

CH-242(b) - Part 1

Lecture 3 - Interfacial Electrochemistry

Resources:

- Butt et al., *Physics and Chemistry of Interfaces*, 3rd (2013) edition, chapter 4

Summary

- Electrocapillarity
 - The surface tension of an interface depends on the electric potential difference across the interface.
 - For a polarizable interface, the surface charge density σ at the interface is related to the applied voltage V and the surface tension by:

$$\sigma = \frac{d\gamma}{dV} \quad (\text{Lippmann's equation})$$

- The differential capacitance c_A of the interface can be calculated using the equation

$$c_A = -\frac{d^2\gamma}{dV^2}$$

- Specific adsorption
 - In general at zero applied voltage there will be a preferential binding to a polarizable metal/aqueous interface of some ions over others.
 - The voltage V_{pzc} is defined to be the voltage required to establish an electrically neutral interface ($\sigma = 0$). For mercury/aqueous interfaces this corresponds to the peak of the associated electrocapillary curve measuring capillary rise/fall as a function of applied voltage.
 - V_{pzc} depends on the species of cations and anions in solution. Because anions typically bind more strongly to metal/aqueous interfaces, V_{pzc} is typically positive.
- The diffuse layer and Debye screening

- Mobile charge carries in solution will redistribute themselves in a “diffuse layer” of thickness λ_D (Debye length) at the interface, where

$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2c_o F^2}}$$

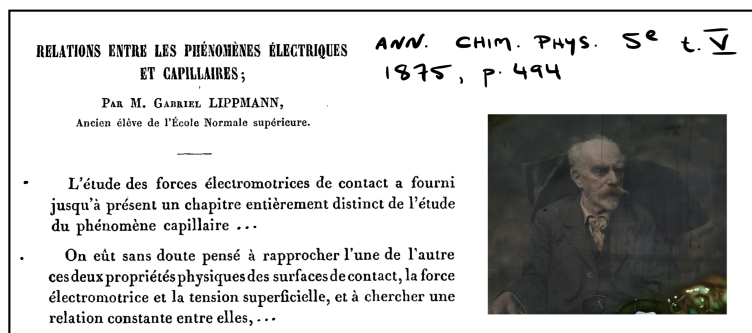
- Inside the diffuse layer, there is a nonzero charge density which acts to “screen” (or block) out the electric field produced by any net surface charge at the interface.
- The differential capacitance c_A of the diffuse layer is ε/λ_D .
- Nonpolarizable interfaces
 - For nonpolarizable interfaces there is a mechanism for charge transfer across the interface.
 - As a result, the interfacial electric potential and the concentrations of ionic species in solution are inter-dependent.
 - For the AgI electrode we have the following equation relating the concentration of Ag^+ ions and the interfacial potential:

$$[\text{Ag}^+] = [\text{Ag}^+]_{\text{pzc}} e^{\frac{F\Delta\phi}{RT}} \quad (\text{Nernst equation})$$

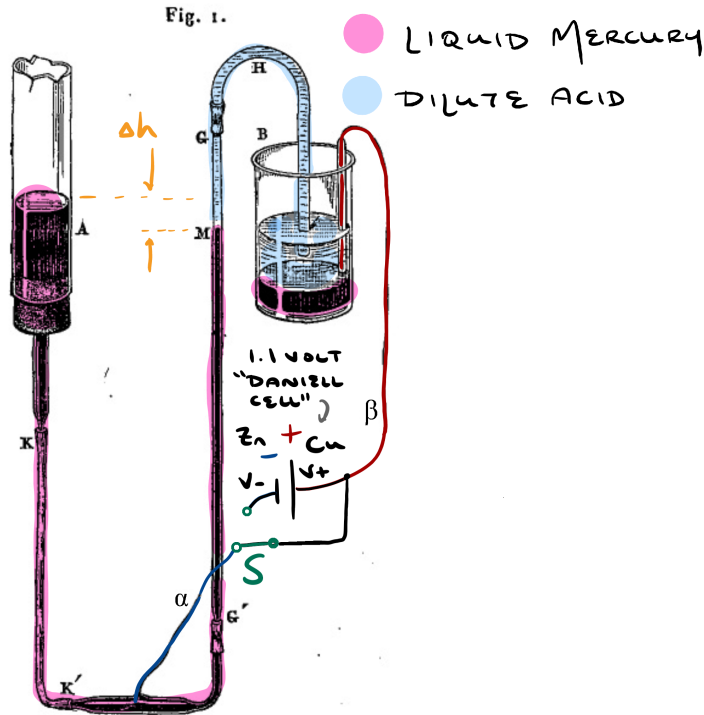
1 Electocapillarity

1.1 Lippmann’s experiment

Franco-Luxembourgish physicist Gabriel Lippmann (1845-1921) performed the first experiments exploring the relationship between electricity and surface tension. Below are a couple excerpts from the introduction of an article announcing his first discoveries in “electrocapillarity”:



Below is Lippmann’s illustration of the apparatus used in his seminal experiments. I’ve colored the diagram to help identify the different elements:



The central component of the apparatus is located at point “M” where one finds a mercury-water meniscus formed in a narrow glass capillary.

Question: What is the approximate inner radius r of the capillary at the point M ? Take the height difference $\Delta h \equiv h_A - h_M$ between the mercury liquid level at A and the meniscus M to be $\Delta h \approx +14.0$ mm, and assume the meniscus is at the same height as the water liquid level at B . Assume, as Lippmann does, that the mercury-water meniscus M has contact angle of $\theta = 0^\circ$. Lippmann in fact adds some sulfuric acid to the water in order to enhance the “wettability” of the water with the walls of the glass capillary and ensure that the contact angle $\theta = 0^\circ$ condition is met. The surface tension γ of the mercury-water interface is 415 mN m^{-1} .

Answer: The pressure P_{Hg} on the mercury side of the meniscus M is $P_o + \rho_{Hg}g\Delta h$ where:

- P_o is the pressure at the gas-mercury interace at A and is simply equal to the atmospheric pressure in the laboratory,
- ρ_{Hg} is the density of liquid mercury, and
- g is the acceleration due to gravity.

The pressure on the water side of the meniscus is simply P_o since the meniscus is at the same height as the water liquid level at B . Therefore the pressure difference ΔP across the interface is just $\rho_{\text{Hg}} g \Delta h$, which by the Young-Laplace equation (lecture 1) is equal to $\frac{2\gamma}{R}$, where R is the radius curvature of the meniscus. The contact angle $\theta = 0^\circ$ condition is equivalent to the assertion that the radius of curvature R is equal to the capillary radius r . Thus we have

$$r = 2\gamma / \rho_{\text{Hg}} g \Delta h$$

There is in fact a unit of pressure called mmHg which is defined to be the pressure difference between two points in a mercury column that are separated by 1 mm in height. We have $1 \text{ mmHg} \approx 133 \text{ Pa}$. Therefore numerically we have

$$r = 2 \times 415 \times 10^{-3} \text{ N m}^{-1} / (133 \text{ Pa mmHg}^{-1} \times 14.0 \text{ mmHg}) \approx 0.44 \text{ mm}$$

which is quite close to Lippmann's estimate of 0.32 mm.

Lippmann inserts into the mercury volume at K' an electrical lead (labeled α) and inserts into the mercury volume below the water reservoir at B another electrical lead labeled β . Connected between the leads α and β is a 1.1 V copper / zinc “Daniell cell” battery, with the positive end of the battery connected to β . With the electrical switch S disconnected from the battery Lippmann observes the capillary drop $\Delta h \approx 14.0 \text{ mm}$. Remarkably, when he connects the switch S to the battery he observes an additional 4.9 mm drop of the meniscus elevation so that we now have $\Delta h = 18.9 \text{ mm}$. Applying a voltage across the interface appears to have the effect of modifying the interfacial surface tension!

