frac{\partial E_{\pm}}{\partial \ln a_{salt}}\right)_{\sigma^M} = \left(\frac{\partial E_{\pm}}{\partial \mu_{salt}}\right)_{\sigma^M}$$

Bockris and Reddy, Plenum Press, 1973, Figure 7.57

pzc

image charges

specific adsorption

0.01 N HCl

1.0 N HCl

0.03 N HCl

0.10 N HCl

2.94 N HCl

Surface tension γ (in dynes cm⁻¹)

Potential difference   (volts vs RHE)

Fig. 7.57. Electrocapillary curves from solutions of different electrolyte (HCl) concentration. The symbol RHE stands for a reversible hydrogen electrode immersed, not in a standard solution, but in the same electrolyte as the electrode under study.

… a new pzc exists, which is the potential required to neutralize charge, due to charges *on both sides of the interface*… specific adsorption! *(SKIPPED)*
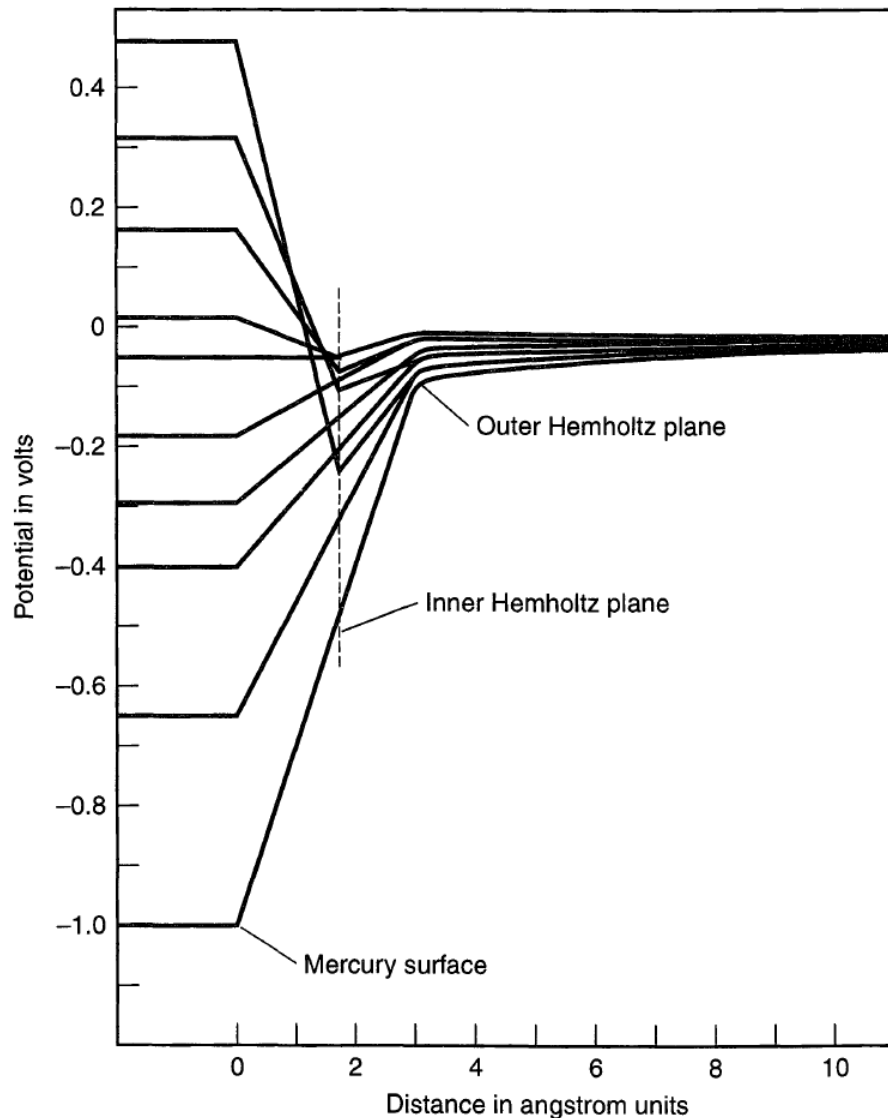
Figure 13.3.8 Calculated potential profiles in the double layer for mercury in contact with aqueous 0.3 *M* NaCl at 25°C. Potentials given with respect to the PZC in NaF. At positive electrode potentials the profile has a sharp minimum because chloride is specifically adsorbed. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.8

