758

Lecture #18 of 20+

758

759

The Double Layer

Chapter 13

759

760

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

760

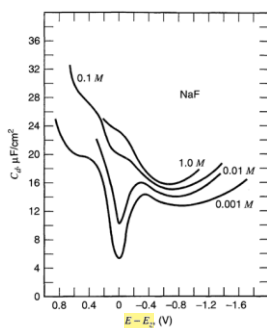... data for aqueous NaF from B&F is qualitatively similar... 761

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

761

RECALL: 762

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.

762

RECALL: 763

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...

763

Models of Electrical Double Layer:

RECALL: 764

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…

http://www.cartage.org.lb/
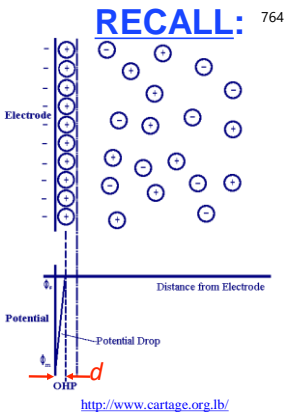
764

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

RECALL:

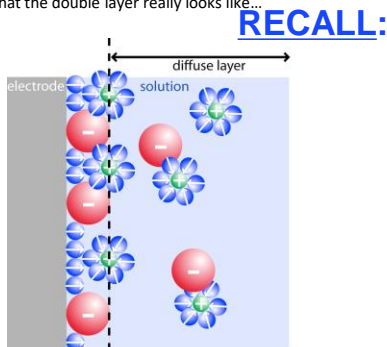$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

… 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?*
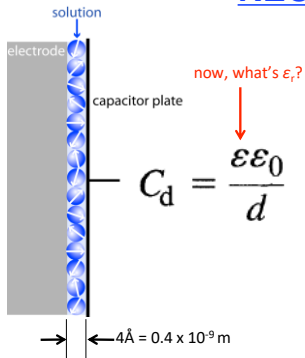
765

… recall, here's what the double layer really looks like…

RECALL: 766

766

… and here's what the double layer looks like in the Helmholtz approximation… **RECALL:** [767]

solution

electrode

capacitor plate

now, what's ε_r?

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

4Å = 0.4 x 10⁻⁹ m

767

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

for water at 20 ºC…

78.4

Rotation and reorientation of dipoles

Libration

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

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

Vibration

Polarisation

Relative permittivity ε_r

5.9

2   4   6   8   10   12   14   16   log ν
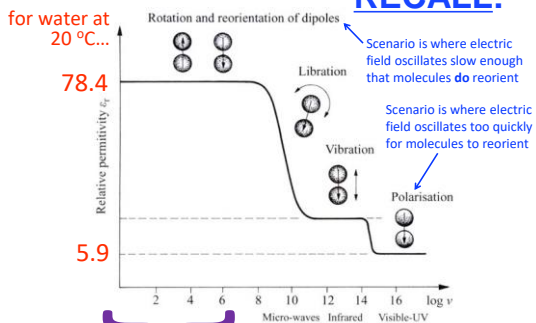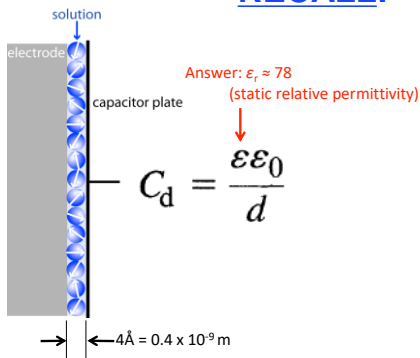Micro-waves   Infrared   Visible-UV

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*

768

… and here's what the double layer looks like in the Helmholtz approximation… **RECALL:** [769]

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

769

… and here's what the double layer looks like in the Helmholtz approximation… 770 **RECALL:**

solution

electrode

capacitor plate

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

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

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

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

$\rightarrow$ $\leftarrow$ 4Å = 0.4 x 10⁻⁹ m

770

… now, what if the water dielectric is saturated, and thus fixed? 771
… so that water cannot rotate…
$\varepsilon_r \approx 6$ **RECALL:**

solution

electrode

capacitor plate

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

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

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

… much more reasonable!