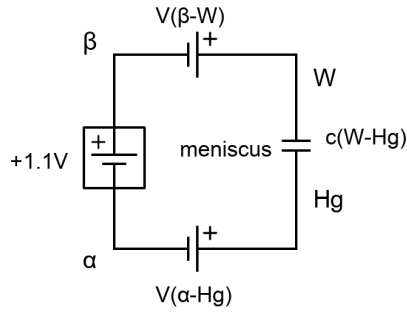
1.2 Aside: contact potentials

Before continuing with the more mathematical analysis of this “electrocapillary” effect, you may be wondering why Lippmann bothers to include a mercury volume at the bottom of the water reservoir at B , and why he connects his electrical lead β to this volume instead of just putting β directly in contact with the water. The reason is that there will in general exist a voltage drop, called a “contact potential”, at the electrical interface (or “junction”) of unlike materials. The origin of this phenomenon can be understood from thermodynamical considerations: if the chemical potentials (see lecture 2) for electrons of the two materials composing the junction are different, then electrons will leave the material of high chemical potential and go to the material of lower chemical potential until the coulomb repulsion due to accumulation of negative charge in the low chemical potential material prevents the flow of further charge*. The flow of charge results in a difference in electric potential between the two materials which we call the contact potential.

The value of this contact potential depends on many factors, including the temperature, pressure, and the composition of the materials composing the

*When this occurs, we say that the difference in “*electro*-chemical potential” of the two materials is zero.

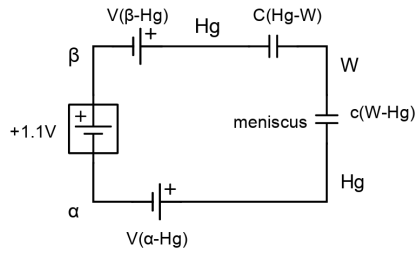
junction[†]. Contact potentials are difficult to measure, so that if one merely inserts lead β directly into the water then, even though there may be a well-defined 1.1 V potential difference between the leads α and β with the switch S connected to the battery, the potential difference across mercury-water interface will be unknown because of the unknown contact potential drops at the junctions between the lead α and the mercury and the lead β and the water. This can be seen by looking at the following simplified electrical diagram:



The voltage drop across the meniscus (represented by the capacitance $c(W - \text{Hg})$) is not 1.1 V but rather $1.1 \text{ V} + V(\beta - W) - V(\alpha - \text{Hg})$ where

- $V(\beta - W)$ is the contact potential across the junction between the lead β and the liquid water (W) and
- $V(\alpha - \text{Hg})$ is likewise the contact potential across the junction between the lead α and the liquid mercury (Hg).

Lippmann's actual experimental arrangement is however represented by the following electrical diagram:



Now the voltage drops created by the contact potentials at the junctions $\alpha - \text{Hg}$ and $\beta - \text{Hg}$ are *equal and opposite* (we presume the electrical leads

[†]The temperature dependence of the contact potential is the operating principle of a *thermocouple*, which is a type of thermometer.

are made of the same material), so that their effects cancel. We do now have however another large mercury-water interface at the water reservoir B , which we represent by a capacitance $C(\text{Hg} - \text{W})$, so that the voltage drop Δv across the meniscus will be 1.1 V minus the voltage drop ΔV across $C(\text{Hg} - \text{W})$.

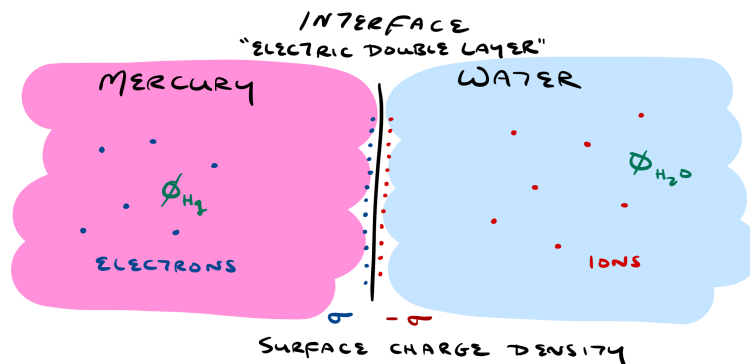
However, for two capacitors in series we have that the charge Q across one capacitor is equal to that of the other. Therefore, from the basic relationship $V = Q/C$ where

- C is the capacitor's capacitance,
- Q is the charge across the capacitor, and
- V is the voltage drop across the capacitor

we have that the voltage drop ΔV over the large mercury-water interface is much smaller than the drop Δv across the meniscus to the extent that capacitance is proportional to surface area and the surface area of the former is much larger than that of the latter (i.e. the $r \approx 300 \mu\text{m}$ meniscus). Therefore to a very good approximation we can say that the voltage drop across the meniscus (with the switch S connected to the battery) is simply equal to that of the 1.1 V battery, independent of whatever might be the contact potential between the mercury and the electrical contacts.

1.3 The Lippmann equation

We now proceed with a thermodynamical analysis of the charged mercury-water interface to try understand this increase in surface tension that Lippmann observed upon applying a voltage across the interface. The picture that will be helpful to keep in your head is that of an *electric double layer* at the mercury-aqueous interface:



where, depending on the difference in the electric potential ϕ on each side of the interface we will have varying amount of electric charge (represented by a surface charge density σ) accumulating at the interface.

We begin the analysis by quoting equation (59) from the typed lecture 2 notes:

$$d\gamma = -\Gamma d\mu^S \quad (1)$$

where γ is the surface tension, Γ is surface excess of a solute, and μ^S is the chemical potential of the ionic solute species at the interface. We generalize this equation in two respects. First we enlarge the equation to include several species: n_{Hg} species from the liquid mercury and n_{Aq} species coming from the aqueous side:

$$d\gamma = -\sum_{i=1}^{n_{\text{Hg}}} \Gamma_i^{\text{Hg}} d(\mu_i^{\text{Hg}})^S - \sum_{j=1}^{n_{\text{Aq}}} \Gamma_j^{\text{Aq}} d(\mu_j^{\text{Aq}})^S \quad (2)$$

The species coming from the mercury side would include negatively charged conduction electrons or positively charged “holes” (i.e. mercury atoms missing a valence electron), while the species in the aqueous side could include any ionic species existing in solution. For Lippmann’s solution we would include among the aqueous ionic species the HSO_4^- hydrogen sulfate anion or H_3O^+ hydronium cation coming from the sulfuric acid added to increase the solution’s wettability.

Second, we generalize μ to now represent the *electrochemical potential* of its associated species. The electrochemical potential μ can, somewhat loosely speaking, be decomposed into two parts $\mu = \mu^o + q\phi$ where:

- μ^o is the “chemical” part equal to the electrochemical potential of the species at zero electric potential, and
- $q\phi$ is the “electric” part, where q is the electric charge of one mole of the species and ϕ is the value of the electric potential in the medium. We recall from introductory electromagnetism that the electric potential $\phi(\mathbf{x})$ is a function defined over a region of space. This function defines the force $\mathbf{F} = q\mathbf{E}$ exerted on a particle of charge q by the surrounding charges via the relation $\mathbf{E} = -\nabla\phi$. The mediums we consider are electrically conductive so that the electric potential is constant throughout a given medium.

At equilibrium the electrochemical potentials of both the mercury- and aqueous-phase species must be equal to the values in their respective bulk phases. Therefore in equilibrium we have

$$d\gamma = -\sum_{i=1}^{n_{\text{Hg}}} \Gamma_i^{\text{Hg}} d\mu_i^{\text{Hg}} - \sum_{j=1}^{n_{\text{Aq}}} \Gamma_j^{\text{Aq}} d\mu_j^{\text{Aq}} \quad (3)$$

where we have dropped the superscript S to indicate that we refer now to the bulk phase electrochemical potentials. If we assume that no changes occur in the chemical part μ^o of the electrochemical potentials, then we have $d\mu = qd\phi$

so that

$$d\gamma = - \left(\sum_{i=1}^{n_{\text{Hg}}} q_i^{\text{Hg}} \Gamma^{\text{Hg}} \right) d\phi^{\text{Hg}} - \left(\sum_{j=1}^{n_{\text{Aq}}} q_j^{\text{Aq}} \Gamma^{\text{Aq}} \right) d\phi^{\text{Aq}} \quad (4)$$

Now molar charge q (charge per mole) times surface excess Γ (moles per unit area) is simply surface charge density σ (charge per unit area) so we have

$$d\gamma = - \left(\sum_{i=1}^{n_{\text{Hg}}} \sigma_i^{\text{Hg}} \right) d\phi^{\text{Hg}} - \left(\sum_{j=1}^{n_{\text{Aq}}} \sigma_j^{\text{Aq}} \right) d\phi^{\text{Aq}} \quad (5)$$

which, setting $\sum_{i=1}^{n_{\text{Hg}}} \sigma_i^{\text{Hg}} \equiv \sigma^{\text{Hg}}$ and $\sum_{j=1}^{n_{\text{Aq}}} \sigma_j^{\text{Aq}} \equiv \sigma^{\text{Aq}}$ yields

$$d\gamma = - (\sigma^{\text{Hg}} d\phi^{\text{Hg}} + \sigma^{\text{Aq}} d\phi^{\text{Aq}}) \quad (6)$$

