

Lecture #17 of 20+

The Double Layer

Chapter 13

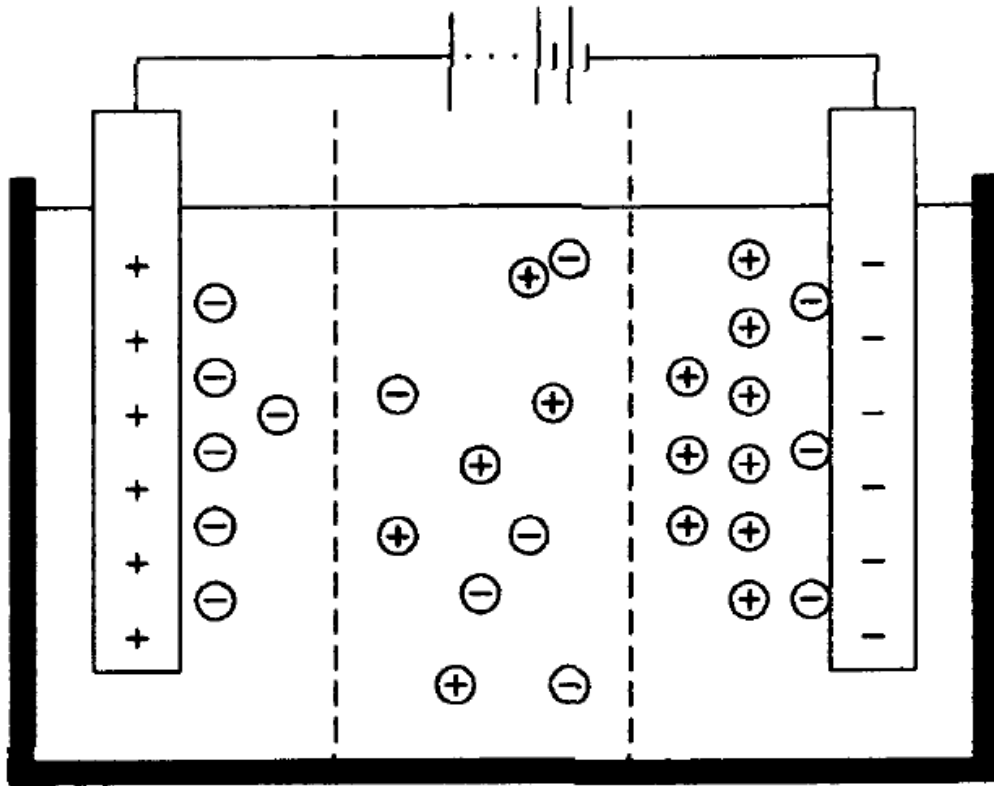
Q: What's in this set of lectures?

A: B&F Chapter 13 main concepts:

- Section 1.2.3: Double layer structure
- Sections 13.1 & 13.2: Gibbs adsorption isotherm, Electrocapillary, 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

the electronic and ionic charge on an electrode, q_M , is compensated by the 703
 accumulation of oppositely charged ions in solution: $q_M = -q_S$

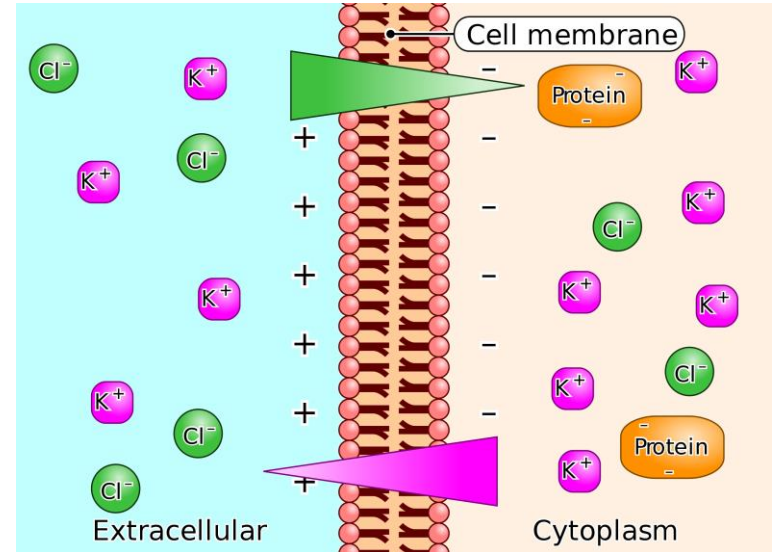
... this sounds just like a **Donnan equilibrated membrane interface** due to
 having a species confined to one side of the membrane (R^- is like e^- in metals)



$$\sum_i q_{ions} = 0 \quad \underbrace{q_M + \sum_i q_{ions}} = 0$$

model this part

... the bulk solution is called "quasi-neutral"

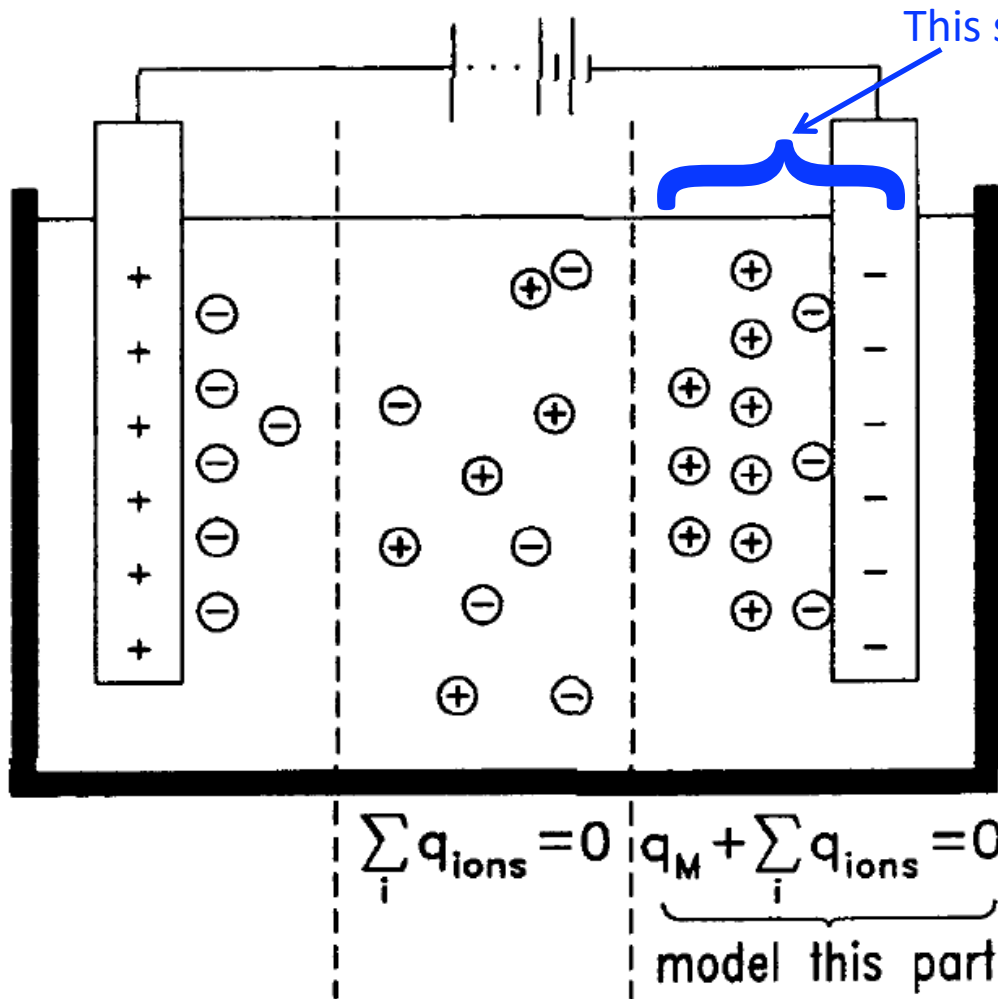


https://en.wikipedia.org/wiki/Gibbs%E2%80%93Donnan_effect

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the electronic and ionic charge on an electrode, q_M , is compensated by the
 accumulation of oppositely charged ions in solution: $q_M = -q_S$
 ... anyway, we should understand the details of how these electrified
 interfaces are structured... and metal-solution interfaces are well understood



This sort of looks like a parallel plate capacitor

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

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

Does a solution reactant located within the double layer “feel” E_{app} or $<E_{app}$?

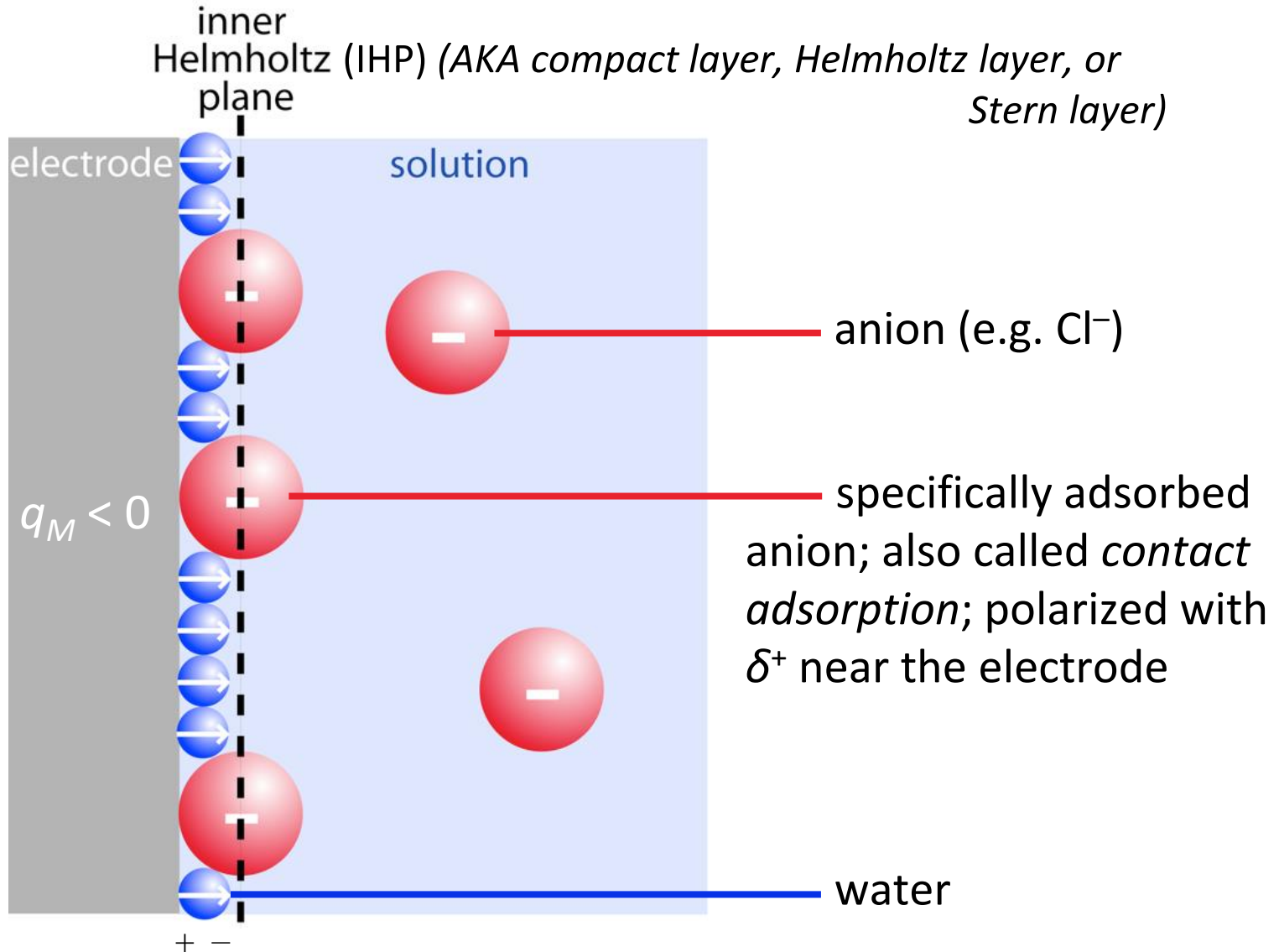
$<E_{app}$... *mind = blown!*

Michael R. Philpott and James N. Gosli†

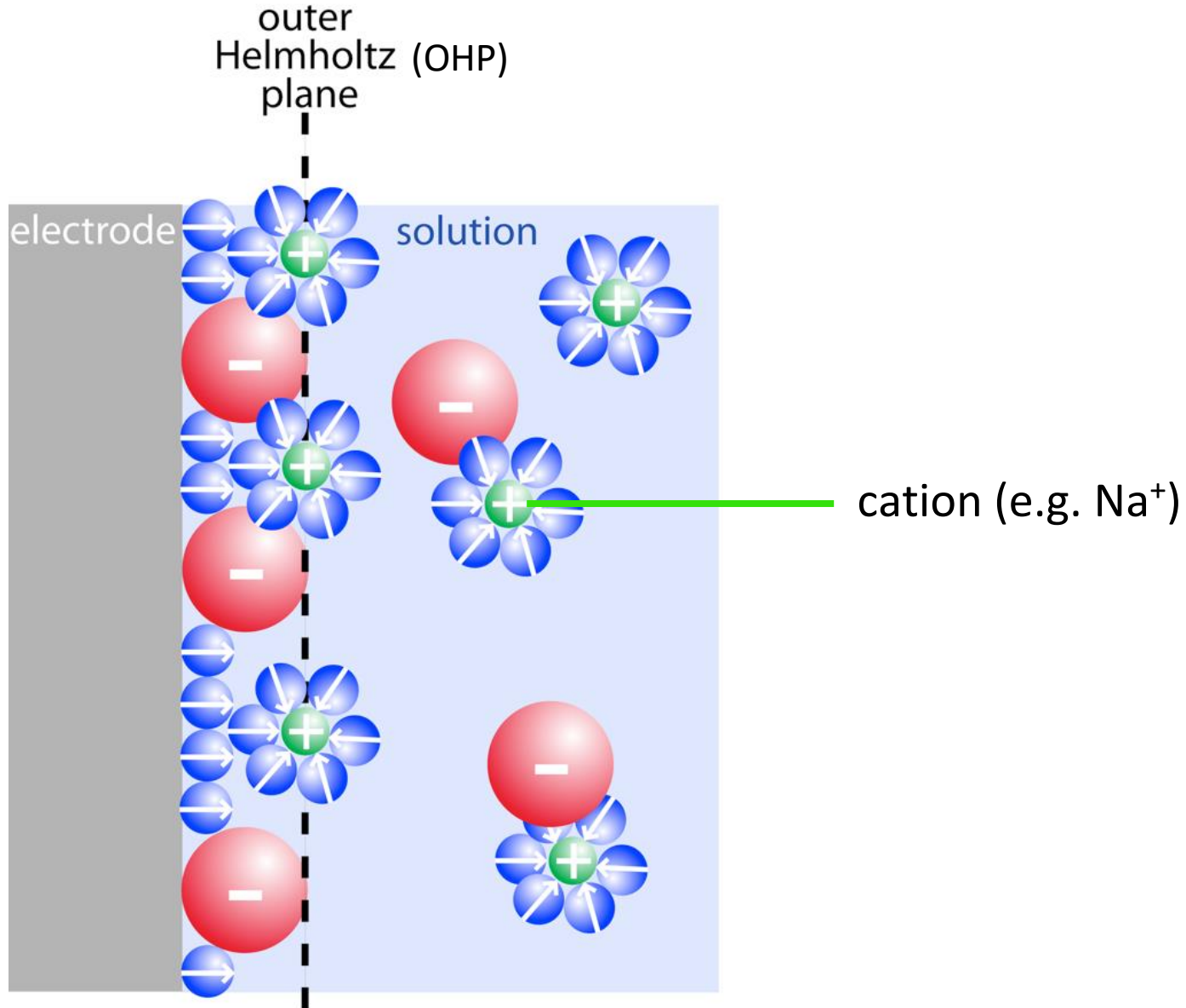
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... the bulk solution is called “quasi-neutral”