$\rightarrow$ $\leftarrow$ 4Å = 0.4 x 10⁻⁹ m

771

… if we can measure γ, we can determine σ_M… **RECALL:** 772
… 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!

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

electrocapillary curve

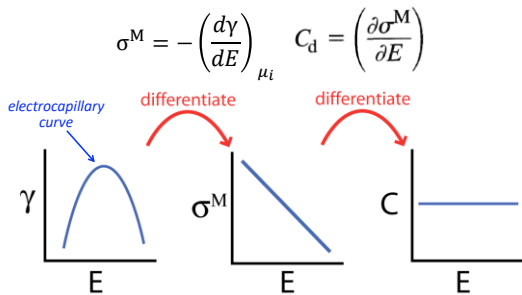differentiate   differentiate

γ

σ^M

C

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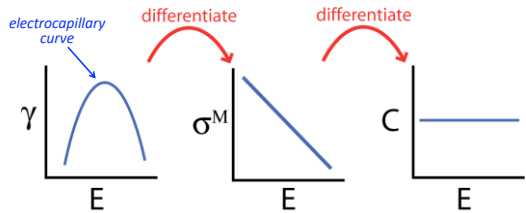
… Aside: One can determine E_{pzc} of a solid electrode using its capacitance

772

… if the Helmholtz model is correct, we'd get this *exactly*: **(BRIEFLY)** 773

RECALL:

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

electrocapillary curve → differentiate → differentiate

773

… here are electrocapillary data for various electrolytes… **(BRIEFLY)** 774
… hey, you can already see that the Helmholtz Model fails a little…
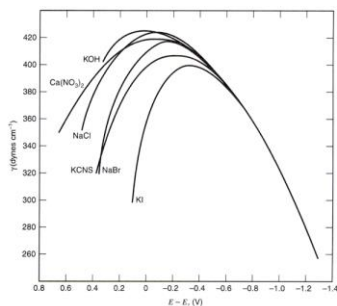
… mostly on the left…

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.]
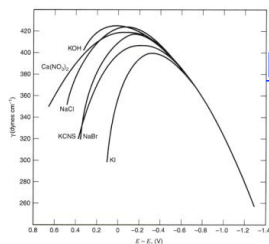
774

(BRIEFLY) 775

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.]
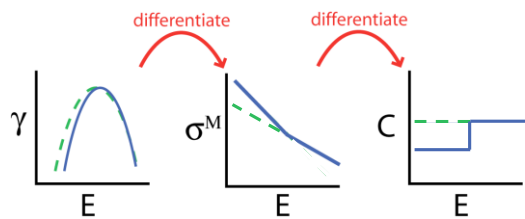
Notwithstanding, notice particularly the following:
  a) the γ vs. E parabola is independent of salt…
      … at potentials negative of the pzc…
  b) … but strongly dependent on salt positive of pzc…
  c) … and pzc itself depends on the electrolyte…
      … we'll get to this shortly…

775

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

… for example…

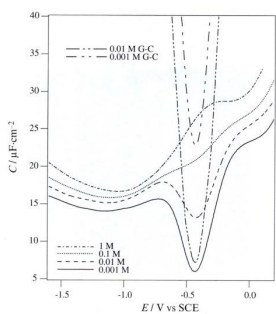… and a flat C_d is in no way observed… *we need a more sophisticated model…*

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

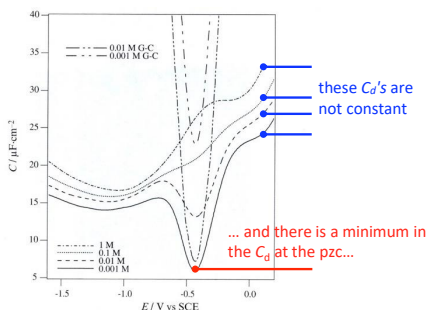… and there is a minimum in the C_d at the pzc…