We now argue that σ^{Hg} must be equal and opposite to σ^{Aq} . This requirement of “electroneutrality” derives from the fact that, though the interface is not necessarily electrically conductive, the individual media are, so that inside either the mercury or aqueous phases we require that the electric field equal zero. We omit here the rigorous demonstration, using Gauss’ law, that the condition of zero electric field outside the interface necessarily implies a perfect cancellation of charge at the interface, and simply assert

$$\sigma^{\text{Hg}} = -\sigma^{\text{Aq}} \equiv \sigma \quad (7)$$

Therefore from (6) we have

$$d\gamma = \sigma d(\phi^{\text{Aq}} - \phi^{\text{Hg}}) \quad (8)$$

Now $\phi^{\text{Aq}} - \phi^{\text{Hg}} = \phi_\beta - \phi_\alpha$ is exactly the external voltage V applied by the experimenter[‡]. Making this substitution we obtain the Lippmann equation

$$\frac{d\gamma}{dV} = \sigma \quad (9)$$

From the Lippmann equation we obtain directly an expression for the “differential interfacial capacitance” c_A :

$$c_A \equiv -\frac{d\sigma}{dV} = -\frac{d^2\gamma}{dV^2} \quad (10)$$

which has units of capacitance per unit area. The negative sign is necessary to ensure that a positive differential capacitance corresponds to an increase in the metallic phase charge density σ when the electric potential in the metallic phase increases relative to the aqueous phase.

In the sections to follow we investigate the consequences of equations (9) and (10), but before continuing it is helpful to quickly pause and enunciate the sign conventions employed in these equations:

[‡]In Lippmann’s original experiment described earlier, the copper cathode is connected to the electrical lead α and the zinc anode is connected to the electrical lead β . Therefore when Lippmann opens the switch S to the battery there is a *positive* voltage V applied across the meniscus interface as we have defined it.

- The surface charge density σ refers to the surface charge density on the mercury side of the interface, or more generally to the metallic side of the interface.
- The polarity of the applied voltage V is such that V is positive if the potential in the aqueous phase is greater than that of the metallic phase.

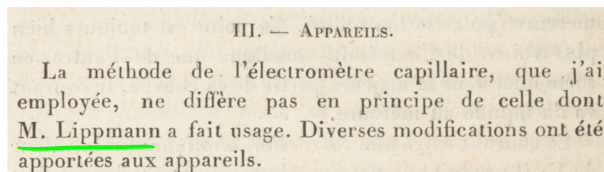
2 Surface charging and specific adsorption

When Lippmann connects the switch S to the battery, he effectively increases V from 0 to 1.1 V. The fact that he observes a further drop in the height of the meniscus upon connecting the switch to the battery implies that an increase in V results in an increase in surface tension γ . This implies via the Lippmann equation that, for the acidic solution used by Lippmann, the interfacial charge density $\sigma = \frac{d\gamma}{dV}(V = 0) \approx \frac{\gamma(1.1 \text{ V}) - \gamma(0 \text{ V})}{1.1 \text{ V} - 0 \text{ V}}$ is positive. Since σ refers to the charge density on the mercury side of the interface, a positive σ implies a *deficit* of negatively-charged electrons at the interface, or equivalently we could say there is a *surplus* of positively-charged mercury ions (i.e. holes).

Likewise, Lippmann's observations imply a negative charging of the aqueous side of the interface. This implies the existence of an anionic species that preferentially binds or *specifically adsorbs* to the interface. Since Lippmann had added sulfuric acid to increase the wettability of his aqueous solution, this anion might be the HSO_4^- hydrogen sulfate ion, though we would need more information about the exact composition of the solution to say more.

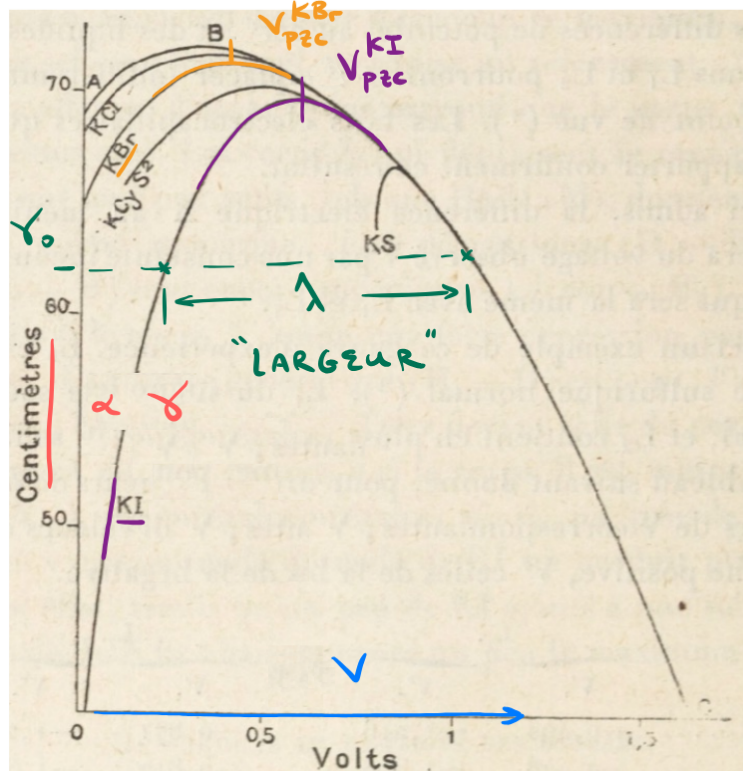
2.1 Guoy's experiments and specific adsorption

At the dawn of the twentieth century French physicist L.G. Gouy (1854-1926) performed a series of experimental investigations on the phenomenon of electrocapillarity. For a wide variety of solutions of widely ranging concentrations Gouy measured "electrocapillary curves" tracing the dependence of the surface tension γ of the mercury-aqueous interface on the interfacial potential difference V . The technique and apparatus used by Gouy are essentially identical to that used by Lippmann:



Here is an example of a series of electrocapillary curves measured by Gouy for several potassium salts:

ANN. CHEM. PHYS. [7] 29, 145 (1903)



We have annotated the diagram to highlight certain properties of these curves that will be of interest to us:

- **Horizontal axis:** the voltage V applied across the mercury-aqueous interface.
- **Vertical axis:** the pressure (in $\text{cmHg} = 10 \text{ mmHg}$) that must be applied to the mercury reservoir in order to keep the meniscus at some fixed height. This pressure is proportional to the surface tension γ of the mercury-water interface.
- **Peak locations:** the voltage V_{pzc} at which the surface tension reaches a maximum.
- **Peak widths** (“largeurs”): the difference λ in voltage at two points of equal reference surface tension γ_0 .

One major result of Gouy’s investigations that is clear from the above curves is that, contrary to the conviction of Chappmann, an electrocapillary curve is not identical from one solution to the next:

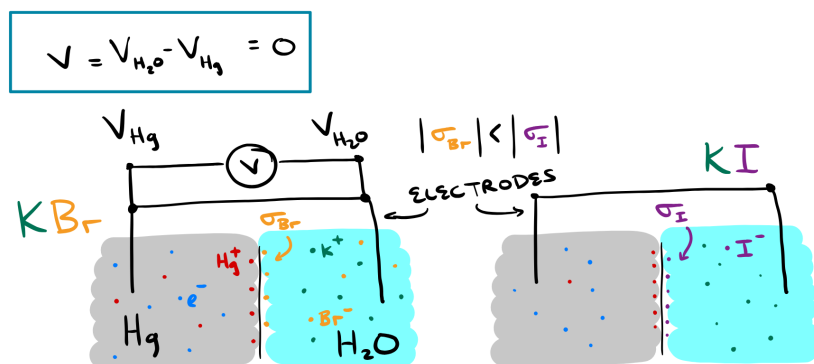
M. Lippmann, à la suite d'expériences peu nombreuses, avait cru que la fonction électrocapillaire était la même, quelle que fût la composition chimique du liquide, et que la dérivée $\frac{d^2\theta}{d\Delta^2}$ était une constante ⁽¹⁾; dès lors toutes les courbes électrocapillaires étaient une même parabole. Dès le début de mes recherches, j'eus l'occasion de constater que les courbes électrocapillaires sont bien différentes les unes des autres, soit par la valeur du maximum, soit par leur forme et leur dissymétrie plus ou moins marquée ⁽²⁾. *Chaque liquide a donc sa courbe électrocapillaire propre*, et leur étude forme un sujet des plus étendus, auquel ce travail est consacré en grande partie.