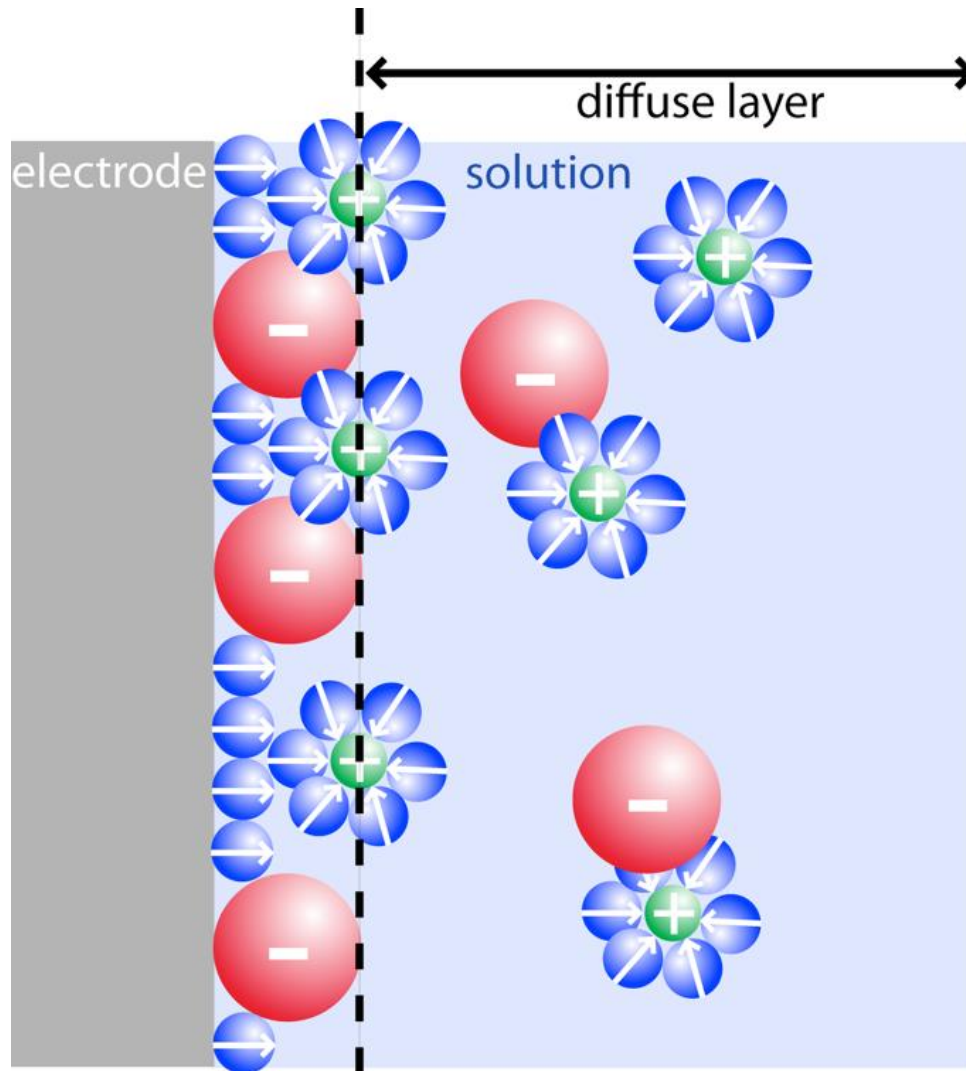
... anyway... in polar solvents, all charged electrode surfaces possess a common structure...



... cations have strongly coordinated waters that exchange slowly...



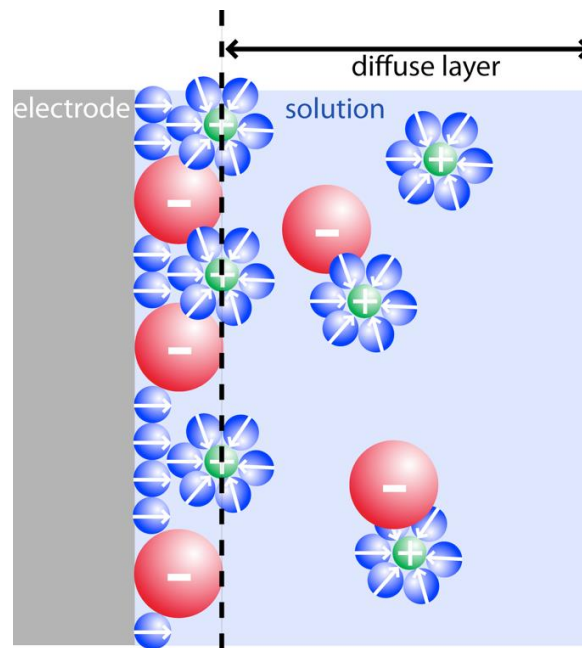
... the (second) layer of solution extending from the OHP that has a composition perturbed from bulk is called the diffuse layer



... follows a Poisson–Boltzmann distribution...

... this is the same idea behind the derivation of the Debye–Hückel equation (to obtain activity coefficients based on the ionic strength) and the Donnan equation (to obtain the electric potential difference across a membrane | solution interface)...

... the general idea for each is that diffusive (thermal) transport (Boltzmann) is equal and opposite to drift (electrostatic) transport (Poisson/Gauss)



Notice particularly the following:

1) A layer of *oriented waters* covers the surface...

... water orientation (O or H) is dictated by the surface charge

2) Anions shed their primary hydration layers and directly adsorb onto the surface. This is called “specific adsorption”...

... with F^- being an exception

3) In general, cations do not specifically adsorb; their primary hydration layers are too strongly attached (by the ion–dipole interaction) to be shed at room temperature. This is an example of “nonspecific adsorption”...

... with $(CH_3)_4N^+$ being an exception

the persistence of water molecules within the first hydration layer is illustrated by the water exchange rate from ions...

$>10^{10}$

I⁻
Cl⁻
Br⁻
(CH₃)₄N⁺

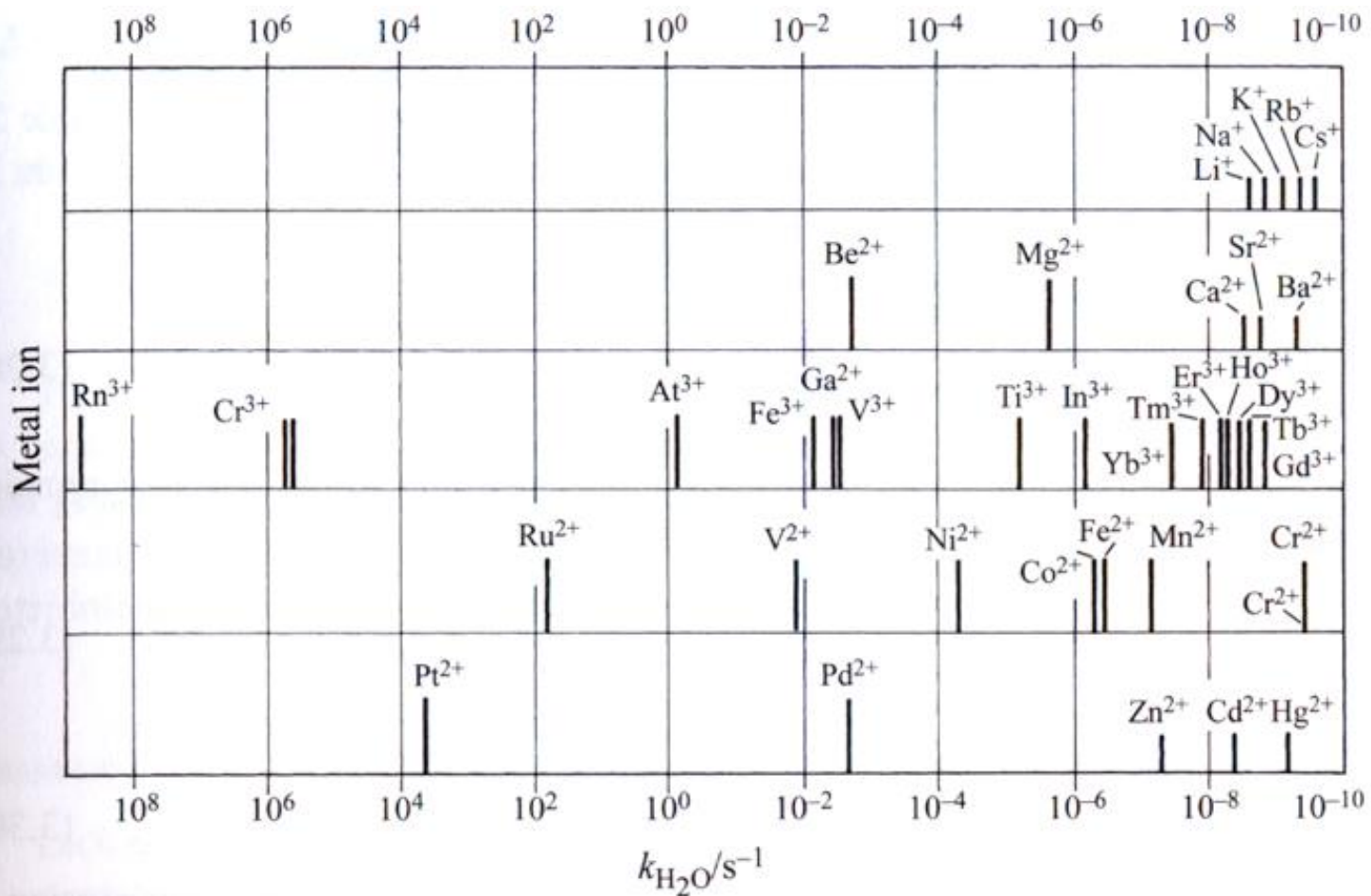


Fig. 3.13 Exchange rate constant for a molecule of water around a metal ion (S.F. Lincoln and A.E. Merbach, *Adv. Inorg. Chem.*, Vol. 42 (1995) 1-87, Academic Press, with permission from Elsevier Science).

The electrode carries a charge, q^M , and a surface charge density σ^M ($\sigma^M = q^M/A$). The total charge (density) of the system is zero, and so...

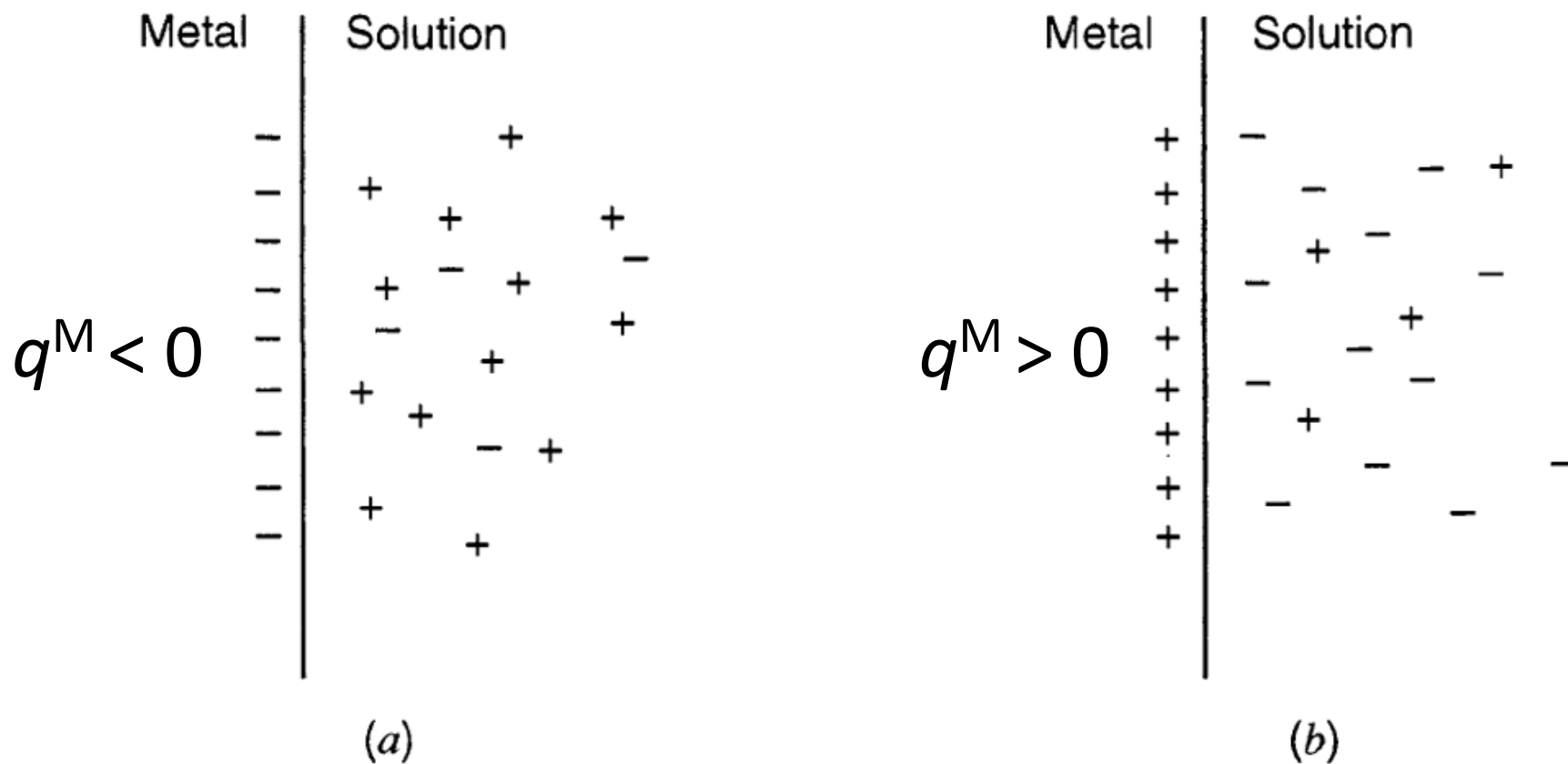
$$\sigma^M = -\sigma^S$$

charge (density)
on metal

excess charge
(density) in solution

The electrode carries a charge, q^M , and a surface charge density σ^M ($\sigma^M = q^M/A$). The total charge (density) of the system is zero, and so...

$$\sigma^M = -\sigma^S$$



... now, what is excess solution charge? There is a technical name for this... 712
... it is called the (Gibbs) Surface Excess, Γ

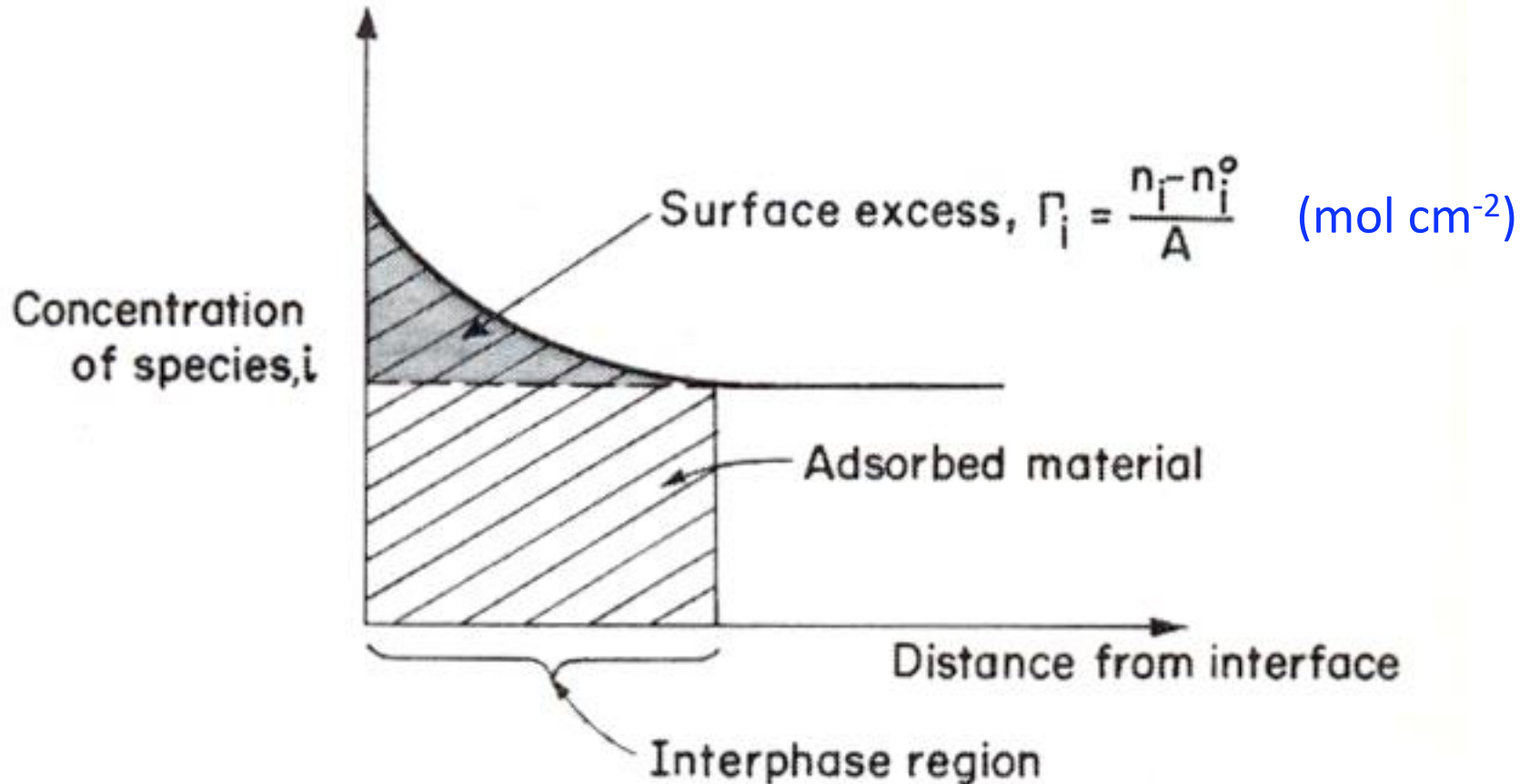


Fig. 7.46. The distinction between the amount of adsorbed material (hatched area) in the interphase region and the surface excess (shaded area).