… what about uncharged adsorbates, like organic molecules?   *(SKIPPED)* 810
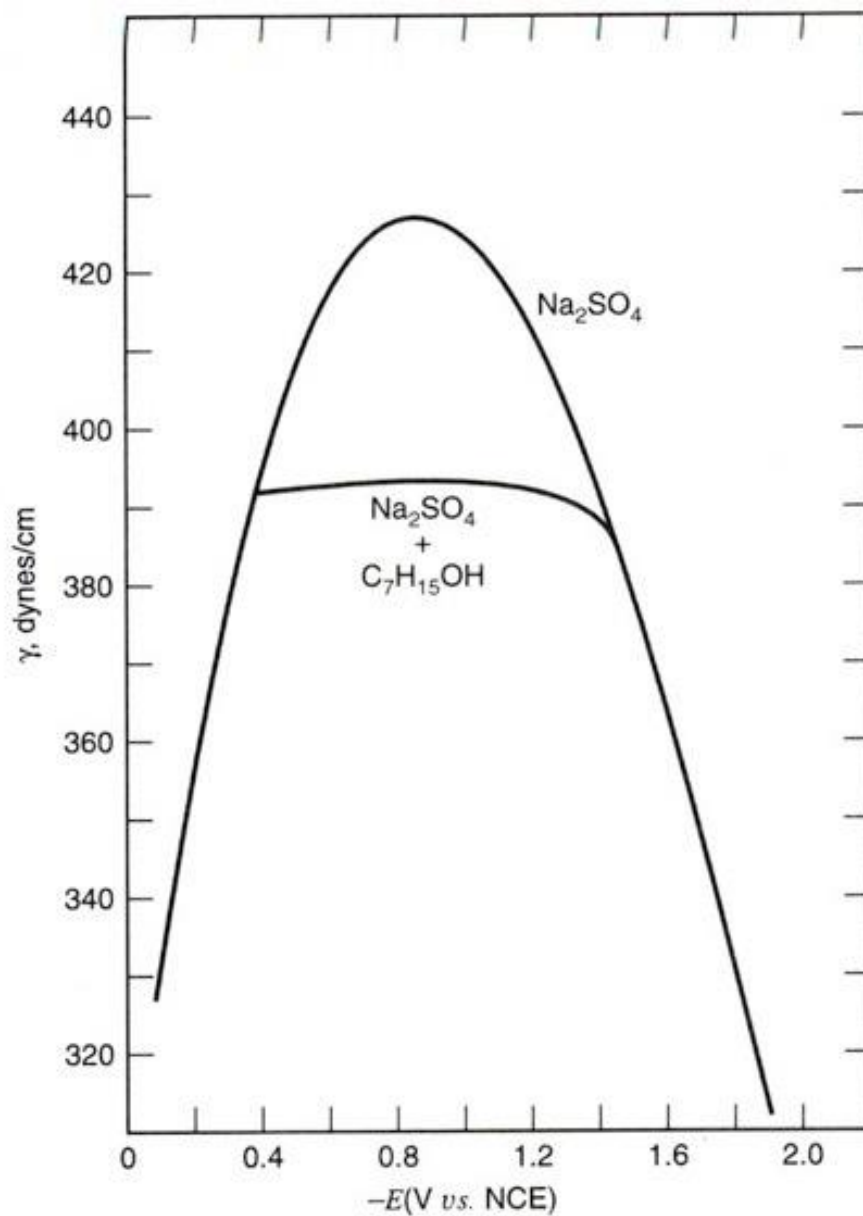
Figure 13.9.1 Electrocapillary curves for mercury in contact with 0.5 *M* Na_2SO_4 in the presence and absence of *n*-heptanol. Data from G. Gouy, *Ann. Chim. Phys.*, **8**, 291 (1906). [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.9.1