The symbols θ and Δ used here by Gouy are what we refer respectively as the surface tension γ and applied voltage V . The next subsection will look at the slopes $\frac{d\gamma}{dV}$ of the electrocapillary curves, which by the Lippman equation (eq. (9)) we know to be equal to the interfacial charge density σ . Following that we then investigate the physical interpretation of the curvature $\frac{d^2\gamma}{dV^2}$ of the curve mentioned in the excerpt above.

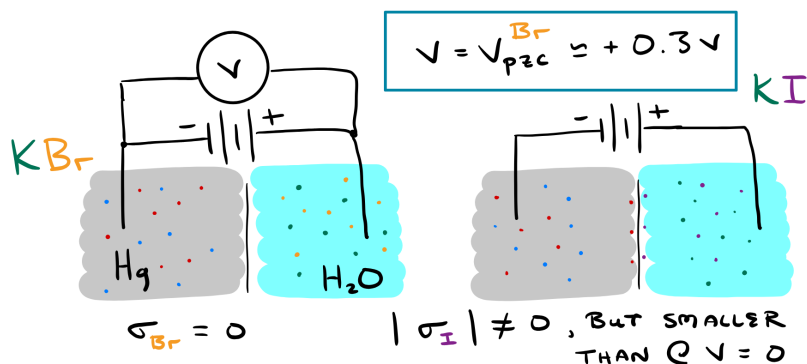
2.2 Point of zero charge and specific adsorption

One feature of the electrocapillary curves shown above which stands out is the relative displacement of the curves from each other. For example, the KI solution peaks at about 0.6 V, while KBr peaks at about 0.3 V. At the peak of a curve we have $\frac{d\gamma}{dV} = 0$, which occurs at V_{pzc} , i.e. the voltage at the “point of zero charge”. At $V = 0$ we have for all curves a positive slope, which according to our convention implies specific adsorption of dissolved anionic species at the interface. When we increase V we put the aqueous phase at a higher electric potential than the mercury phase, which has the effect of repelling negatively charged anions from the interface. Evidently the voltage required to reach $\sigma = 0$, i.e. to reach a state of equal and opposite anion and cationic charge density at the interface, is greater for the KI solution than for KBr. Since both solutions share the same potassium K^+ cation, the electrocapillary curves seem to suggest in other words that iodine binds more strongly than bromine to the interface.

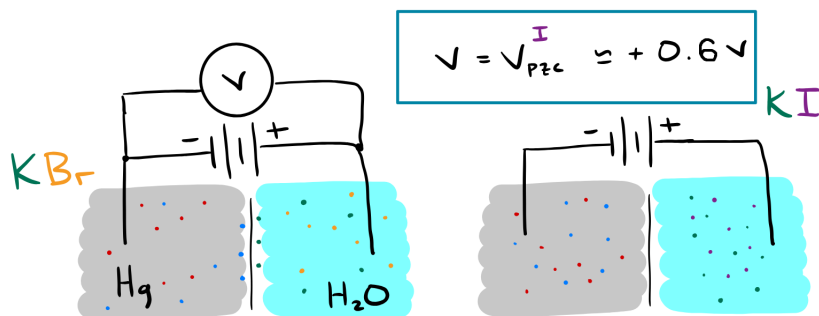
We offer the following series of diagrams to help the reader visualize the charge state of the interface at various applied voltages V :



With no zero applied voltage, the binding at the interface is determined purely by chemical affinity, which for iodine is greater than bromine. This reflected in the steeper γ vs. V slope for KI than KBr, which implies a greater surface charge density σ . The negative charge from the bound anions repels free electrons in the mercury, leaving behind an excess of positively charged Hg^+ cations.



In the above diagram we apply a positive voltage $V \approx 0.3V$, so that positive charge appears on the electrode in the aqueous phase and negative charge appears on the electrode in the mercury. Anions bound at the interface are attracted to the positive charge and repelled by the negative charge, resulting in net force acting to pull anions back into the aqueous phase. This force is strong enough to eliminate any preference for the adsorption of Br^- over the K^+ counterion, resulting in an overall charge density $\sigma = 0$. The selective adsorption of the more strongly bound I^- ions is on the other hand reduced but not completely eliminated.



Finally, increasing the voltage to $V \approx 0.6$ V eliminates any preference for I^- adsorption over K^+ . The electrical force attracting positively charged ions to the interface is now strong enough to preferentially adsorb K^+ cations, which in turn attracts free electrons in the mercury phase to the interface. Glancing back at Gouy's graph of electrocapillary curves reproduced at the beginning of the section, we note that at sufficiently positive applied voltages the measured surface tension is independent of the salt solution, i.e. on the right hand side the curves all trace over one another. This we can explain by arguing that at sufficiently positive applied voltages the dense layer of (negatively charged) electrons on the metallic side of the interface prevent any significant occupation of anionic species on the aqueous side of the interface. It is thus only the cationic species which can populate the interface, which, for the curves displayed on the graph in question, is always the potassium K^+ ion. Therefore for these voltages we expect identical electrocapillary behavior.

According to *PCI*, the preference for specific adsorption of anionic species over cationic species is a general one. The trend is observed not only for mercury but for other metals as well, including gold, platinum, silver, etc. One influence thought to play a role in this preference is the tendency for cations to form stronger hydration shells. Binding to the surface would require an ion to "shed" its hydration shell of water molecules, which for cations is often too expensive energetically.

3 "Largeur des courbes" and solute concentration

In addition to the peak location, Gouy also studied the voltage difference ("largeur") λ between two points of equal surface tension γ_o (see e.g. the annotated diagram above). He tabulates the results for potassium nitrate (KNO_3) solutions for a series of different concentrations in the excerpt below:

200 GOUY.

On y a inscrit, pour les hauteurs 940, 900, 860 et 820, les largeurs λ des courbes, et les accroissements $\delta\lambda$ que prennent ces largeurs quand la concentration devient 10 fois plus petite.

CONCENTRATION
1 M \equiv 1 g/liter

TABLEAU V.

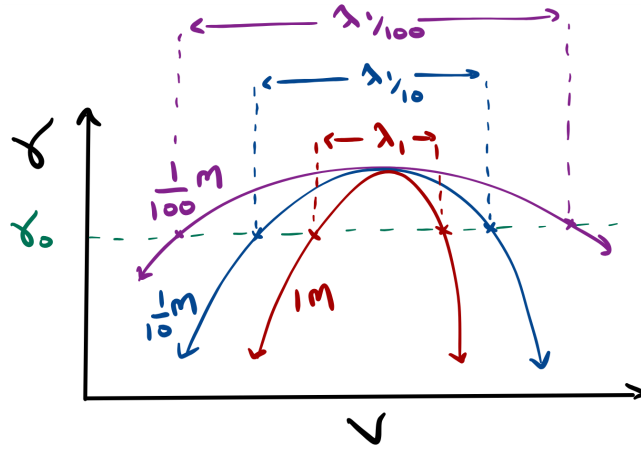
	940.		900.		860.		820.
$h.$	$\lambda.$	$\delta\lambda.$	$\lambda.$	$\delta\lambda.$	$\lambda.$	$\delta\lambda.$	$\lambda.$
K Az O ₃ ($\frac{1}{10}$ M) ...	0,933		1,211		»		»
id. ($\frac{1}{10}$ M) ...	0,862	0,071	1,149	0,062	1,377	»	»
id. (1 M) ...	0,767	0,095	1,059	0,090	1,296	0,081	1,497

* SURFACE TENSION MEASURED AS CAPILLARY FALL OF MENISCUS, NORMALIZED TO PURE WATER SOLUTION, SET EQUAL TO 1000.