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

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

779

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…

779

780

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…

780

781

RECALL: Debye–Hückel equation

(in water at 25 °C) $-\log\gamma_x = \dfrac{0.51z_x^2\sqrt{I}}{1 + 3.3\alpha_x\sqrt{I}}$

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

781

… d) ions are distributed according to Maxwell–Boltzmann statistics… 782

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

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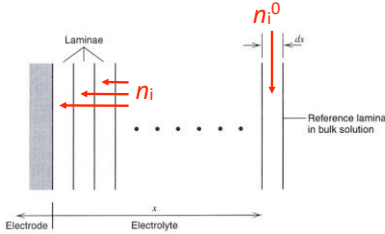

Figure 13.3.2 View of the solution near the electrode surface as a series of laminae.

782

---

the charge density, i.e. charge per unit volume, $\rho(x)$, is defined as: 783

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

… 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)*…

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

783

… if we apply the Poisson–Boltzmann Equation to a 1:1 electrolyte, we obtain the following (see B&F, pp. 547–548): 784

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

… and if we further assume that ϕ^0 is small, we get…

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

… where

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

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

784

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

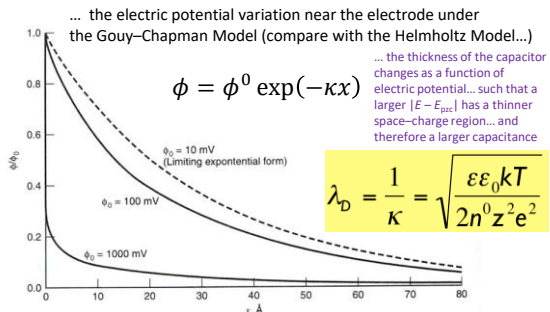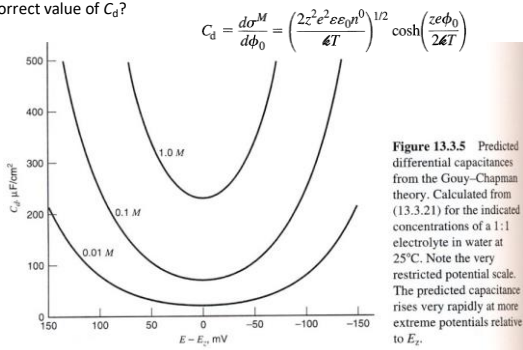… the electric potential variation near the electrode under the Gouy–Chapman Model (compare with the Helmholtz Model…)

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

… 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

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

Figure 13.3.3 Potential profiles through the diffuse layer in the Gouy–Chapman model.
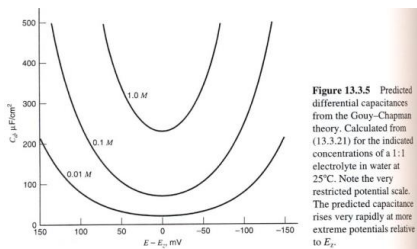
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.3

… 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.
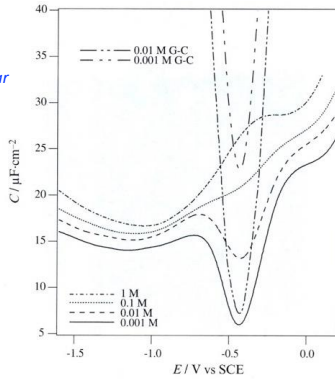
About Gouy–Chapman Theory we can say the following:
  a) it predicts a "dip" in C_d, that becomes more capacitive with increased ionic strength = **Good!**
  b) but it predicts a C_d that is WAY too high as the potential becomes far from the pzc = **Bad!**…
  c) and the C_d is symmetrical about the pzc (why?); this is not what is observed experimentally…

Getting close?

… Notably, near the pzc?

788

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].

788

… example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO$_4$ solution?

789

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

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

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

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

789

… example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO$_4$ solution?