... now put it all together, and what do we have? ...

electrochemical potential ($\bar{\mu}$)

$$d\bar{G}^R = \left(\frac{\partial \bar{G}^R}{\partial T}\right) dT + \left(\frac{\partial \bar{G}^R}{\partial P}\right) dP + \sum_i \left(\frac{\partial \bar{G}^R}{\partial n_i^R}\right) dn_i^R$$

$$d\bar{G}^S = \left(\frac{\partial \bar{G}^S}{\partial T}\right) dT + \left(\frac{\partial \bar{G}^S}{\partial P}\right) dP + \left(\frac{\partial \bar{G}^S}{\partial A}\right) dA + \sum_i \left(\frac{\partial \bar{G}^S}{\partial n_i^S}\right) dn_i^S$$

... where R is in a reference system, and S is in the actual system

... and at constant temperature and constant pressure, but variable A...

$$d\bar{G}^\sigma = d\bar{G}^S - d\bar{G}^R = \gamma dA + \sum_i \bar{\mu}_i d(n_i^S - n_i^R)$$

total
differential

differential
excess
free energy


$$= \gamma dA + \sum_i \bar{\mu}_i dn_i^\sigma$$

$$d\bar{G}^\sigma = \gamma dA + \sum_i \bar{\mu}_i dn_i^\sigma + A d\gamma + \sum_i n_i^\sigma d\bar{\mu}_i$$

... now put it all together, and what do we have? ...


... and setting the two forms of the differential equation equal to each other...

$$-d\gamma = \sum_i \Gamma_i d\bar{\mu}_i$$


 surface excess (mol cm⁻²)

= Gibbs Adsorption Isotherm

$$d\bar{G}^\sigma = d\bar{G}^S - d\bar{G}^R = \gamma dA + \sum_i \bar{\mu}_i d(n_i^S - n_i^R)$$

 differential excess free energy

$$= \gamma dA + \sum_i \bar{\mu}_i dn_i^\sigma$$

 total differential

$$d\bar{G}^\sigma = \gamma dA + \sum_i \bar{\mu}_i dn_i^\sigma + A d\gamma + \sum_i n_i^\sigma d\bar{\mu}_i$$

... now put it all together, and what do we have?

... recasting the difference in electric potential ($d\phi$) as the change in applied potential (dE)...

... we have the **electrocapillary equation** (B&F pp. 537–538)...

Recall $\bar{\mu} = \mu + zF\phi$

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

the *surface tension* (units: energy/area, typically J m^{-2} or N m^{-1} ... these are identical)

$$\left(\gamma = \frac{\partial G}{\partial A} \right)$$

... now put it all together, and what do we have?

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Recall $\bar{\mu} = \mu + zF\phi$

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

the *surface excess concentration* of species i (units: moles/area), and sometimes called the *Gibbs surface excess*

... now put it all together, and what do we have?

... recasting the difference in electric potential ($d\phi$) as the change in applied potential (dE)...

... we have the *electrocapillary equation* (B&F pp. 537–538)...

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

Recall $\bar{\mu} = \mu + zF\phi$

the *chemical potential* of species i

... but where is the electric potential (ϕ) term?

... now put it all together, and what do we have?

... recasting the difference in electric potential ($d\phi$) as the change in applied potential (dE)...

... we have the *electrocapillary equation* (B&F pp. 537–538)...

Recall $\bar{\mu} = \mu + zF\phi$

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

the change in potential between
the WE and the RE

... now put it all together, and what do we have?

... recasting the difference in electric potential ($d\phi$) as the change in applied potential (dE)...

... **we have the *electrocapillary equation*** (B&F pp. 537–538)...

$$-d\gamma = \sigma^M dE + \sum_i \Gamma_i d\mu_i$$

(this means
at constant
chemical
potential of
all species)

... so measurement of the **surface tension** (γ) of a variable-area electrode as a function of its **potential** (E) is a direct way to get at its surface charge (density), σ^M . This is called *Lippmann's Equation*:

We want to know this...

... or better yet, q^M

... or better yet, q^S

$$\sigma^M = - \left(\frac{d\gamma}{dE} \right)_{\mu_i}$$

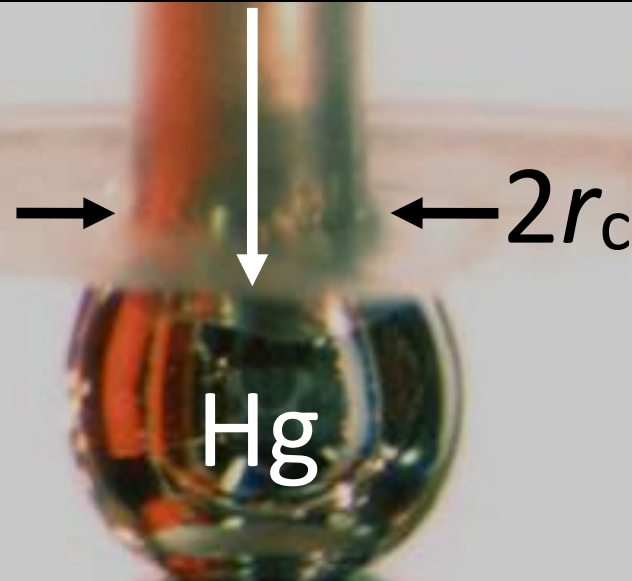
Key Point: *Measuring γ is easy if the electrode is a liquid...*

... thus, our window into the double layer structure is the dropping mercury electrode (DME)... Seriously!

B&F used "m," but IUPAC prefers q_m



q_m = mass flow rate (kg/s)



<http://gmwgroup.harvard.edu/>

... since drop moves slowly, $F_\gamma \approx F_{(g)\text{ravity}}$ (recall that $F_g = mg = (q_m t_{\text{max}})g$)

... and just before dropping...

circumference
of the capillary

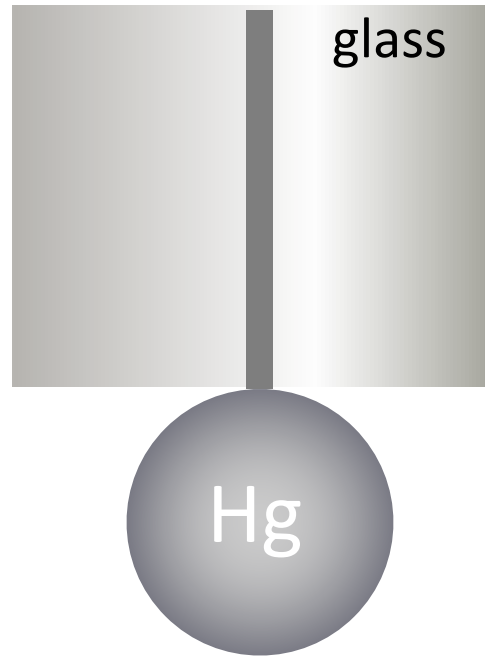
$$t_{\text{max}} = \frac{2\pi r_c}{q_m g} \gamma$$

acceleration
due to gravity

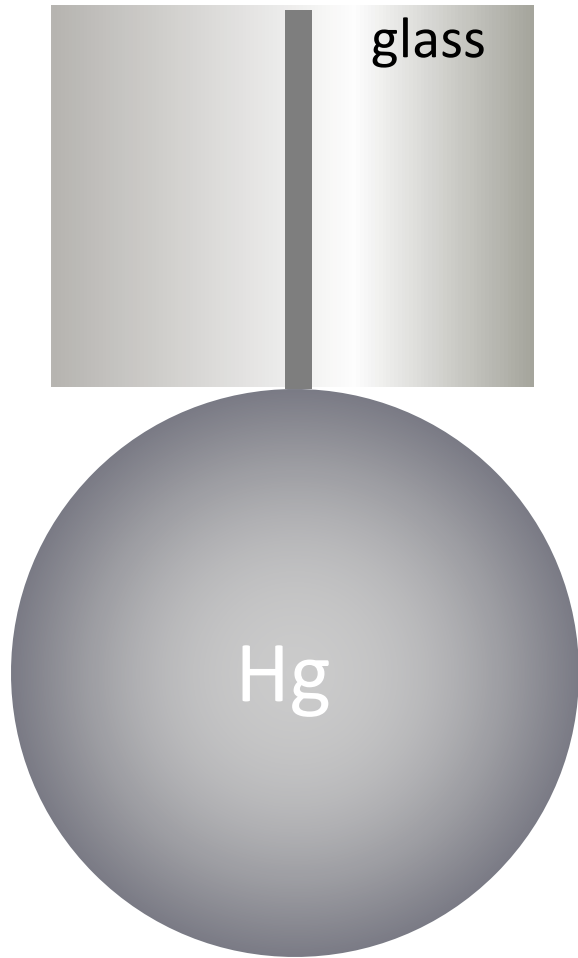
(... recall that γ has units of N m^{-1})

... now, in a *dropping mercury electrode*, as the name implies...

721

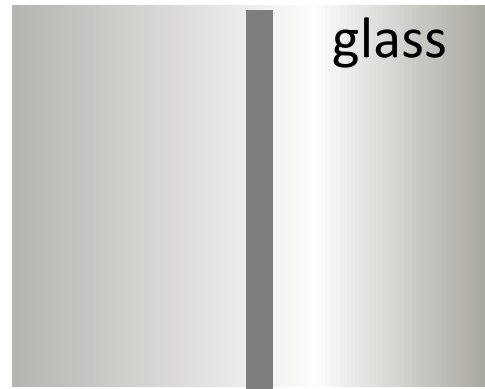


... now, in a *dropping mercury electrode*, as the name implies...



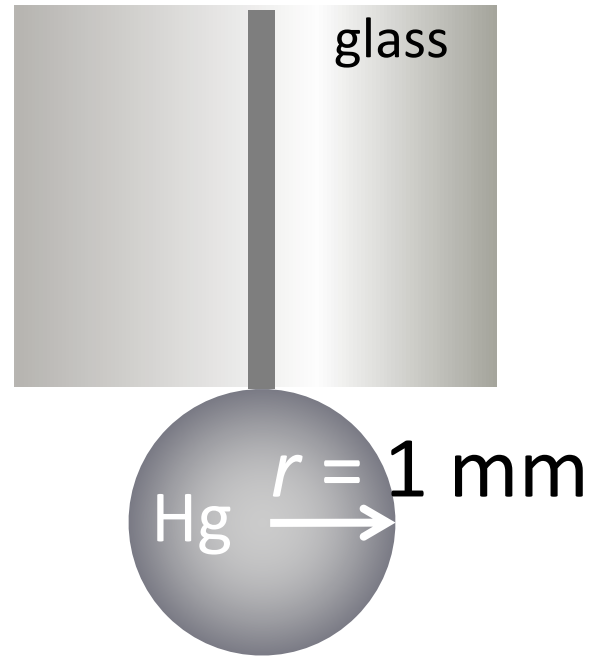
... now, in a *dropping mercury electrode*, as the name implies...

723



... what do we measure during this process?

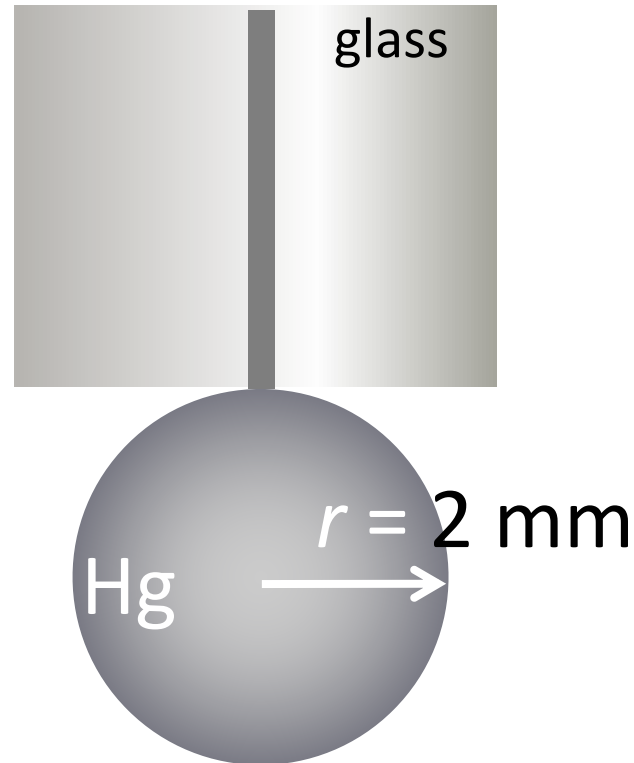
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... suppose the electrode is at a potential where $\sigma^M = q^M/A = 25 \mu\text{C}/\text{cm}^2$
... *what is the surface charge, q^M ?*

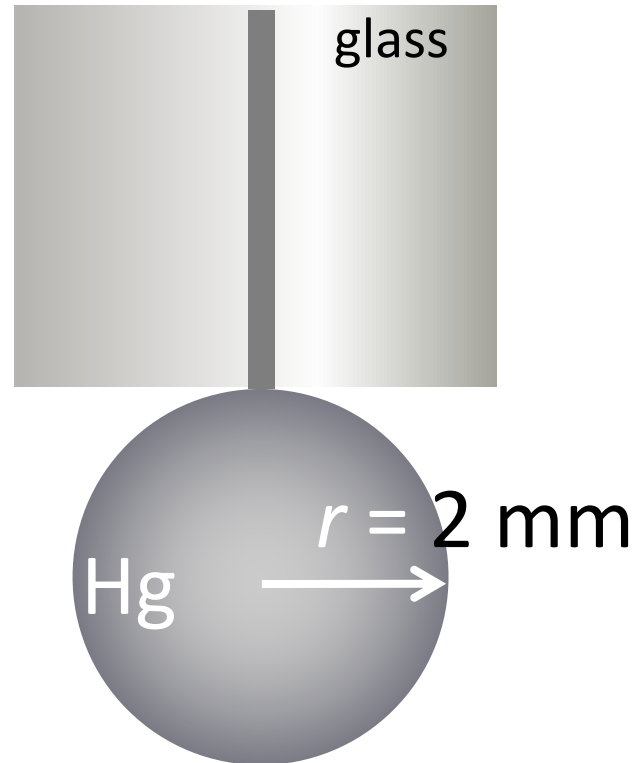
... what do we measure during this process?