Inspection of the table shows a systematic decrease in the largeur λ with increasing KNO₃ ("KAzNO₃") concentration. This trend was found to hold in general for the wide array of solutions Gouy investigated. What is the physical interpretation of this observation? In general, near the peak of a curve the surface tension has the following dependence on the applied voltage:

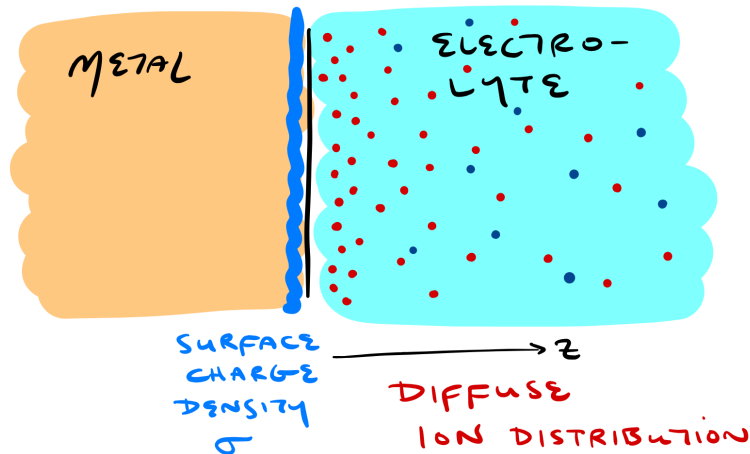
$$\gamma(V) \approx \gamma(V_{pzc}) + \frac{1}{2} \frac{d^2\gamma}{dV^2} (V_{pzc}) \times (V - V_{pzc})^2 \quad (11)$$

This comes from a Taylor expansion of the function $\gamma(V)$, taking into account that at the peak, i.e. at $V = V_{pzc}$, we have $\frac{d\gamma}{dV} = 0$. If we take into account that $\gamma(V_{pzc})$ is found to be mostly independent of concentration, then the primary influence of changing the solute concentration is apparently to modify the curve's curvature $\frac{d^2\gamma}{dV^2} (V_{pzc})$. We illustrate this in the following diagram, which qualitatively illustrates the electrocapillary curves tabulated in the table above:



The diagram illustrates that a smaller λ corresponds to a higher absolute curvature $|\frac{d^2\gamma}{dV^2}(V_{pzc})|$, and that these curves have a negative curvature. But we also have from equation (10) that the differential capacitance c_A is $-\frac{d^2\gamma}{dV^2}$. So increasing the solute concentration appears to increase the capacitance of the electric double layer at the metal-aqueous interface. To explain this correlation (among others), Gouy along with English chemist D. L. Chapman (1869-1958) worked out the theory of the *diffuse* layer at the interface, which we will treat in the following section.

4 Diffuse electric double layer and Debye screening

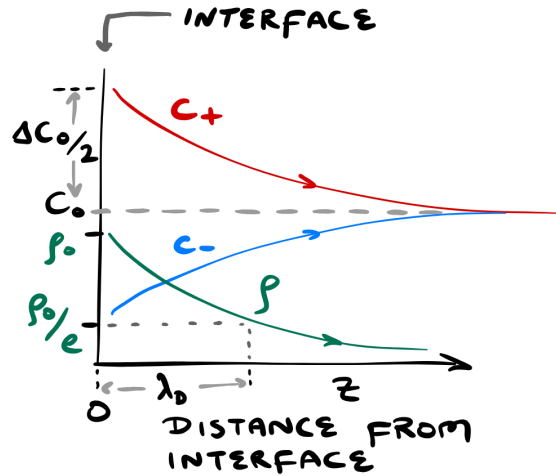


4.1 Qualitative description

The Gouy-Chapman theory of the electric double-layer in essence describes an interplay between two complimentary driving forces:

- *Energy*: Coulombic forces (unlike charges attract, like charges repel) tend to *concentrate* charged particles at regions of low potential energy.
- *Entropy*: At high temperatures particles tend to *diffuse* or *disperse* – there is a pseudo “entropic force” acting to encourage a uniform distribution of particles.

The physical result of the theory is the following: in addition to a possible layer of specifically adsorbed ions located at the interface, there is a *diffuse* layer of thickness λ_D^* existing just outside the interface in the aqueous phase where there is an imbalance of negative and positive ions which decreases gradually as one gets further from the interface. The following diagram attempts to illustrate what a diffuse aqueous layer might resemble in response to the application of a positive voltage V which produces layer of negative charge on the metallic side:



In the diagram, c_+ and c_- represent respectively the concentration of positively and negatively charged ions in the aqueous phase as a function of the distance z from the interface. For the moment we assume for simplicity that the solute is a fully-dissolved monovalent salt (e.g. NaCl) so that there is a single cation and single anion species of charge $+e$ and $-e$ respectively. In this case the net electric charge density ρ is proportional to the difference $c_+ - c_-$ of the cation and anion concentrations. In response to the layer of negative charge on the metallic side of the interface, there is attracted to the interface a surplus Δc of positive ions that act to “screen” or block this negative charge, and at distances $z \gg \lambda_D$ sufficiently far from the surface the concentrations approach their bulk value c_0 .

*Not to be confused with Gouy’s “largeur” symbol λ from section 3.

4.2 The Debye length

For mathematical convenience we restrict consideration to small applied voltages so that the maximum concentration difference Δc is much smaller than the bulk concentration c_o . In this case the thickness of the diffuse layer λ_D is equal to the “Debye length”[†], given by

$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2c_o F^2}} \quad (12)$$

where:

- ε is the permittivity of the aqueous medium. Attraction/repulsion between mobile charges is modified in dielectric materials (like water) so that the constant ε_o in the Coulomb force law $F = \frac{q_1 q_2}{4\pi\varepsilon_o r^2}$ is replaced by the permittivity ε characteristic of the medium. Therefore in mediums of high permittivity the force of attraction/repulsion between mobile charges is reduced.
- R is the universal gas constant.
- T is the absolute temperature of the aqueous medium.
- c_o is the bulk molar concentration of the salt.
- $F = eN_A$ is the Faraday constant[‡], where e is the unit of elementary charge and N_A is Avogadro’s number.

For solutions not merely consisting of a single monovalent salt we have the more general expression

$$\lambda_D = \sqrt{\frac{\varepsilon RT}{F^2 \sum_n c_n^o Z_n^2}} \quad (13)$$

where c_n^o is the bulk concentration of the n^{th} ionic species of valency Z_n .

Plugging in the values for the various constants for a monovalent salt dissolved in water at room temperature, we have

$$\lambda_D \approx \frac{3 \text{ \AA}}{\sqrt{c_o}} \quad (14)$$

where c_o is the salt concentration in units of mol L^{-1} . Before beginning a mathematical derivation of expression (12) for the Debye length, we take a qualitative look at this expression and analyze how the result is consistent with our picture unenacted earlier of a balance between the energetic force of electric attraction/repulsion and the entropic force of diffusion:

[†]Named after American physicist Peter Debye (1884-1966).

[‡]Named after English scientist Michael Faraday (1791-1867).

- A large value for the permittivity ε means a weaker attraction/repulsion between mobile charges. Ions are therefore less driven to concentrate themselves in regions of low electric potential energy, resulting in a broader Debye length.
- A larger temperature increases the entropic force which discourages large gradients in concentration, which also leads to a thicker diffuse layer.
- A larger concentration c_o of mobile charges improves the electrolyte's ability to screen the charge layer present on the metallic side of the interface, leading to a thinner diffuse layer.

Qualitatively we thus see that the dependence of the thickness λ_D of the diffuse layer on the different properties of the solution reflects this interplay between an electric driving force and a thermodynamic driving force acting respectively to shrink and expand the diffuse layer.

4.3 Gouy-Chapman theory

In this subsection we offer a mathematical derivation of the expression (12) for the Debye length. We continue for simplicity to assume that we are dealing with a monovalent salt. We begin with the expression for the electrochemical potentials $\mu_+(z)$ and $\mu_-(z)$ for the cationic and anionic species at a distance z from the interface:

$$\mu_{\pm}(z) = \mu_{\pm}^o + RT \ln c_{\pm}(z) \pm F\phi(z) \quad (15)$$

The first two terms comprise the “chemical” part of the electrochemical potential, while the third term, which depends on the electric potential $\phi(z)$ is the “electrical” part. Contrary to our approach in our derivation of the Lippmann equation (equation (9)), we explicitly take in account the dependence of the chemical potential on the local concentration $c_{\pm}(z)$ of particles via the second term, which is, strictly speaking, accurate only in the limit of low solute concentrations*. The first term is a simple constant, independent of z .