what is the origin of these sharp C_d peaks?
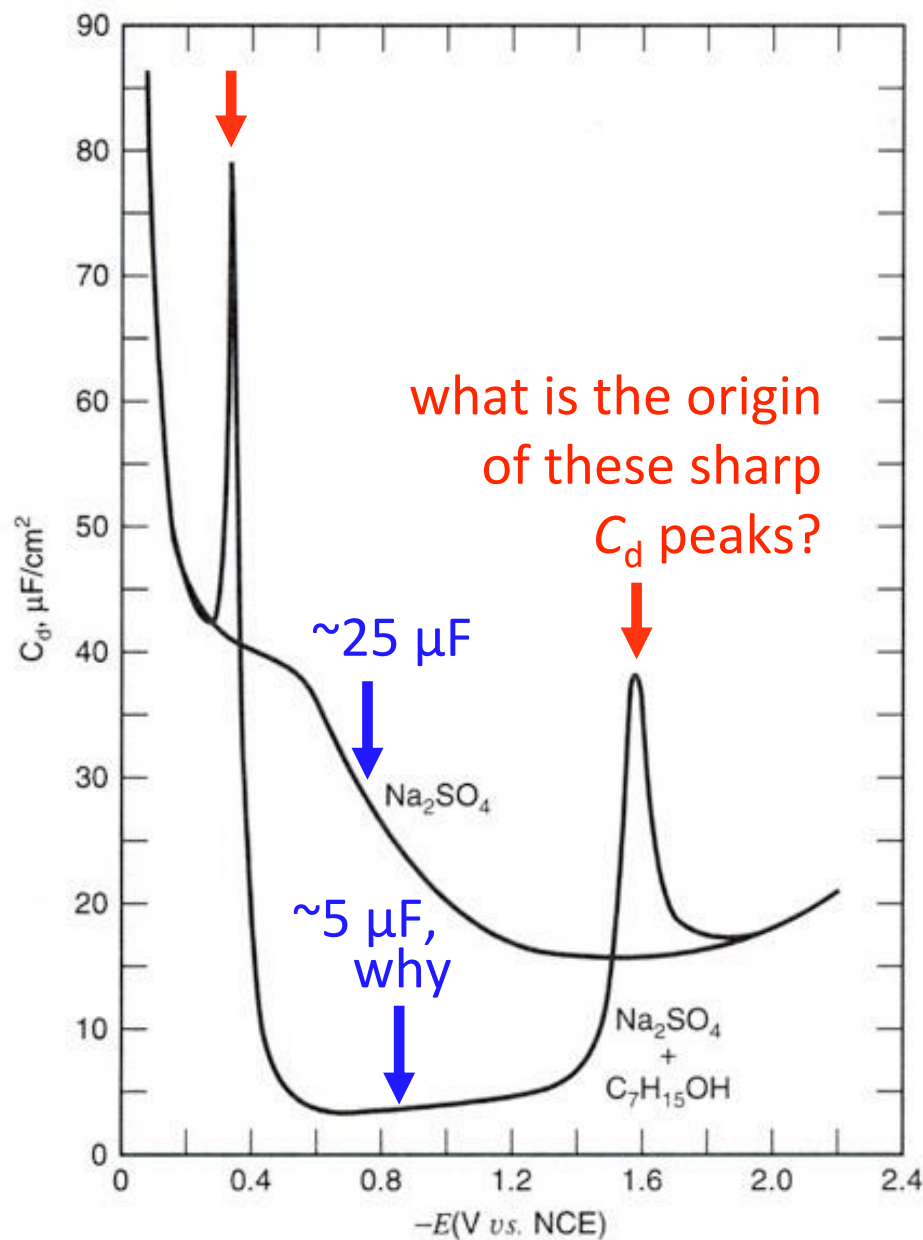
… Gunk that is redox-active… and whose capacitance is called *chemical, or quantum, capacitance*

… Gunk is blocking ~80% of surface!

~25 µF

~5 µF, why

Figure 13.9.2 Differential capacitance curves corresponding to the systems of Figure 13.9.1. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.9.2

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power…

…. but don't forget my questions from the start of this series of lectures on the double layer…

… What is the potential difference between the two sides? E_{app}

What is the potential difference between one side and near the middle? $\sim E_{app}/2$