725



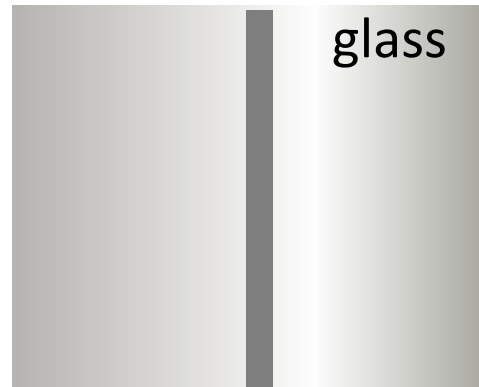
$$\begin{aligned}q^M &= (25 \times 10^{-6} \text{ C / cm}^2)(4\pi r^2) \\&= (25 \times 10^{-6} \text{ C / cm}^2)4\pi(0.1)^2 \\&= (25 \times 10^{-6} \text{ C / cm}^2)(0.126 \text{ cm}^2) \\&= 3.14 \times 10^{-6} \text{ C} = 3.14 \mu\text{C}\end{aligned}$$

... what happens as the electrode grows?



... so even though the *potential is constant*,
... and even though *no Faradaic electrochemistry* is occurring,
... the Hg droplet grows (*surface area increases*),
... and thus current flows to its surface...
... and this current is proportional to q^M

... what happens as the electrode grows?



... after it falls, off, the current drops to a small value...

... and then the process repeats...

... okay, so let's do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

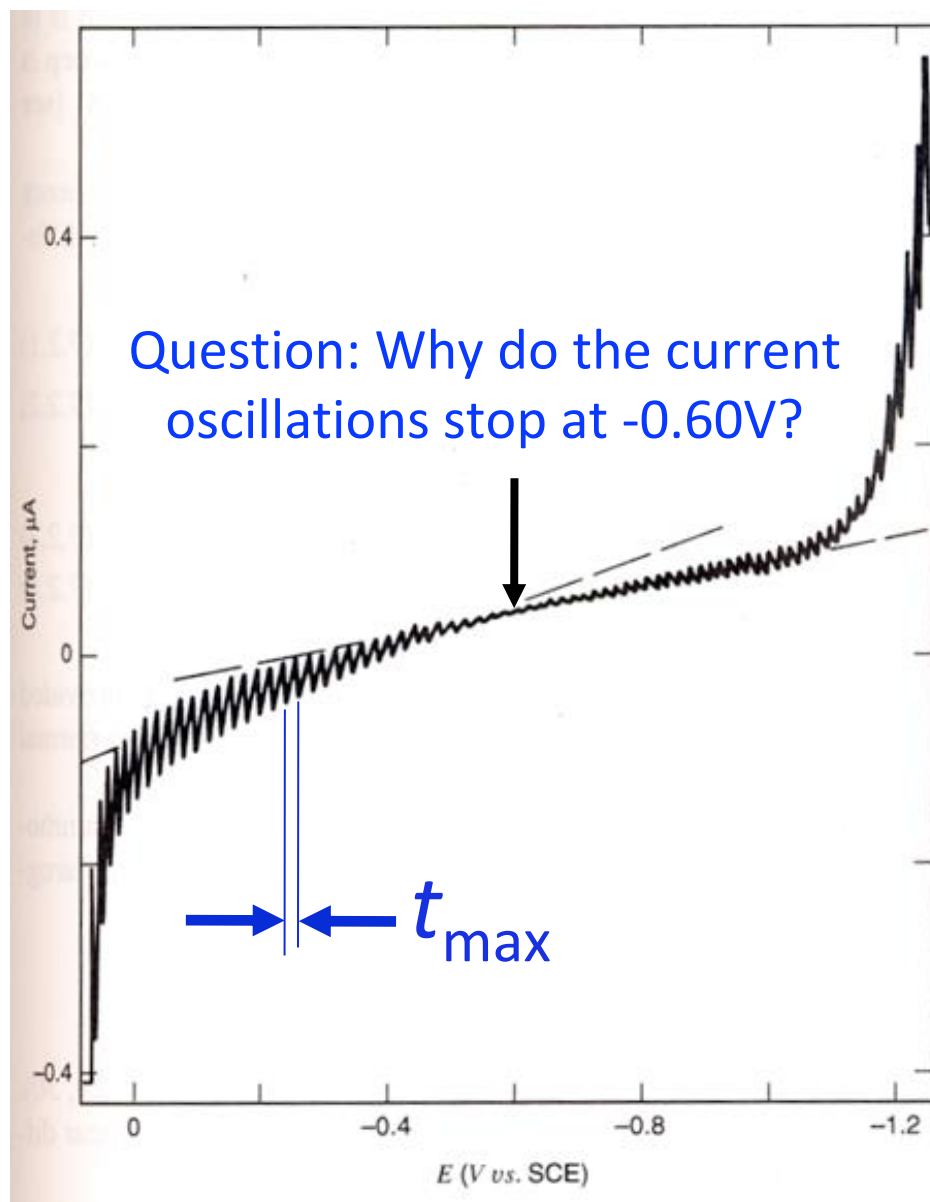


Figure 7.1.5 Residual current curve for 0.1 M HCl. The sharply increasing currents at potentials more positive than 0 V and more negative than -1.1 V arise from oxidation of mercury and reduction of H^+ , respectively. The current between 0 V and -1.1 V is largely capacitive. The PZC is near -0.6 V vs. SCE. (From L. Meites, "Polarographic Techniques," 2nd ed., Wiley-Interscience, New York, 1965, p. 101, with permission.)

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

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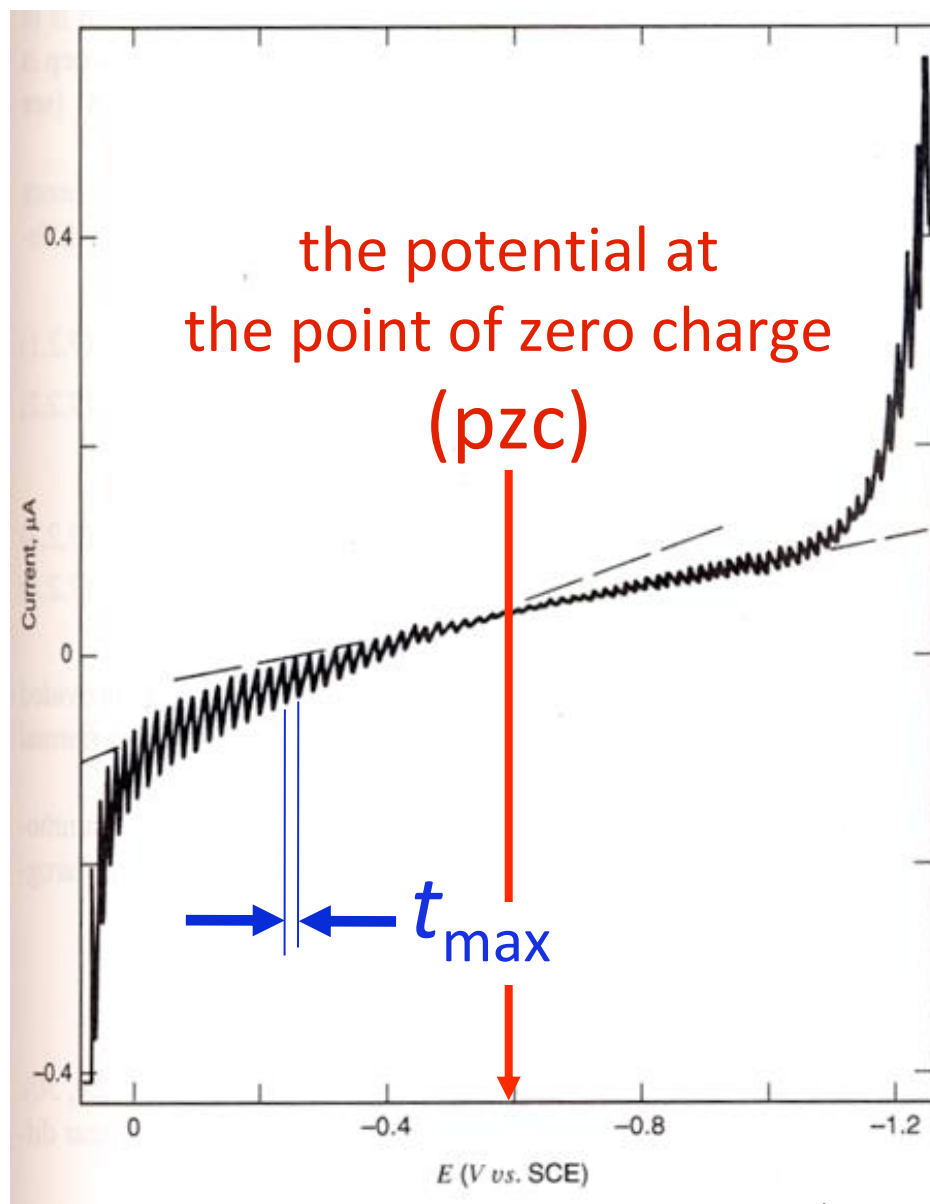
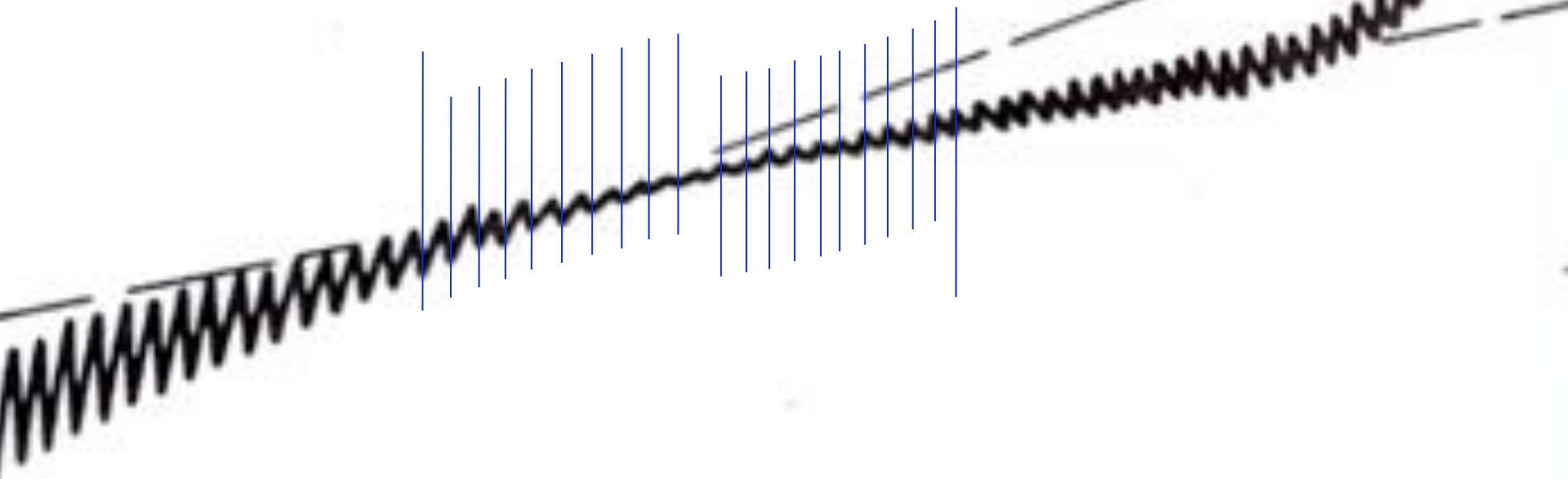


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... okay, so let's do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

notice also that the *phase* of the current oscillation inverts as E crosses the PZC...



... a linear scan voltammogram acquired with a DME (and therefore called a *polarogram*)

... DMEs are "self-cleaning"

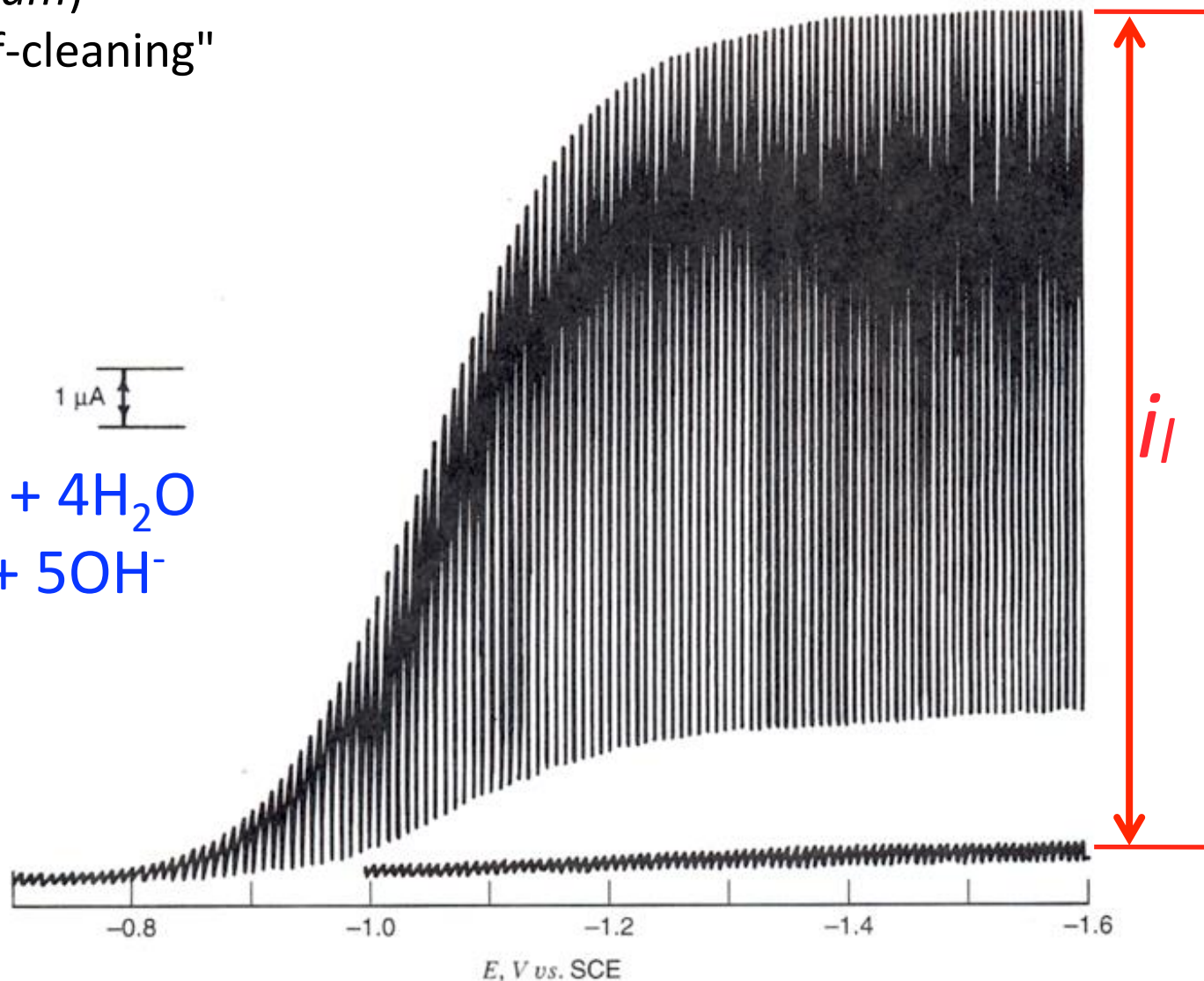
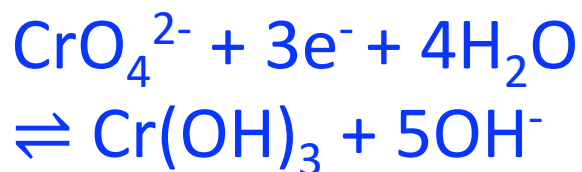


Figure 7.1.4 Polarogram for 1 mM CrO_4^{2-} in deaerated 0.1 M NaOH, recorded at a DME.