The electric potential $\phi(z)$ profile is not independent of the concentration profiles $c_{\pm}(z)$. By definition, the electric potential ϕ is related to the electric field \mathbf{E} via

$$\mathbf{E} = -\nabla\phi \quad (16)$$

We assume a flat interface[†], so that ϕ does not depend on the coordinates x and y , so that

$$E_x = E_y = 0 \quad (17)$$

$$E_z(z) = -\frac{d\phi}{dz}(z) \quad (18)$$

*See brief discussion in section 2.3 of the lecture 2 notes.

[†]Or, more precisely, we assume the interface's radius of curvature is much larger than the Debye length λ_D

Gauss' law in turn relates changes in electric field to the local electric charge density. In its differential form in “homogeneous media”, i.e. in materials of constant permittivity ε , it reads

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon} \quad (19)$$

where ρ is the charge density. This specializes for flat interfaces to

$$\frac{dE_z}{dz}(z) = \frac{\rho(z)}{\varepsilon} \quad (20)$$

The charge density $\rho(z)$ in the aqueous phase is determined by the ion concentrations $c_{\pm}(z)$. For monovalent salts we simply have

$$\rho(z) = F(c_+(z) - c_-(z)) \equiv F\Delta c(z) \quad (21)$$

so that, from the preceding equations we have

$$\frac{d^2\phi}{dz^2} = -\frac{F}{\varepsilon}\Delta c(z) \quad (22)$$

We now turn to the term $\ln c_{\pm}(z)$ appearing in equation (15). We define $\Delta c_{\pm}(z)$ so that $c_{\pm}(z) = c_o + \Delta c_{\pm}(z)$, where c_o is still the bulk salt concentration (i.e. $c_o = c_{\pm}(z \rightarrow \infty)$). Assuming $|\Delta c_{\pm}| \ll c_o$ and recalling $\ln(1+x) = x$ as $x \rightarrow 0$, we have

$$\begin{aligned} \ln c_{\pm}(z) &= \ln(c_o + \Delta c_{\pm}(z)) \\ &= \ln\left(c_o \left(1 + \frac{\Delta c_{\pm}(z)}{c_o}\right)\right) \\ &= \ln c_o + \ln\left(1 + \frac{\Delta c_{\pm}(z)}{c_o}\right) \\ &\approx \ln c_o + \frac{\Delta c_{\pm}(z)}{c_o} \end{aligned} \quad (23)$$

From here we take the difference $\mu_+(z) - \mu_-(z) \equiv \Delta\mu(z)$, obtaining (after some algebra)

$$\Delta\mu(z) = \mu_+^o - \mu_-^o + RT \frac{\Delta c(z)}{c_o} + 2F\phi(z) \quad (24)$$

Taking the second derivative of the previous equation yields

$$\frac{d^2}{dz^2}\Delta\mu(z) = \frac{RT}{c_o} \frac{d^2}{dz^2}\Delta c(z) + 2F \frac{d^2}{dz^2}\phi(z) \quad (25)$$

Which by equation (22) becomes

$$\frac{d^2}{dz^2}\Delta\mu(z) = \frac{RT}{c_o} \frac{d^2}{dz^2}\Delta c(z) - 2\frac{F^2}{\varepsilon}\Delta c(z) \quad (26)$$

Now in thermodynamic equilibrium the electrochemical potentials $\mu_{\pm}(z)$ of both species must be equal throughout, and must therefore be independent of z . This in turn implies that $\frac{d^2}{dz^2}\Delta\mu(z) = 0$, which upon plugging into equation (26) yields the *linearized Poisson-Boltzmann* equation[‡]

$$\frac{d^2}{dz^2}\Delta c(z) = \frac{2F^2c_o}{\varepsilon RT}\Delta c(z) = \lambda_D^{-2}\Delta c(z) \quad (27)$$

This differential equation has for solutions the linear combination

$$\Delta c(z) = \Delta c^+ e^{+\frac{z}{\lambda_D}} + \Delta c^- e^{-\frac{z}{\lambda_D}} \quad (28)$$

for arbitrary constants Δc^{\pm} . Our boundary condition $c_{\pm}(z) \rightarrow c_o$ as $z \rightarrow \infty$ however imposes the requirement $\Delta c^+ = 0$ so that we have finally for our solution

$$\Delta c(z) = \Delta c_o e^{-\frac{z}{\lambda_D}} \quad (29)$$

Where Δc_o is some constant representing the concentration difference at $z = 0$. Note also that from equation (22) we have for the electric potential

$$\frac{d^2\phi}{dz^2} \propto \Delta c \propto e^{-\frac{z}{\lambda_D}} \quad (30)$$

since the aqueous fluid is conductive the electric field $E_z \propto \frac{d\phi}{dz}$ must vanish at $z \rightarrow \infty$ where $\rho \rightarrow 0$. Since the potential is defined by equation (16) we are also free to fix the potential at a given point so we therefore choose $\phi \rightarrow 0$ as $z \rightarrow \infty$. The general solution for the electric potential in the aqueous medium consistent with equation (30) and the boundary conditions just enunciated is

$$\phi(z) = \Delta\phi e^{-\frac{z}{\lambda_D}} \quad (31)$$

where from equation (22) we have

$$\Delta\phi = -\frac{F\lambda_D^2\Delta c_o}{\varepsilon} \quad (32)$$

4.4 Capacitance of diffuse layer

Let us model the interface as a capacitor with a surface charge density σ and $-\sigma$ on the metallic and aqueous sides of the interface respectively. The surface

[‡]Named after French mathematician and physicist Siméon Denis Poisson (1781-1840) and Austrian physicist Ludwig Boltzmann (1844-1906).

charge density $\bar{\sigma} = -\sigma$ in the diffuse layer is given by

$$\begin{aligned}
\bar{\sigma} &= \int_0^\infty dz \rho(z) \\
(\text{eq. 21}) &= \int_0^\infty dz F \Delta c(z) \\
(\text{eq. 29}) &= F \Delta c_o \int_0^\infty dz e\left(-\frac{z}{\lambda_D}\right) \\
&= F \lambda_D \Delta c_o \\
(\text{eq. 32}) &= -\frac{\varepsilon \Delta \phi}{\lambda_D}
\end{aligned} \tag{33}$$

so that

$$\sigma = -\bar{\sigma} = \frac{\varepsilon}{\lambda_D} \Delta \phi \tag{34}$$

If we assume the charge on the metallic side of the interface is confined to a layer much thinner than the diffuse layer*, then the potential drop $V = \phi(z \rightarrow -\infty) - \phi(z \rightarrow +\infty)$ across the entire interface is approximately equal to the drop $-\Delta\phi$ going from $z = -\infty$ to $z = 0$. Taking $V = -\Delta\phi$, the differential capacitance c_A (equation (10)) of the interface is therefore

$$c_A = -\frac{d\sigma}{dV} = \frac{\varepsilon}{\lambda_D} \tag{35}$$

It is instructive to compare the above expression with that of the capacitance C of a parallel plate capacitor. In this case we have $C = \frac{\varepsilon A}{d}$ where

- A is the area of the plate electrodes,
- d is the separation between the plates, and
- ε is the permittivity of the dielectric filling the space between the plates.

Therefore we can conveniently interpret the diffuse layer as being effectively a parallel plate capacitor with plate separation λ_D .

Finally we are in a position to understand Gouy's observation of a decreasing largeur λ of his measured electrocapillary curves with increasing salt concentration (subsection 3). An increase in the salt concentration c_o decreases the Debye length λ_D which in turn increases the differential capacitance c_A which results in a decreased curve largeur λ .

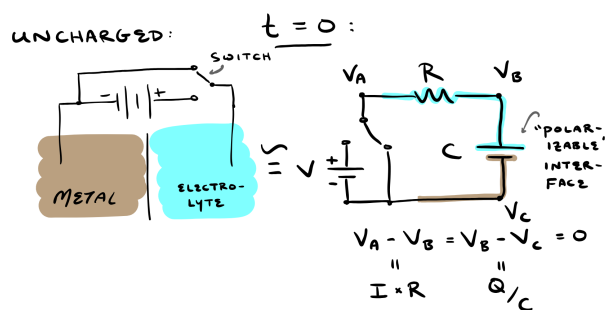
*This is a good assumption to the extent that the concentration of mobile charge carriers in metals (i.e. conduction electrons and holes) typically much higher than the carrier concentration in aqueous solution. In metals there is typically at least one conduction electron and one hole per atom, while an electrolyte solution that is, e.g., one molar in concentration will only have one anion or per 1000/18 \approx 50 water molecules. The Debye length of the diffuse layer of conduction electrons on the metallic side of the interface is therefore much shorter than that of the aqueous phase.