NEW QUESTION: **Can anyone explain how a corrosion reaction can be potential dependent when the electron never transfers across the metal|solution interface?**

diffuse layer

electrode

solution

R

R

M⁺

OHP

IHP
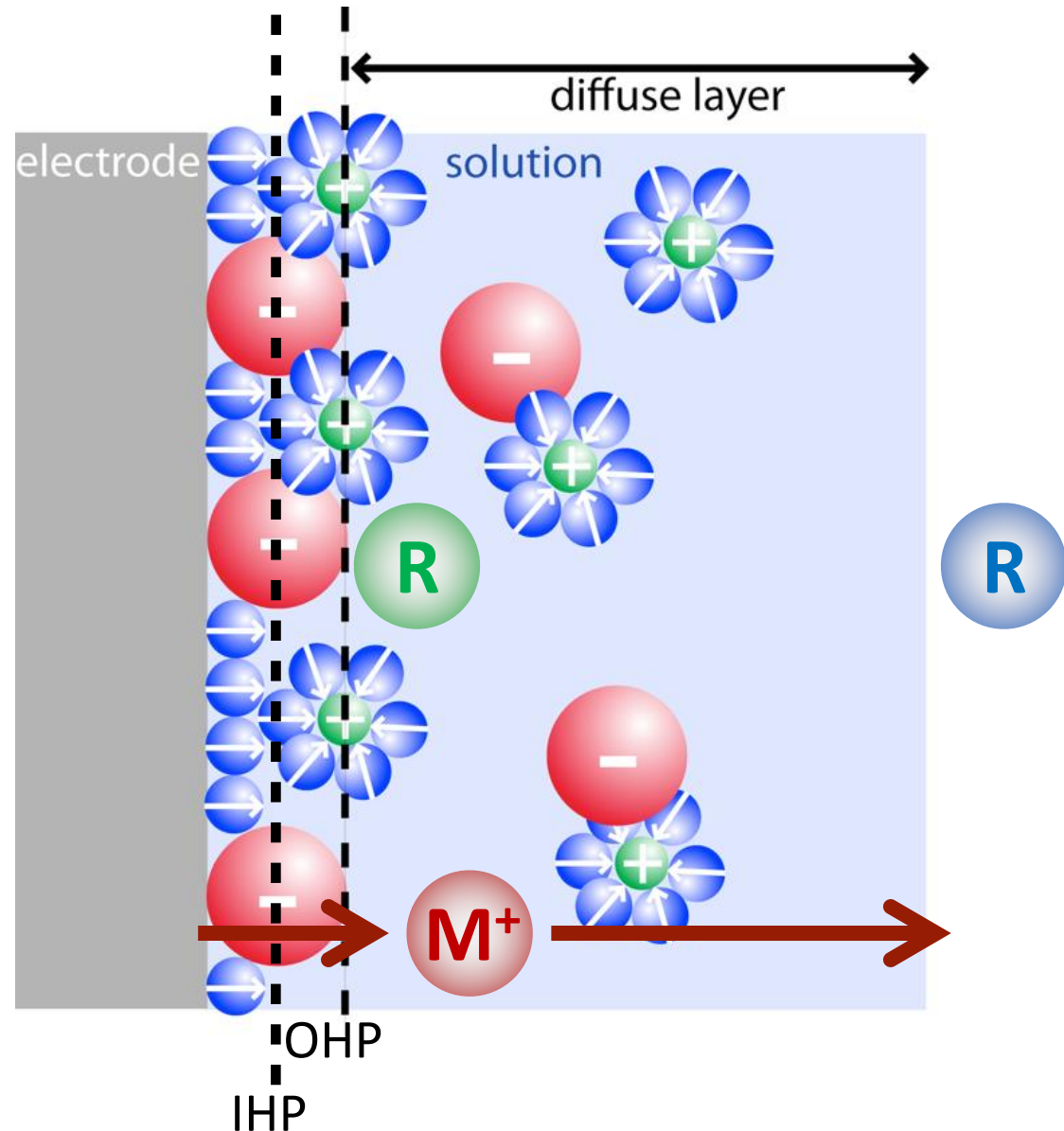
An ion transfers across the double layer… *mind = blown, again!*

Q: What *was* in this set of lectures?

A: B&F Chapter 13 main concepts:

- Section 1.2.3:   Double layer structure

- Sections 13.1 & 13.2: Gibbs adsorption isotherm,
  Electrocapillar(it)y, Surface excess,
  Lippmann's equation, Point of Zero Charge

- Section 13.3:   Models: Helmholtz, Gouy–Chapman
  (Poisson–Boltzmann), Gouy–Chapman–Stern

- Section 13.5:   Specific adsorption

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power…

(BRIEFLY)

Now what about starting with this approximate behavior (an active area of research)…

… plus adding in Faradaic charge-transfer reaction kinetics?!?!?!

… Oh yeah!!! … Now we're talking!

… still don't forget about the location of the reactants and products within/outside of the double layer during Faradaic charge transfer