... look familiar? ... It's just this:

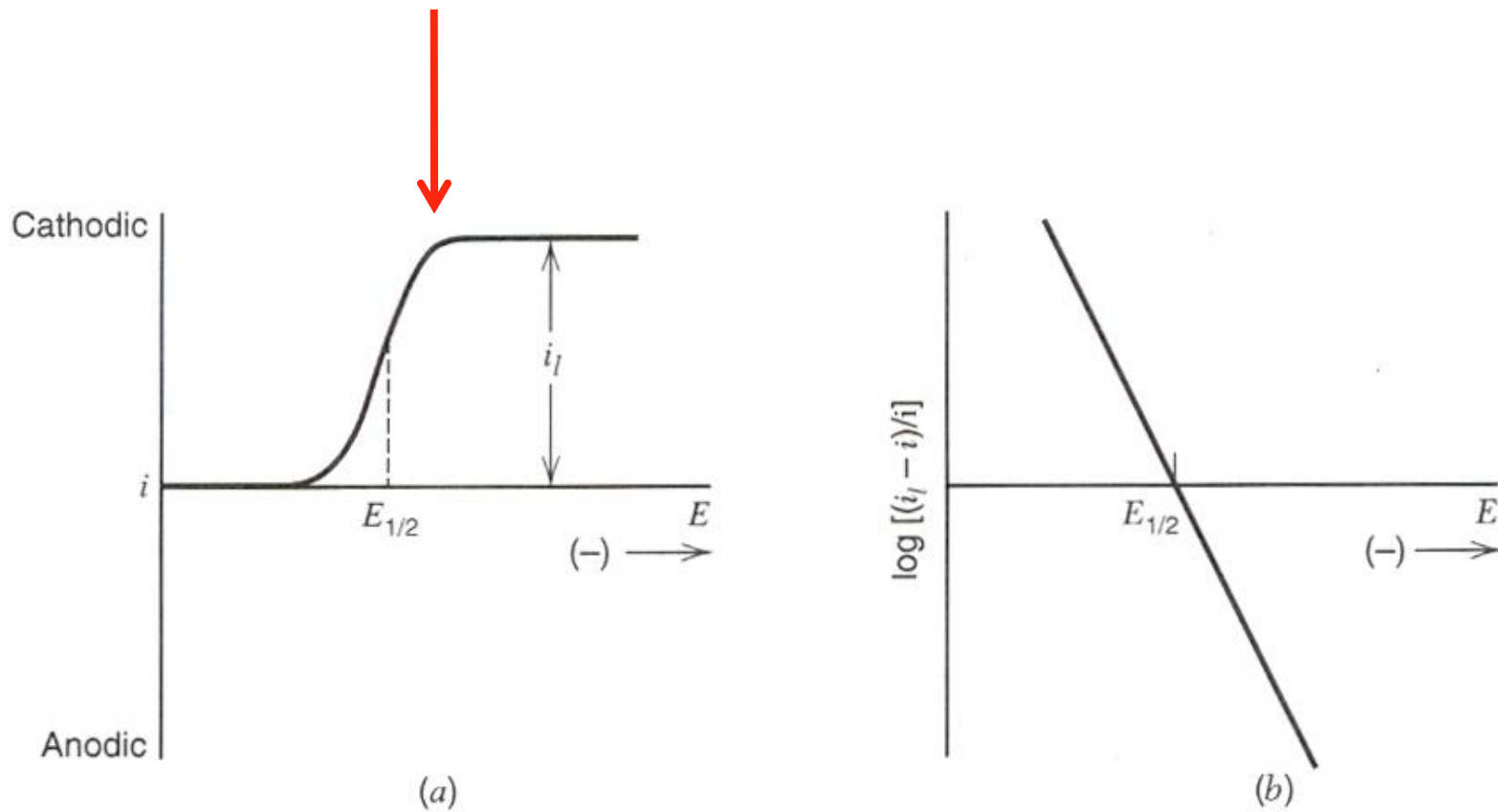
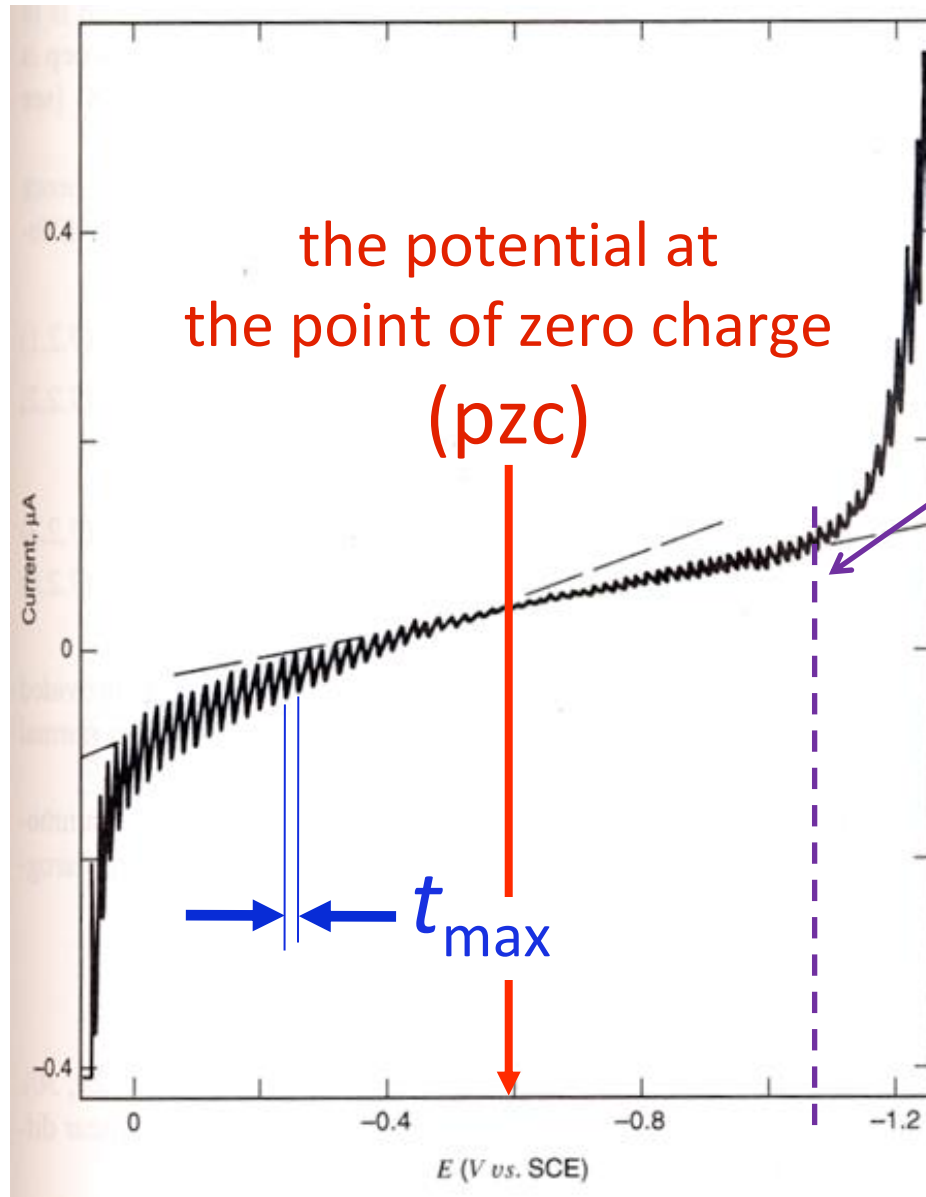


Figure 1.4.2 (a) Current-potential curve for a Nernstian reaction involving two soluble species with only oxidant present initially. (b) $\log[(i_l - i)/i]$ vs. E for this system.

... okay, now going back to the case of 0.10 M HCl, let's measure the drop time, t_{\max} , as a function of potential...



... this huge kinetic overpotential for H_2 evolution helps to minimize Faradaic reactions

Figure 7.1.5 Residual current curve for 0.1 M HCl. The sharply increasing currents at potentials more positive than 0 V and more negative than -1.1 V arise from oxidation of mercury and reduction of H^+ , respectively. The current between 0 V and -1.1 V is largely capacitive. The PZC is near -0.6 V vs. SCE. (From L. Meites, "Polarographic Techniques," 2nd ed., Wiley-Interscience, New York, 1965, p. 101, with permission.)

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... take the t_{\max} versus E data and make a plot... and voila!...

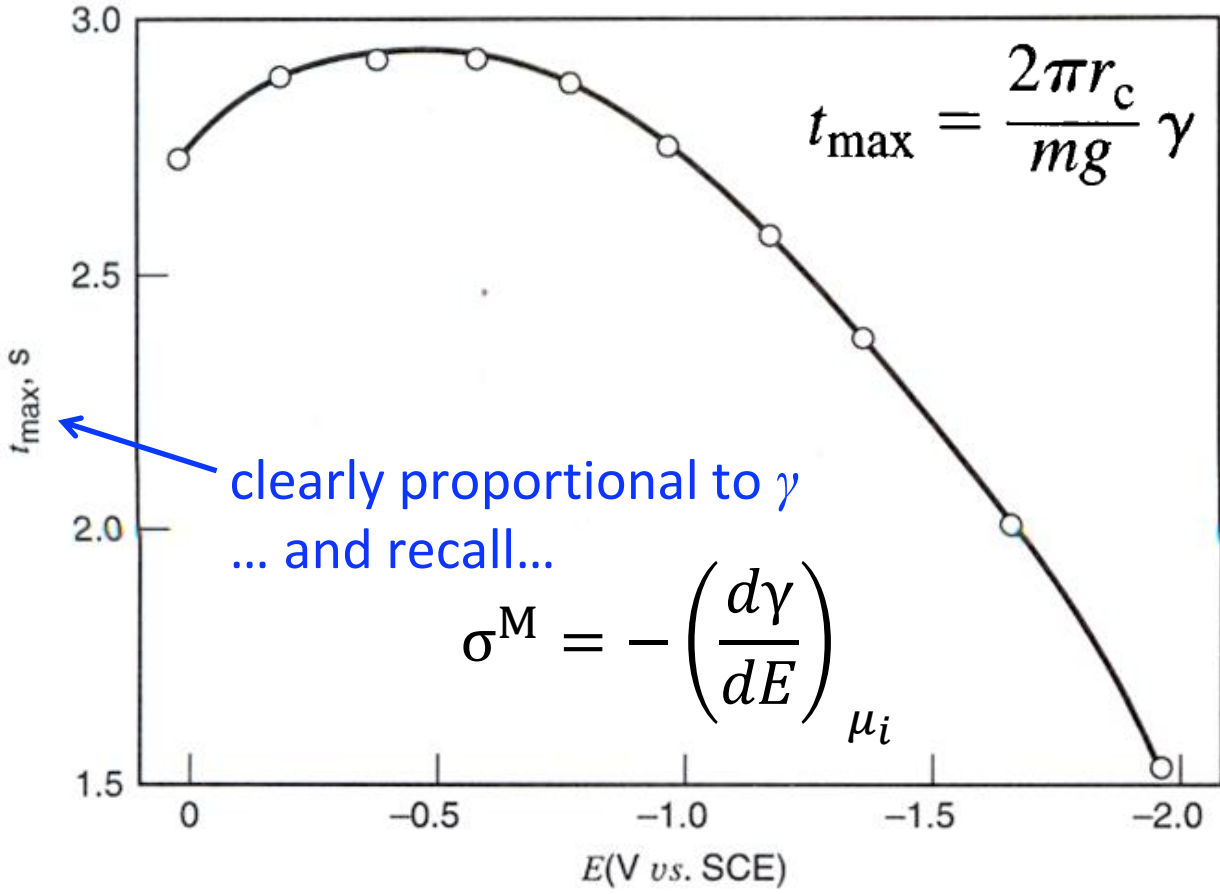
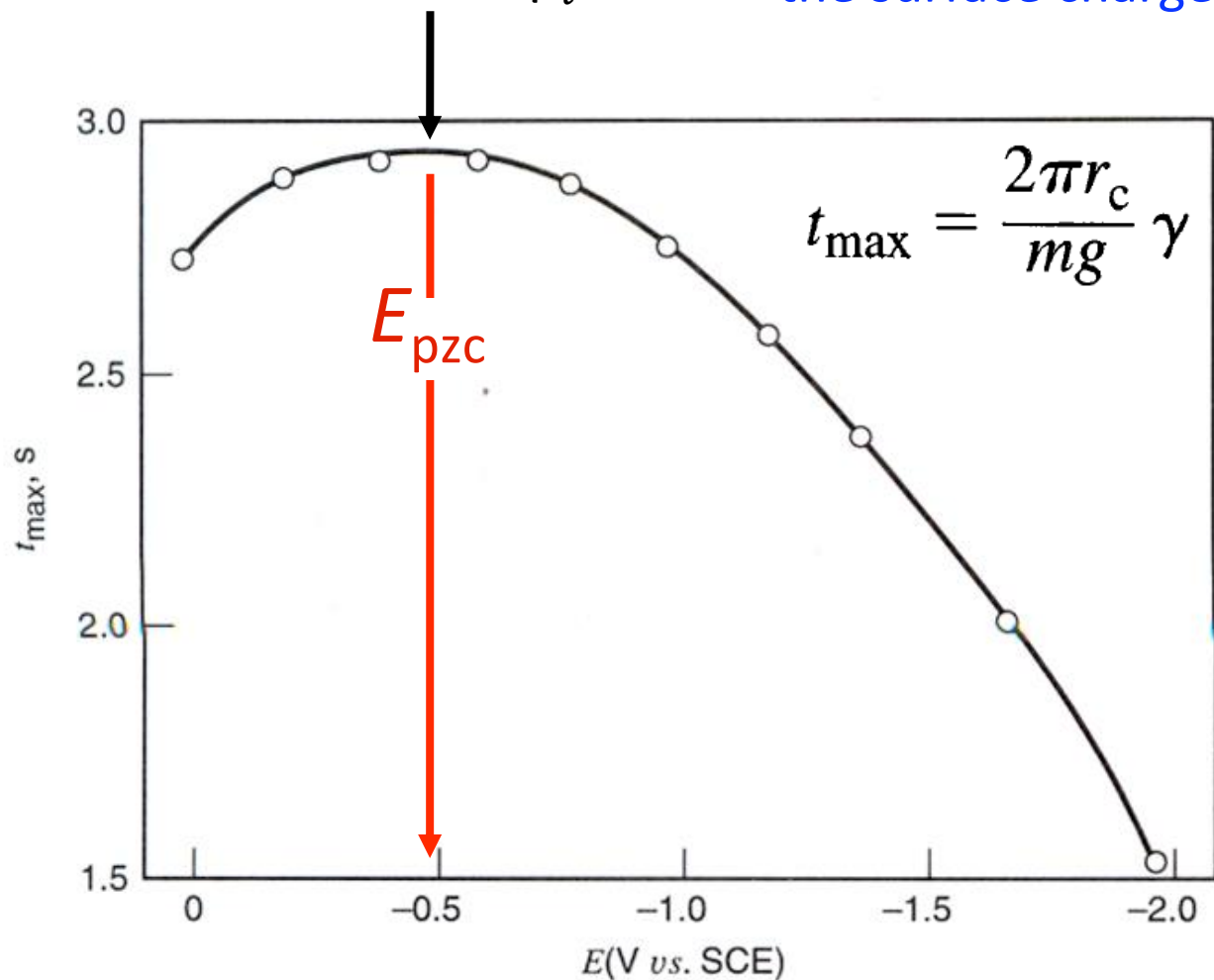


Figure 13.2.1
 Electrocapillary curve of drop time vs. potential at a DME in 0.1 M KCl. [Data of L. Meites, *J. Am. Chem. Soc.*, **73**, 2035 (1951).]

... take the t_{\max} versus E data and make a plot... and voila!...

$$\sigma^M = - \left(\frac{d\gamma}{dE} \right)_{\mu_i} = 0$$

Why is the surface tension largest when the surface charge is smallest?



... the intermolecular cohesive forces between solvent molecules is large but...
... like charges repel!

Figure 13.2.1

Electrocapillary curve of drop time vs. potential at a DME in 0.1 M KCl. [Data of L. Meites, *J. Am. Chem. Soc.*, **73**, 2035 (1951).]

... okay, what can we do with this information? Well, a plot of charge (q) versus potential (E) has a slope of... What? Capacitance (C)

$$\frac{q}{E} = C$$

... but this is the *integral / total capacitance*... the capacitance that applies for a given applied potential versus E_{pzc} . For a real capacitor, C is virtually E -independent, but that may not be (*and in fact, is not*) true for an electrical double layer.