5 Polarizable vs. non-polarizable interfaces

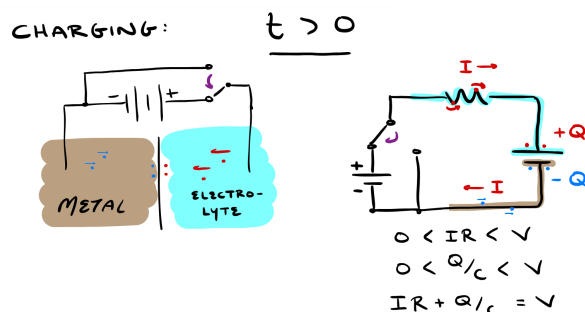
5.1 Polarizable interfaces

The mercury/electrolyte interface discussed at length so far in this lecture is an example of a *polarizable* interface. For polarizable interfaces there is no significant mechanism available for charge *transfer* across the interface. As a result, a change in the voltage applied across an interface is reflected in the potential difference across the interface. For nonpolarizable interfaces the situation is qualitatively different.

An analogy in terms of an electrical circuit is helpful. Take a polarizable interface, where we assume for simplicity that the surface charge density σ at the interface is zero when the applied voltage is zero, i.e. $V_{pzc} = 0$. We can then model the response of the interface to a change in applied potential by the following circuit analogy. If the applied voltage is zero, then in steady-state the interface is uncharged there is no flow of charge (i.e. no current) anywhere in the system:



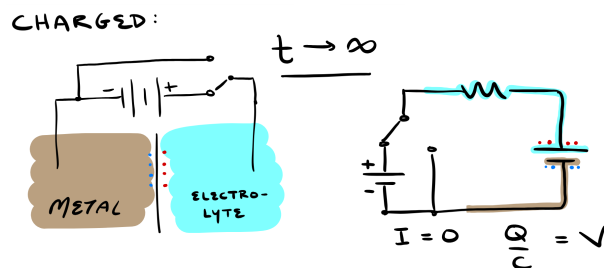
If we flip the switch, there is now an electromotive force pushing cations towards the interface on the aqueous side, which attracts electrons on the metallic side:



The symbol R here represents the resistance to flow of electric charge. Note that for a polarizable interface the effective resistance *across* the interface is *infinite*, since there is no mechanism for charge transfer. As time goes on, more

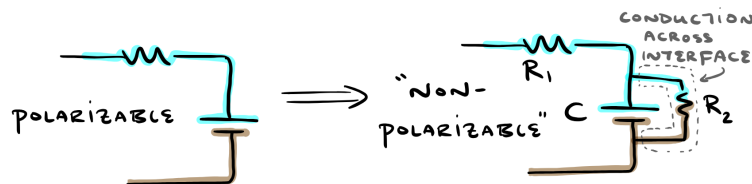
and more charge Q accumulates at the interface, which reduces the electromotive force $V - \frac{Q}{C}$ which drives the current $I = \left(V - \frac{Q}{C}\right) / R$ that charges the interface.

As $t \rightarrow \infty$, $\frac{Q}{C} \rightarrow V$ so that there is no more current I to further charge the interface:

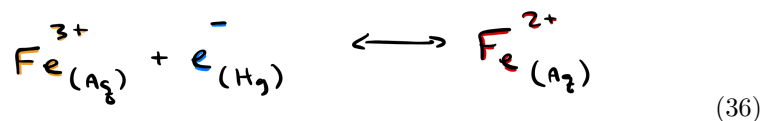


5.2 Non-polarizable interfaces

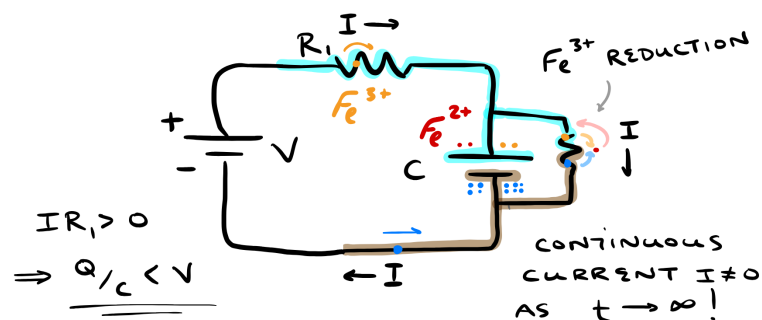
As you might have guessed, a *non-polarizable* interface is one where charge transfer is permitted by some mechanism. We now say that there is a finite electrical conductance across the interface, which in terms of our qualitative electrical circuit analogy implies some non-infinite resistance *across* the interface:



As an example, suppose we have in our aqueous solution the redox pair Fe_2^+ and Fe_3^+ , so that the following chemical reaction can take place at a water/mercury interface:



When this reaction proceeds from left to right, we end up with the net charge transfer of $-e$ from the mercury phase to the aqueous phase, and vice versa. Intuitively we expect that an increase in the applied potential $V = \phi_{Aq} - \phi_{Hg}$ will act to encourage the transfer of electrons from the mercury phase of lower electric potential to the aqueous phase of higher electric potential, i.e. the reaction in figure 36 should shift towards left-to-right. Indeed this is what our qualitative electrical circuit analogy suggests:

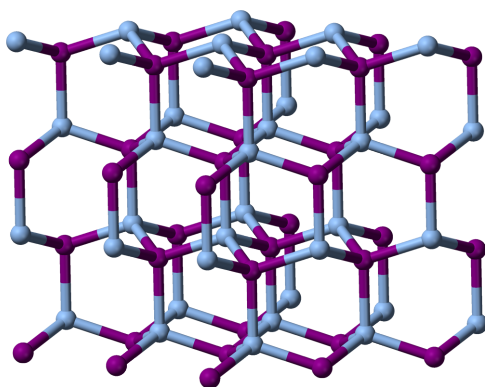


The above diagram illustrates the *non-polarizability* of an interface across which charge transfer is permitted. An applied voltage of V is not reflected in a voltage drop V across the interface, even as $t \rightarrow \infty$. There is a non-zero electromotive force $V - Q/C$ leading to a continuous current I across the interface which depends on the mobility of ions in solution (R_1) and the kinetics of the oxidation reaction (R_2). Of course if all of the Fe_3^+ in solution becomes oxidized, the oxidation reaction comes to a halt (i.e. $R_2 \rightarrow \infty$) and the interface becomes effectively polarizable.

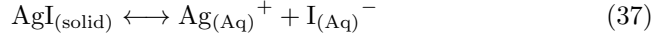
In the next section we analyze the non-polarizable interface in a more precise mathematical context, using the silver iodide (AgI) electrode as an example. We will make more clear the ideas discussed qualitatively in this subsection and in the process derive the Nernst equation relating electrode potentials to reactant concentrations.

6 The AgI electrode and the Nernst equation

Consider the silver iodide (AgI) crystal, which at room temperature takes the following wurtzite structure:



Silver iodide is partially soluble in water, so that the following reaction



is characterized by the solubility product

$$[\text{Ag}_{(\text{Aq})}^{+}][\text{I}_{(\text{Aq})}^{-}] \approx 10^{-16} \text{M}^2 \quad (38)$$

Since the simultaneous dissociation of silver cation and iodine anion produces no net charge transfer from the solid AgI electrode to the aqueous solution, this solubility product is independent of any voltage difference V between the two phases.

It is however also possible that only one of the ions, say Ag^{+} , dissolves into solution[†]:



This reaction of course does lead to a transfer of charge across the interface. As we have done many times already in this course, we analyse the conditions under which chemical equilibrium[‡] is established. This occurs when the electrochemical potentials of the Ag^{+} and I^{-} species are constant across the interface, i.e. when

$$\mu_{\text{Ag}^{+}}^{\text{solid}} = \mu_{\text{Ag}^{+}}^{\text{liquid}} \quad (40)$$

$$\mu_{\text{I}^{-}}^{\text{solid}} = \mu_{\text{I}^{-}}^{\text{liquid}} \quad (41)$$

Now in the solid we have

$$\mu_{\text{Ag}^{+}}^{\text{solid}} = \mu_{\text{Ag}^{+}}^{o,s} + F\phi^s \quad (42)$$

where

- ϕ^s is the electric potential in the solid AgI electrode, and
- $\mu_{\text{Ag}^{+}}^{o,s}$ is a constant independent of the potential.