790

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

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

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

$$= 9.589x10^{-10}m = 9.6\text{Å}$$

≈ 1 nm… about the same thickness as the compact layer…
Wow!

790

11

... example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO$_4$ solution?

791

TABLE 13.3.1 Characteristic Thickness of the Diffuse Layer[a]

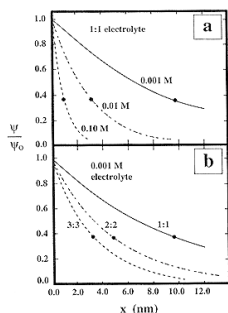| C*(M)[b]	$1/\kappa$(Å)
1	3.0
10^{-1}	9.6
10^{-2}	30.4
10^{-3}	96.2
10^{-4}	304

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

791

... 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

792

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

792

793

Three traditional models for double layer structure:

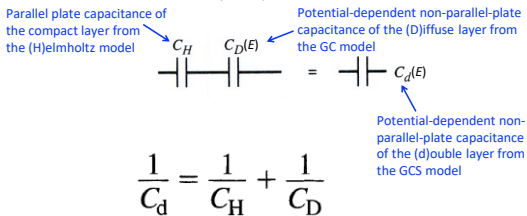1) Helmholtz

2) Gouy–Chapman (GC)

3) Gouy–Chapman–Stern (GCS)

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

793

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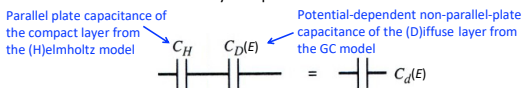
Parallel plate capacitance of the compact layer from the (H)elmholtz model → C_H

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

$= $ $C_d(E)$

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

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

794

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 → C_H

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

$= $ $C_d(E)$

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…

795

… our three models for the potential distribution near a charged electrode immersed in an electrolyte solution…

A

B

C

Helmholtz (H)   Gouy–Chapman (GC)   Gouy–Chapman–Stern (GCS)

http://electrochem.cwru.edu/
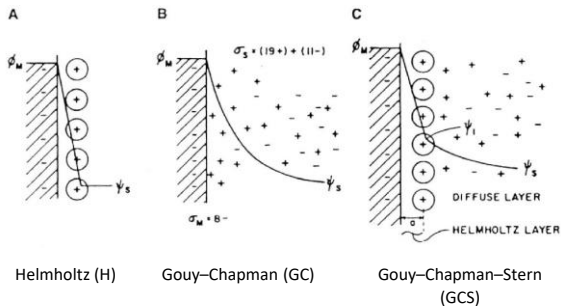
796

… History…

Physician & Physicist

Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)

Physicist

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

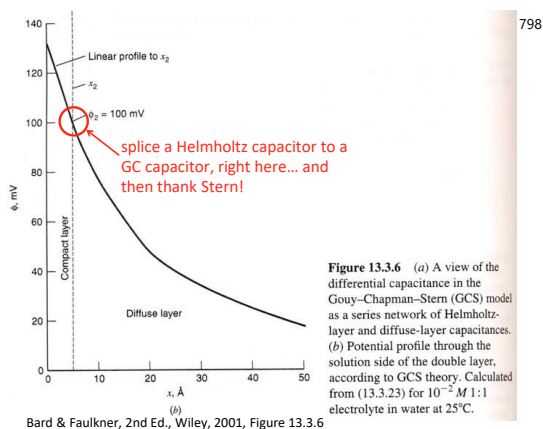Physicist

Louis Georges Gouy
(1854–1926)

P-Chemist

David Leonard Chapman
(1869–1958)

from Wiki

797

797

splice a Helmholtz capacitor to a GC capacitor, right here… and then thank Stern!