... in anticipation of this, let's define a *differential capacitance* (C_d), which is the correct term to use, as follows:

$$C_d = \left(\frac{\partial \sigma^{\text{M}}}{\partial E} \right) = - \left(\frac{\partial^2 \gamma}{\partial E^2} \right)_{\mu_i}$$

Let's compare *total capacitance* (C) and *differential capacitance* (C_d) as follows:

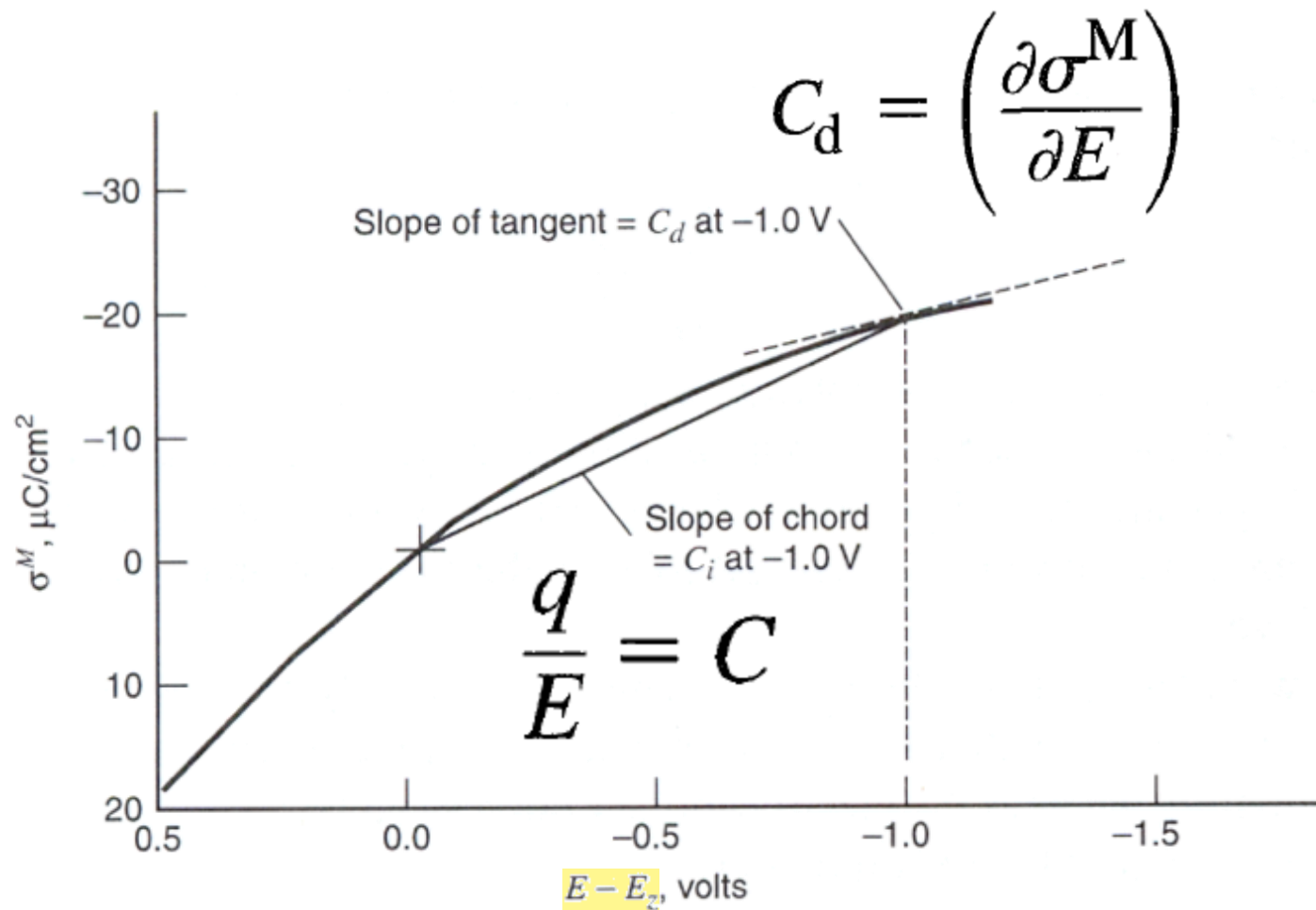


Figure 13.2.4 Schematic plot of charge density vs. potential illustrating the definitions of the integral and differential capacitances.

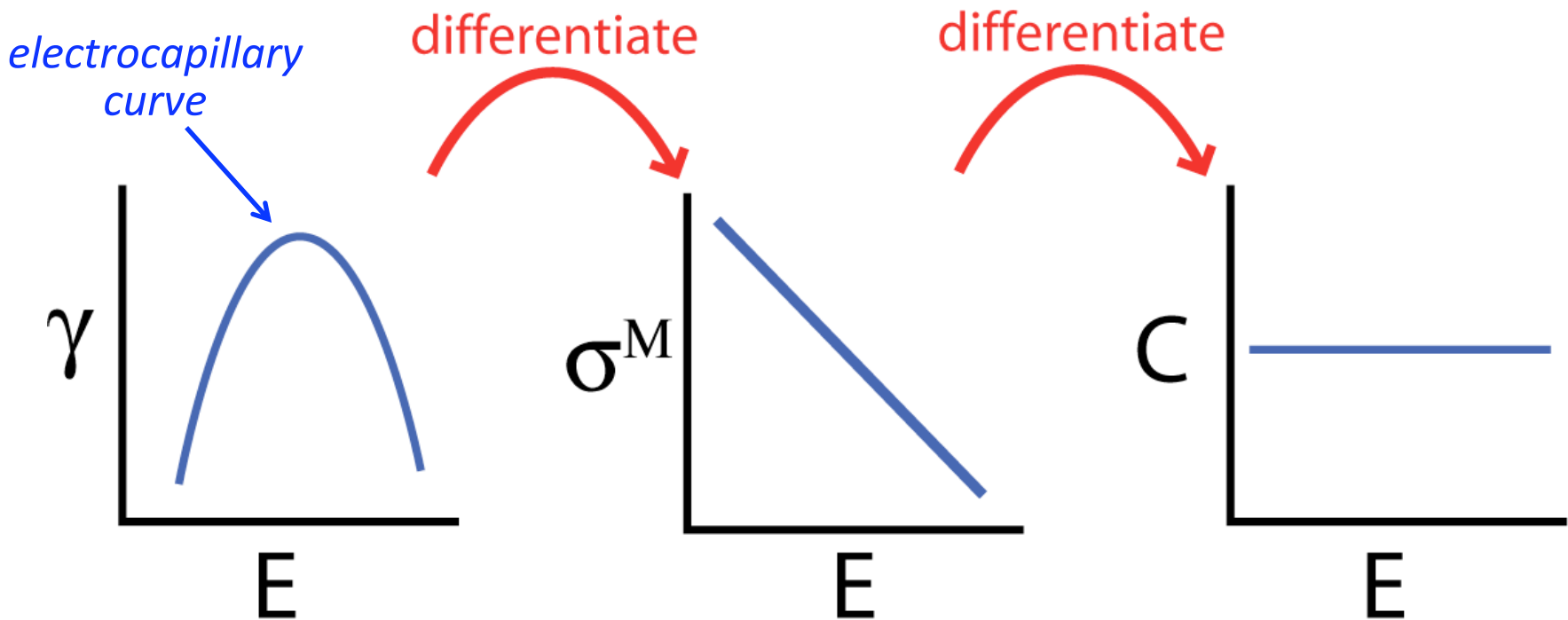
E_z is the potential at the pzc

... 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!

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



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

... here's what the C vs. E data actually look like as a function of concentration, for aqueous KF at a DME...

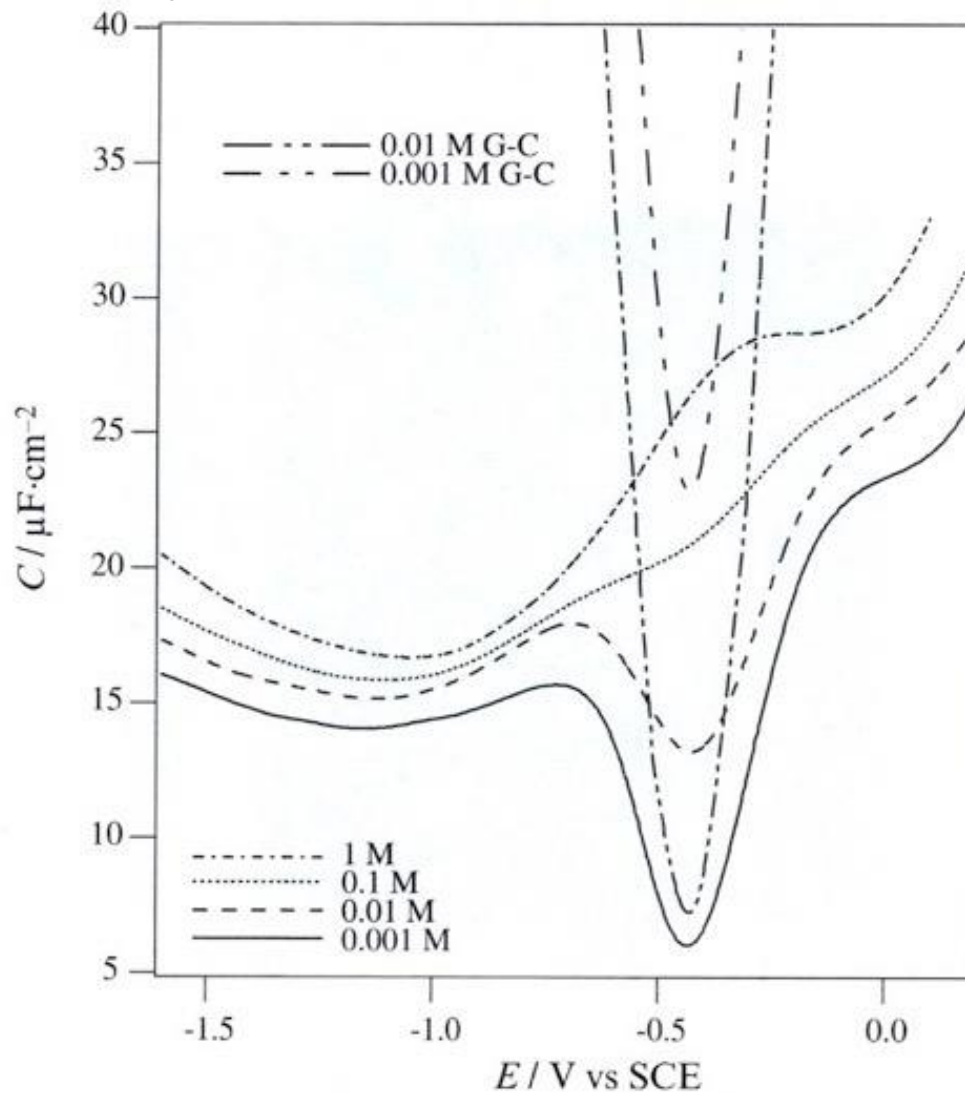
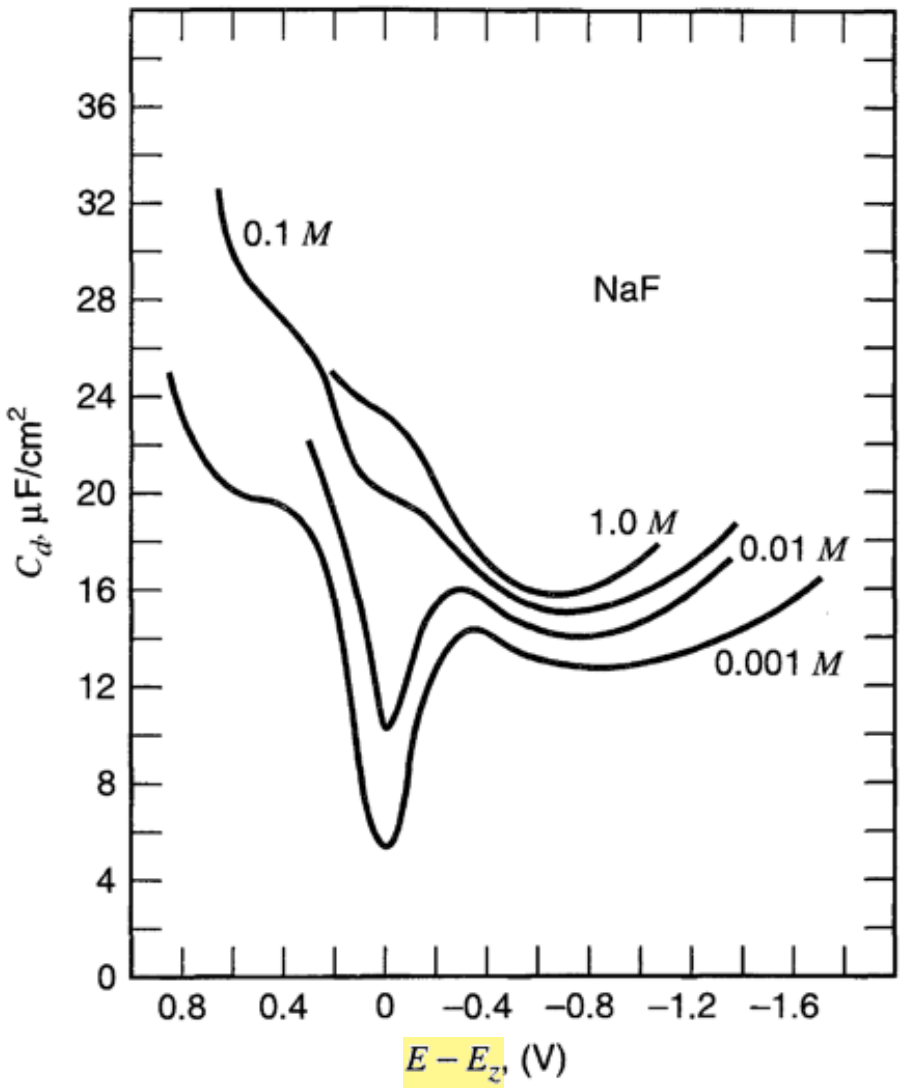


Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433\text{V}$) with the respective Gouy-Chapman capacity [Paolo Galletto, EPFL thesis].



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.]

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.

... do you want to understand the details of C_d away from the pzc?

Do you want to understand *the hump*? There is a book for that...

J. O'M. BOCKRIS / A. K. N. REDDY

**MODERN
ELECTROCHEMISTRY • 2**



John Bockris



Three traditional models for double layer structure:

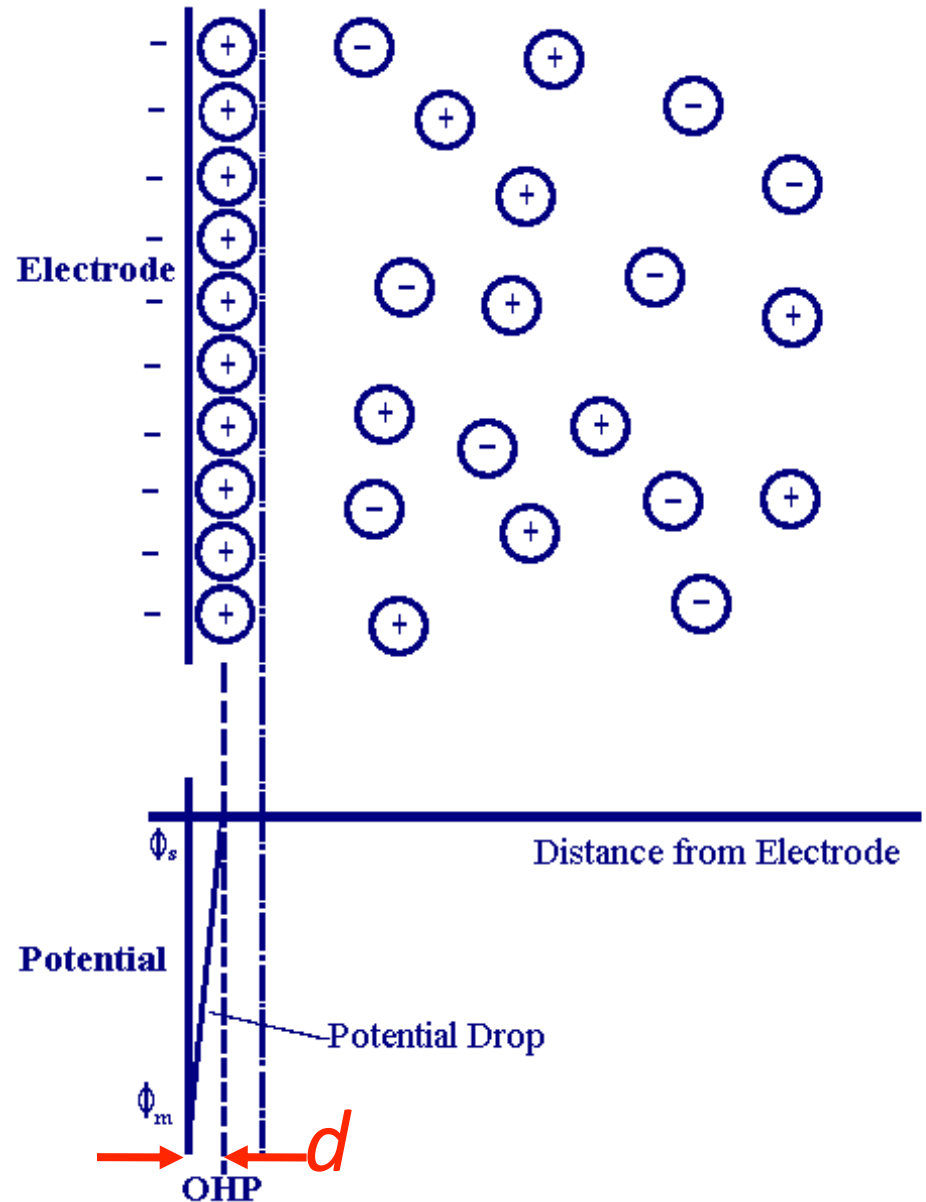
- 1) Helmholtz
- 2) Gouy–Chapman (GC)
- 3) Gouy–Chapman–Stern (GCS)

... let's take a look at each of these...