Similarly, in the liquid phase we have

$$\mu_{\text{Ag}^{+}}^{\text{liquid}} = \mu_{\text{Ag}^{+}}^{o,l} + RT \ln[\text{Ag}^{+}] + F\phi^l \quad (43)$$

where $\mu_{\text{Ag}^{+}}^{o,l}$ and $F\phi^l$ are defined analogously, but in addition we have a term $RT \ln[\text{Ag}^{+}]$, valid at low ion concentrations, which depends on the concentration $[\text{Ag}^{+}]$ of Ag^{+} cations in solution[§].

[†]Iodine dissociation $\text{I}_{(\text{solid})}^{-} \longleftrightarrow \text{I}_{(\text{Aq})}^{-}$ of course being simply the combination of the other two reactions.

[‡]Or, rather, *electrochemical* equilibrium

[§]There is no analogous term in the solid phase because the Ag^{+} concentration in AgI, which is a crystalline solid, is fixed.

We will find it convenient to define a concentration $[\text{Ag}^+]_{\text{pzc}}$ with the following defining property:

$$\mu_{\text{Ag}^+}^{o,l} = \mu_{\text{Ag}^+}^{o,s} - RT \ln[\text{Ag}^+]_{\text{pzc}} \quad (44)$$

In this case we have

$$\mu_{\text{Ag}^+}^{\text{liquid}} - \mu_{\text{Ag}^+}^{\text{solid}} = RT \ln ([\text{Ag}^+]/[\text{Ag}^+]_{\text{pzc}}) - F\Delta\phi \quad (45)$$

where $\Delta\phi \equiv \phi^s - \phi^l$. From the equilibrium condition (40) for the Ag^+ cations we obtain

$$[\text{Ag}^+] = [\text{Ag}^+]_{\text{pzc}} e^{\frac{F\Delta\phi}{RT}} \quad (46)$$

The concentration $[\text{I}^-]$ of iodine anions is incidentally determined by inserting the above equation into the solubility product (equation 38) and solving for $[\text{I}^-]$.

Equation (46) is a specific case of what is known as the Nernst equation*, which in general describes the relationship between reaction quotients and oxidation potentials†. What does the equation tell us? Apparently the potential drop $\Delta\phi$ across the interface and the concentration $[\text{Ag}^+]$ of silver cations in solution are not independently variable. If for instance we apply a positive potential $\delta\phi > 0$ across the interface, then the electric potential will be lower in the liquid phase, attracting Ag^+ ions. Vice versa for $\Delta\phi = -\delta\phi < 0$. We therefore expect $[\text{Ag}^+](\delta\phi) > [\text{Ag}^+](-\delta\phi)$, and indeed from equation (46) we have

$$\frac{[\text{Ag}^+](+\delta\phi)}{[\text{Ag}^+](-\delta\phi)} = e^{+2\frac{F\delta\phi}{RT}} > 1 \quad (47)$$

for $\delta\phi > 0$. So the Nernst equation is in line with our intuitive expectations regarding the influence of electric potential on concentration of dissolved product.

Incidentally, what is our interpretation of $[\text{Ag}^+]_{\text{pzc}}$? Indeed at zero applied voltage ($\Delta\phi = 0$) we apparently have $[\text{Ag}^+] = [\text{Ag}^+]_{\text{pzc}}$, but from section 2 we know that, due of the phenomenon of specific adsorption‡, an applied voltage of zero does not necessarily imply zero surface charge. Nonetheless, in the simplified scenario considered here where the only participating charge carriers in both phases are the $[\text{Ag}^+]$ and $[\text{I}^-]$ ions, we can indeed identify the “point of zero charge” with the Ag^+ concentration at which $\Delta\phi = 0$.

Measurements indicate that $[\text{Ag}^+]_{\text{pzc}} \approx 10^{-5.5}\text{M}$, so that, for AgI in pure water where $[\text{Ag}^+] = [\text{I}^-] \approx \sqrt{10^{-16}\text{M}^2} = 10^{-8}\text{M}$ we have

$$\Delta\phi = \frac{RT}{F} \ln(10^{-8}/10^{-5.5}) \approx -140 \text{ meV} \quad (48)$$

at $T = 300 \text{ K}$. The AgI surface will thus be negatively charged, suggesting that I^- ions dissolve into solution less easily than Ag^+ ions.

*Named after German physicist Walter Nernst (1864-1941)

†The curious are referred the supplementary “Electrochemistry Primer” document for more info.

‡As well that of *surface dipoles*, which we do not discuss.

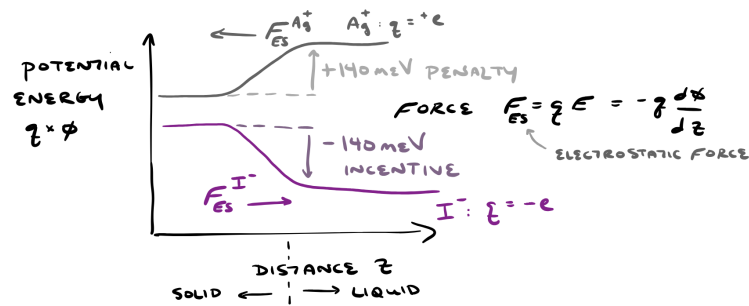
What is mathematically expressed by the Nernst equation is a reflection of the following qualitative description of electrochemical equilibrium at the non-polarizable interface:

- An interfacial potential difference $\Delta\phi$ acts an incentive or penalty to dissociation or adsorption, depending on the sign of $\Delta\phi$ and the sign of the charged particle adsorbing or desorbing from the interface.
 - An interfacial potential difference $\Delta\phi \equiv \phi^s - \phi^l > 0$ will for example enhance (inhibit) dissociation of positively (negatively) charged ions, and vice versa for $\Delta\phi < 0$.
- The rate of adsorption of an ionic species increases with increasing concentration of that species in solution[§].
- At equilibrium, the rate of adsorption of each ionic species onto the interface is exactly balanced by the corresponding rate of dissociation.
- Therefore, if an ion appears at sufficiently high concentrations*, then its rate of adsorption exceeds its rate of dissociation. This net in-flow of charged particles will alter the interfacial potential difference so that dissociation is enhanced and adsorption is inhibited. This occurs until the adsorption and desorption rates are equalized, thus establishing equilibrium.
- Similarly, if the voltage $\Delta\phi$ applied across the interfacial is sufficiently high, then the rate of I^- dissociation will exceed that of I^- adsorption. The concentration of I^- ions in solution will therefore increase until the rate of adsorption matches the rate of dissociation. The effect will be exactly the opposite for the Ag^+ cations.

The following diagram qualitatively illustrates the influence of the interfacial potential $\Delta\phi = -140 \text{ meV}$ on adsorption/desorption:

[§]This can be understood as a simple consequence of statistics: the more ions of a given species there are in solution, the more frequently that ions of that species will strike the interface, thus the greater chance that an ion adsorbs onto the interface over a given interval in time.

*The astute reader may object that, for concentrations $[\text{Ag}^+]$ or $[\text{I}^-]$ not equal to the square root of the solubility product, we will have a non-zero charge density in the bulk of the aqueous phase due to an imbalance between Ag^+ and I^- ions. This is indeed true if these are only ions present in solution. In practice the ion concentrations are manipulated by addition of salts (e.g. AgNO_3). See the example problem at the end of the section.



Question:

When AgI particles are added to pure water, preferential dissociation of Ag^+ cations over I^- anions leads to a negative spontaneous charging of the AgI / aqueous interface, as discussed. Up to what concentration we would need to add AgNO_3 salt to our solution in order to reach a point where the AgI / aqueous interface is uncharged?

Answer:

AgNO_3 dissociates readily in water, so by adding this salt to our solution up to a concentration of $10^{-5.5}\text{M}$ we increase the concentration of Ag^+ ions from 10^{-8}M to $10^{-5.5}\text{M} \approx [\text{Ag}^+]_{\text{pzc}}$ so that the AgI particle surfaces become uncharged. Even though the concentration of Ag^+ cations now greatly outweighs that of I^- anions ($[\text{I}^-] \approx 10^{-16}\text{M}^2 / 10^{-5.5}\text{M} = 10^{-10.5}\text{M}$), the bulk of the solution is still electrically neutral thanks to the NO_3^- counterions.