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

798

798

… 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 $C_{D(GC)}$…

799

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

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

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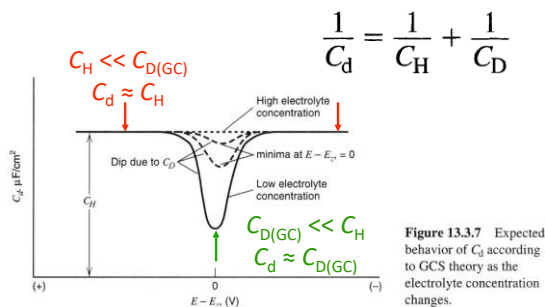
Figure 13.3.7 Expected behavior of C_d according to GCS theory as the electrolyte concentration changes.

799

14

And lastly, what effect does *specific adsorption* have on the pzc? 800
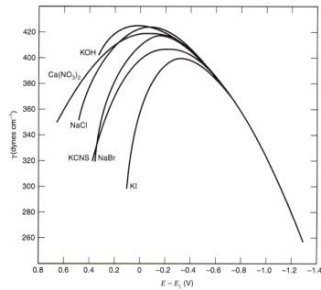The answer is hinted at in the data that we saw earlier…

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

800

… 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:

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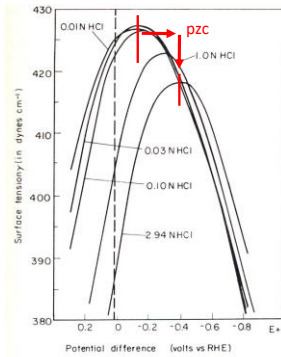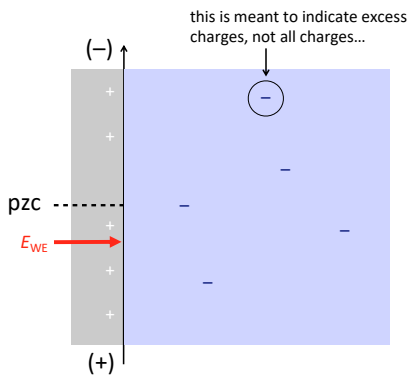

Fig. 7.57. Electrocapillary curves from solutions of different electrolyte (HCl) concentration. The symbol RHE stands for a reversible hydrogen electrode immersed, not in a standard solution, but in the same electrolyte as the electrode under study.

Bockris and Reddy, Plenum Press, 1973, Figure 7.57

801

… why a negative shift with anion adsorption? 802

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

802

… why a negative shift with anion adsorption?   803

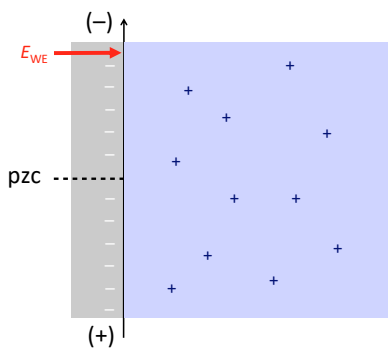this is meant to indicate excess charges, not all charges…

803
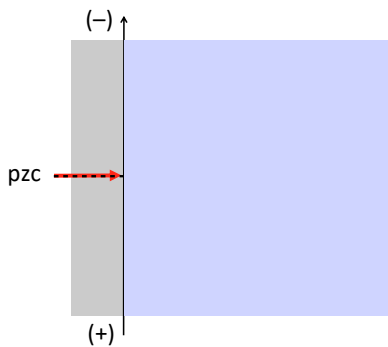
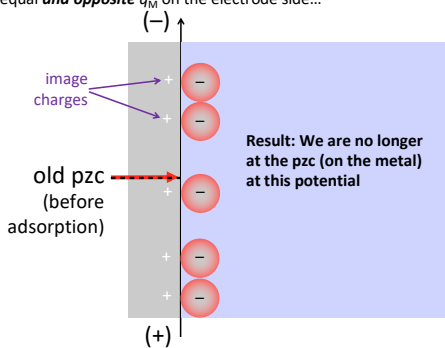… why a negative shift with anion adsorption?   804

804

… at the pzc, $q_M = 0$ and there is no excess positive or negative charge in the solution…   805
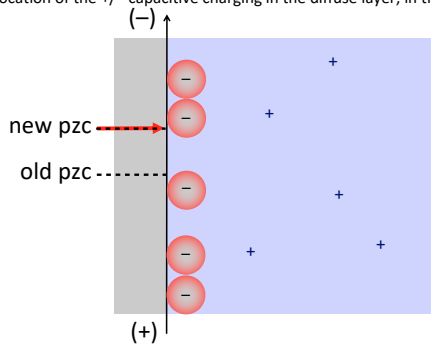

805

... 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...