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:

$$C_d = \frac{\epsilon\epsilon_0}{d}$$

... for a parallel plate capacitor, C is independent of E because the permittivity of the capacitor, $\epsilon\epsilon_0$, and its spacing, d , are both independent of applied potential...



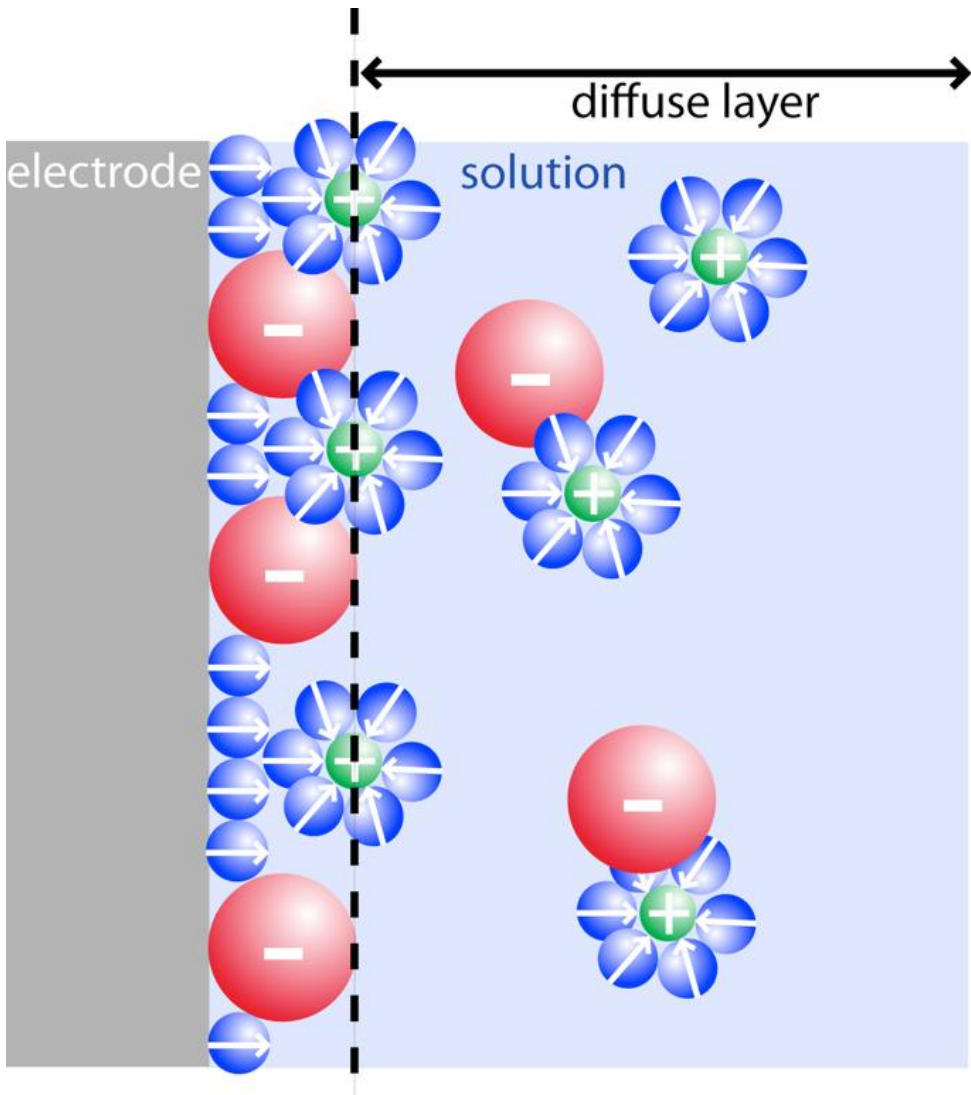
... the Helmholtz model says that the electrical double layer acts like, and looks like (*rare in EChem*), a parallel plate capacitor...

$$C_d = \frac{\epsilon\epsilon_0}{d}$$

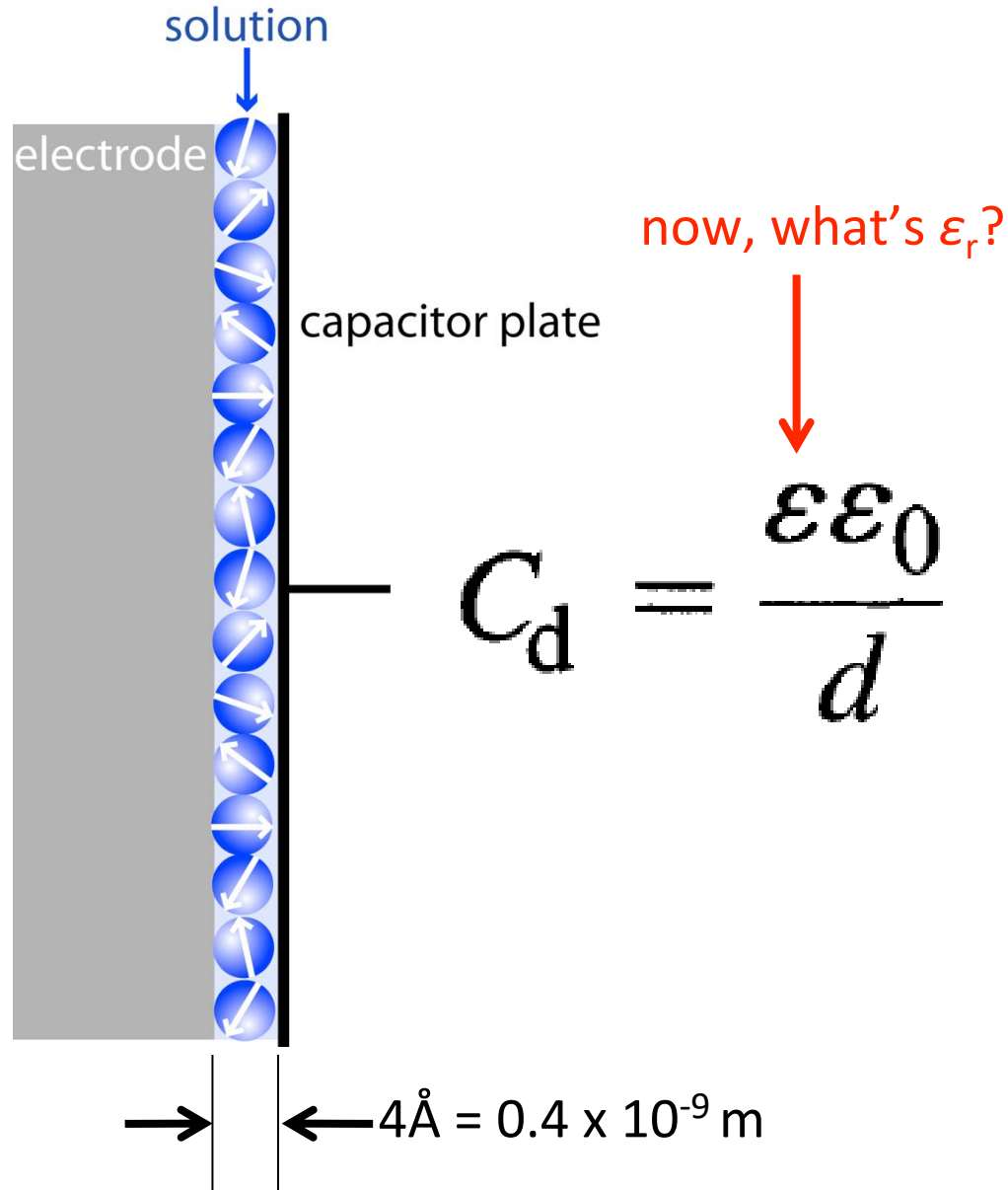
... C_d is therefore independent of E because the permittivity of the capacitor, $\epsilon\epsilon_0$, and its spacing, d , are both independent of applied potential...

... 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...



... first, what's ϵ_r for water? Well, that depends... *can it rotate?* (**BRIEFLY**) 748

for water at
20 °C...

78.4

5.9

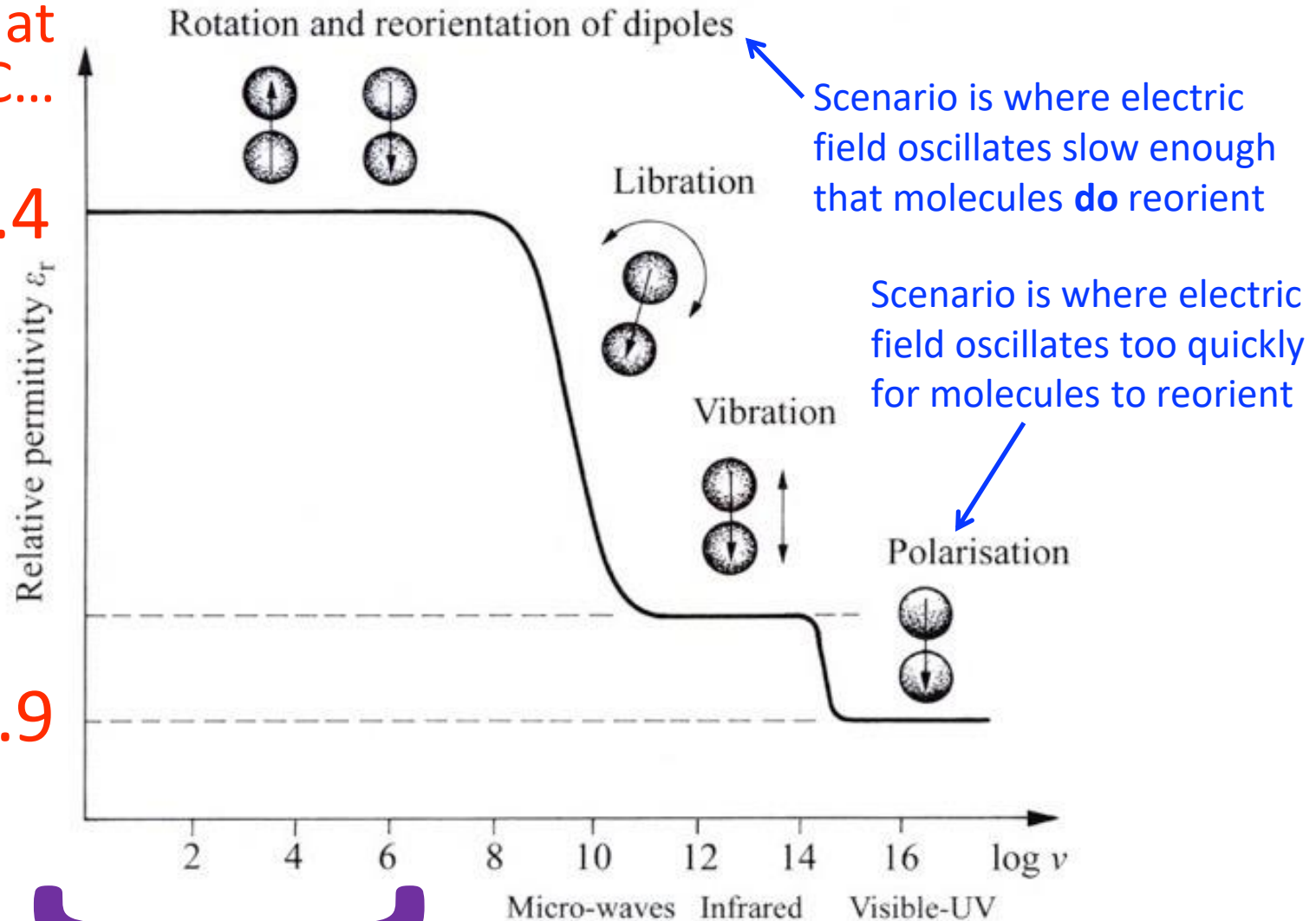
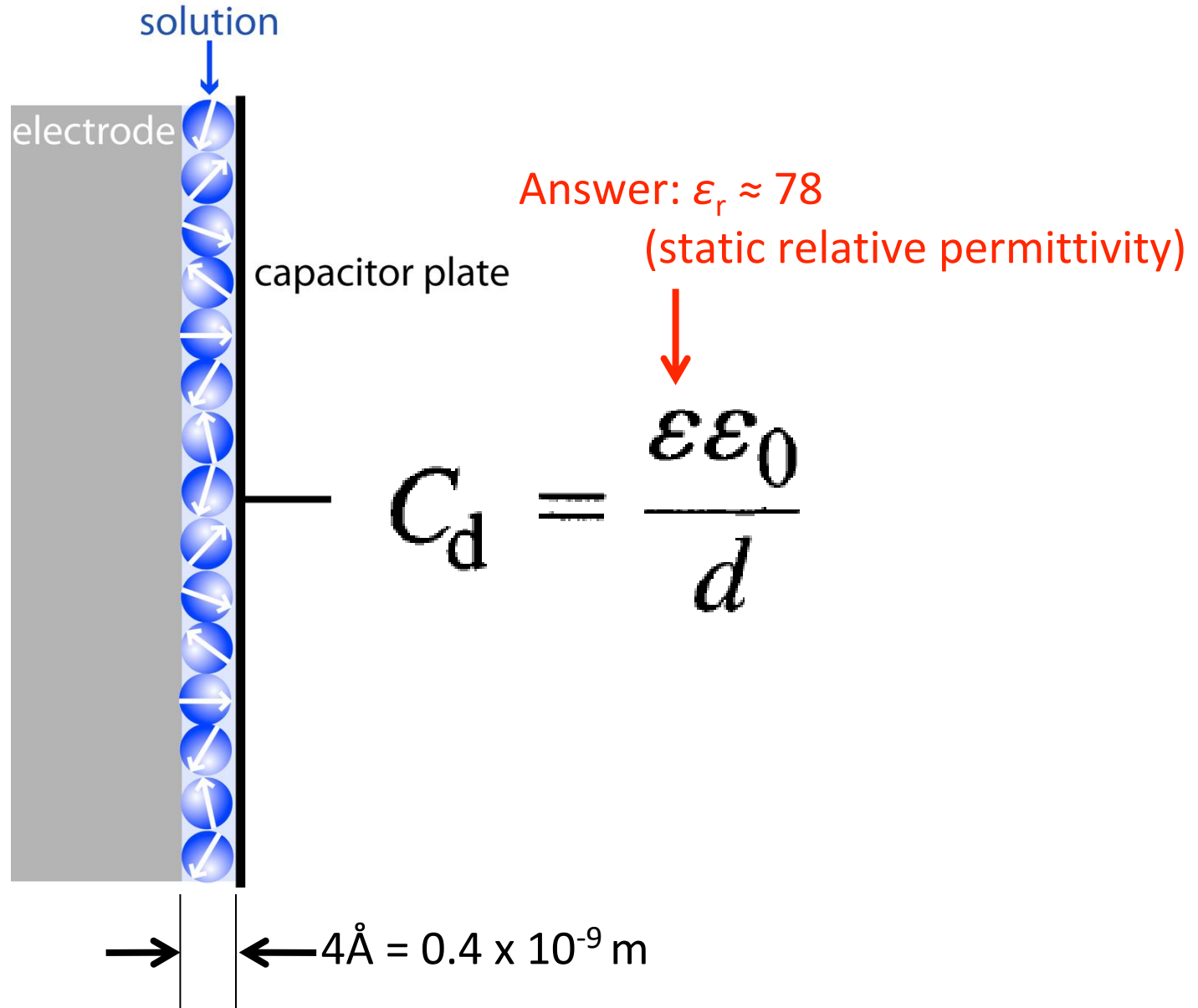


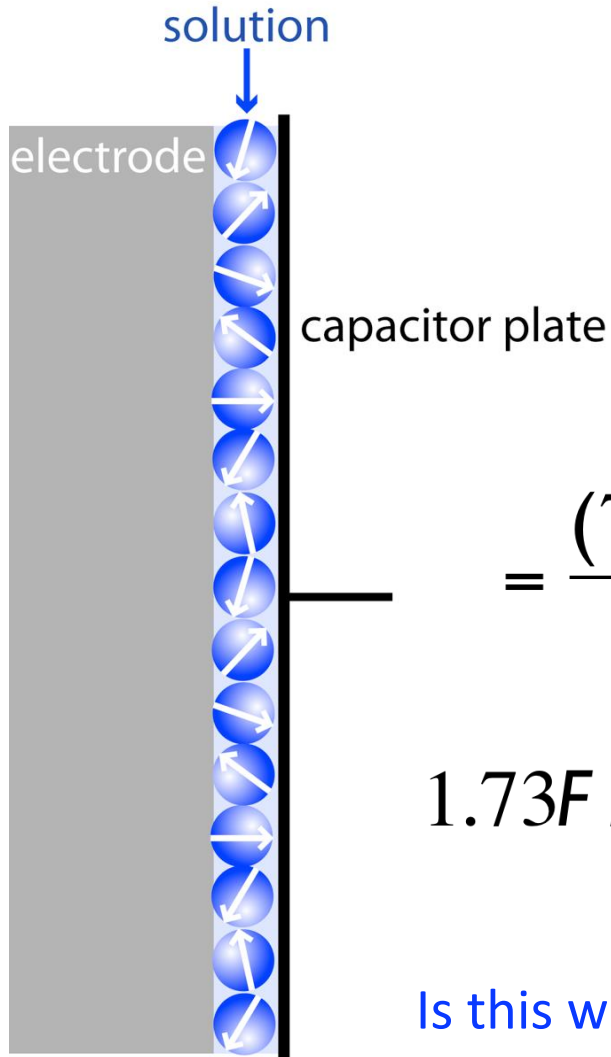
Fig. 1.7 Variation of the relative permittivity of water as a function of the frequency of the applied electric field.

Electrochemical impedance spectroscopy range

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



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



$$C_d = \frac{\epsilon \epsilon_0}{d}$$

$$= \frac{(78)(8.854 \times 10^{-12} \text{ F/m})}{0.4 \times 10^{-9} \text{ m}} = 1.73 \text{ F/m}^2$$

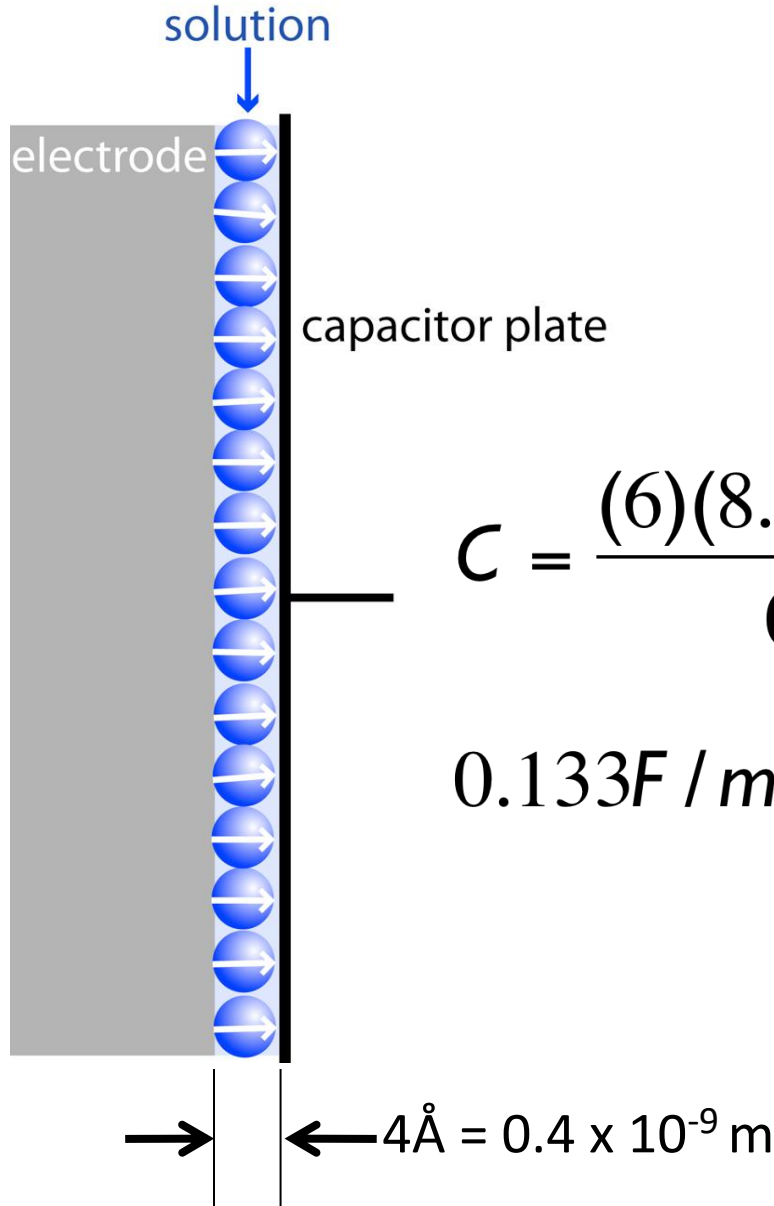
$$1.73 \text{ F/m} \frac{10^6 \mu\text{F}}{\text{F}} \frac{\text{m}^2}{100^2 \text{ cm}^2} = 172.6 \mu\text{F/cm}^2$$

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

$$\longleftrightarrow 4 \text{ \AA} = 0.4 \times 10^{-9} \text{ m}$$

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

... so that water cannot rotate...



$$C_d = \frac{\epsilon_r \epsilon_0}{d}$$

$$C = \frac{(6)(8.854 \times 10^{-12} \text{ F/m})}{0.4 \times 10^{-9} \text{ m}} = 0.133 \text{ F/m}^2$$

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

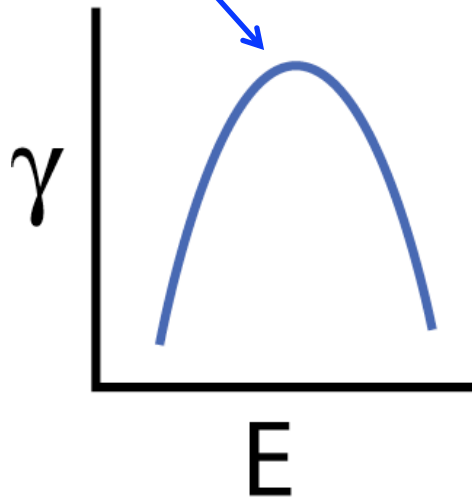
... much more reasonable!

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

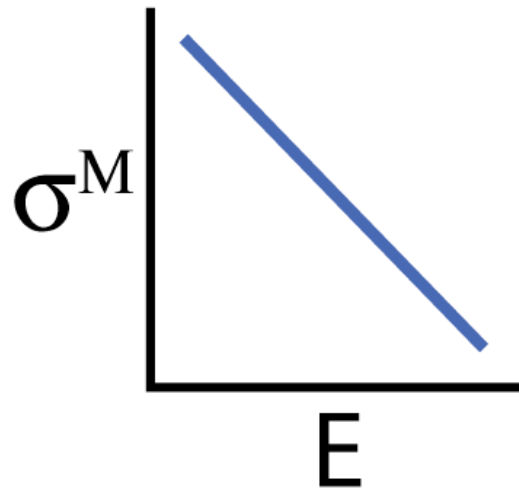
(BRIEFLY) 752

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

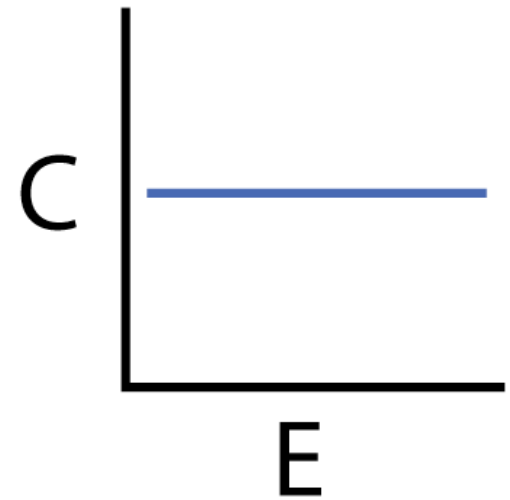
*electrocapillary
curve*



differentiate



differentiate



... here are electrocapillary data for various electrolytes...

(BRIEFLY) 753

... hey, you can already see that the Helmholtz Model fails a little...

... mostly on the left...

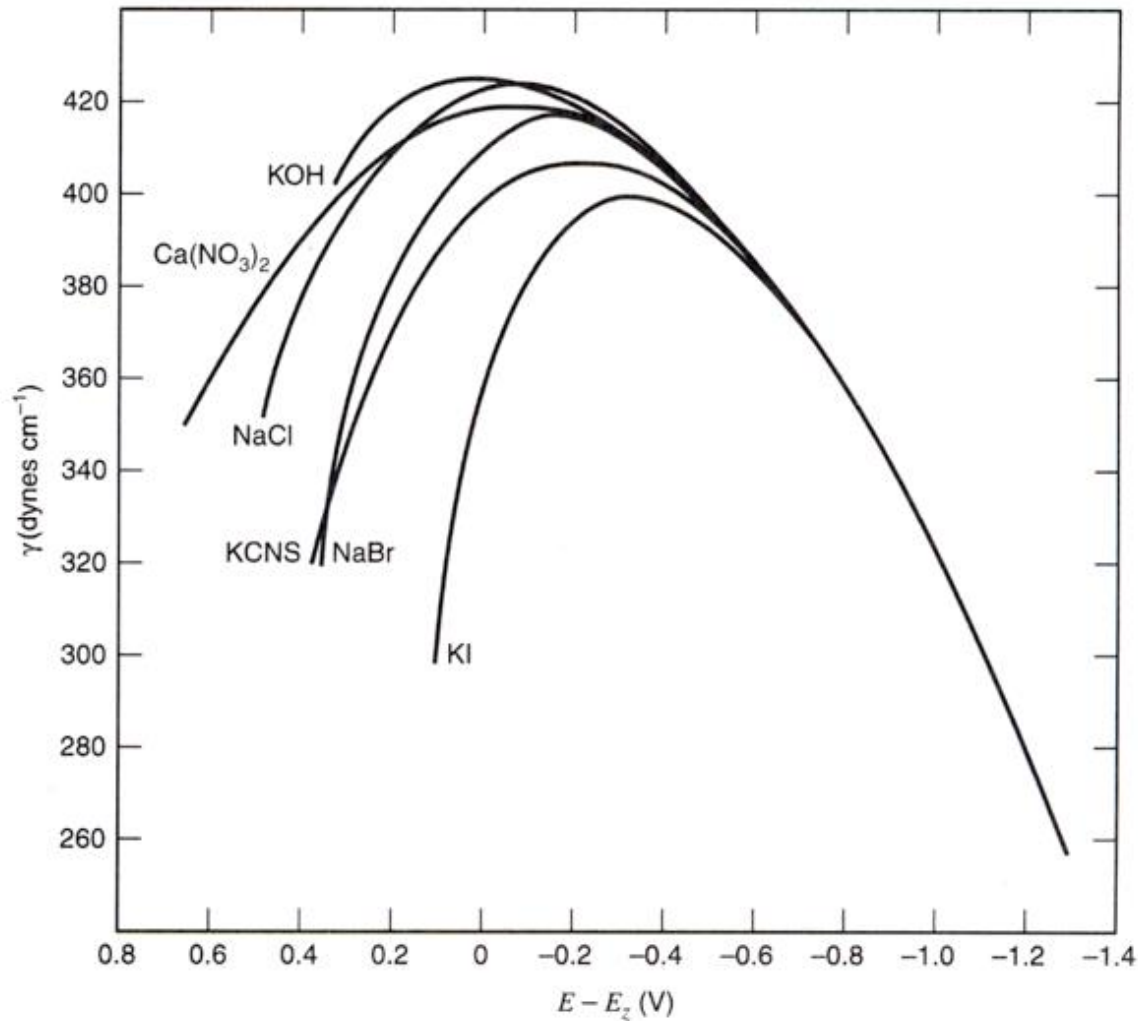


Figure 13.2.2 Electrocapillary curves of surface tension vs. potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947,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

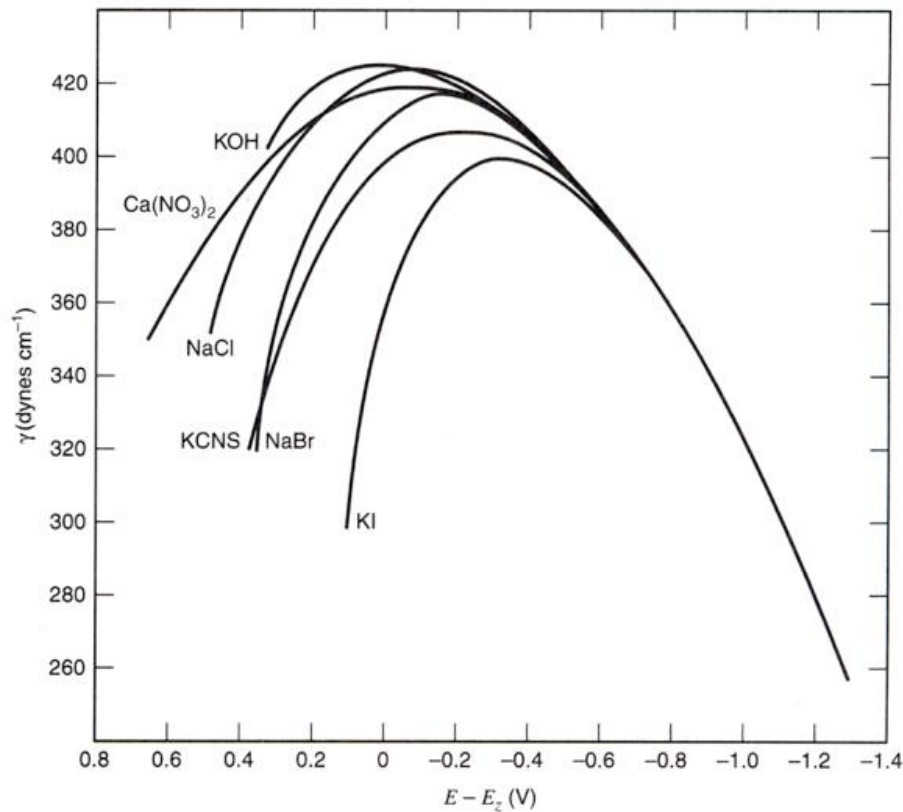


Figure 13.2.2 Electrocapillary curves of surface tension vs. potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947,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