806

... 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

807

... 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:

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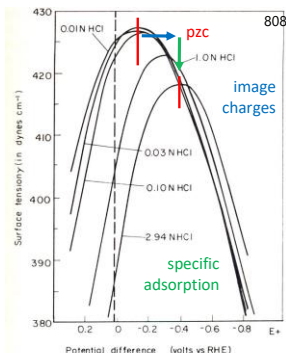

Fig. 7.57. Electrocapillary curves from solutions of different electrolyte (HCl) concentration. The symbol RHE stands for a reversible hydrogen electrode immersed, not in a standard solution, but in the same electrolyte as the electrode under study.

Bockris and Reddy, Plenum Press, 1973, Figure 7.57

808

17

… a new pzc exists, which is the potential required to neutralize charge, 809
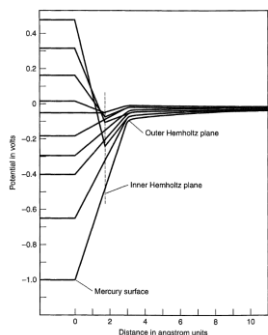due to charges *on both sides of the interface*… specific adsorption! **(SKIPPED)**

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

809

… what about uncharged adsorbates, like organic molecules?   **(SKIPPED)** 810
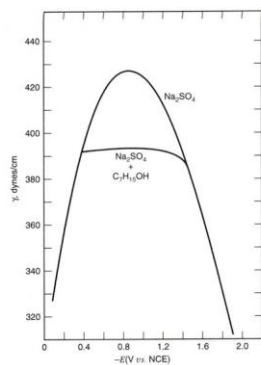

Figure 13.9.1 Electrocapillary curves for mercury in contact with 0.5 *M* Na$_2$SO$_4$ in the presence and absence of *n*-heptanol. Data from G. Gouy, *Ann. Chim. Phys.*, **8**, 291 (1906). [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]
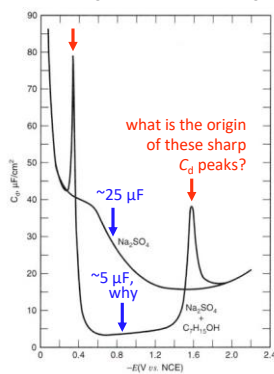
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.9.1

810

… what about uncharged adsorbates, like organic molecules?   811

what is the origin of these sharp C_d peaks?

~25 µF

~5 µF, why

… Gunk that is redox-active… and whose capacitance is called *chemical, or quantum, capacitance*

… Gunk is blocking ~80% of surface!

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

811

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power…   812

…. 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!*
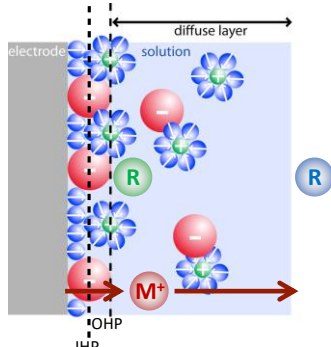
812

813

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
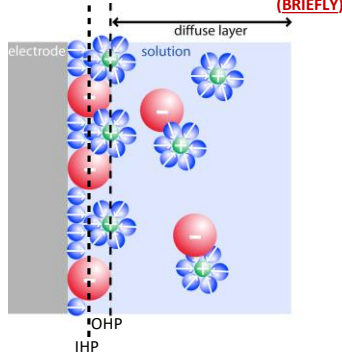
- Section 13.5:   Specific adsorption

813

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power…   814

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

(BRIEFLY)

diffuse layer

electrode   solution

−

−

−

OHP

IHP

814