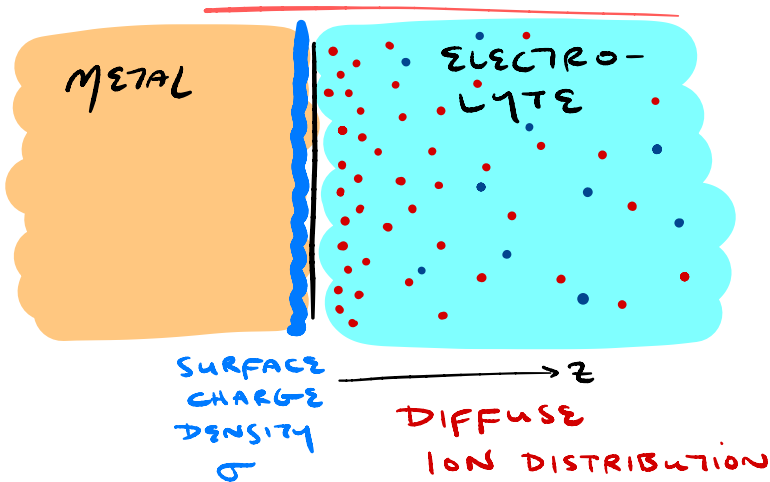- ## LECTURE 3 - PT. II

  - Gouy - Chapman Theory of Diffuse Layer, Poisson - Boltzmann Equation, Reversible Electrodes & the Nernst Eqn.

• DIFFUSE ELECTRIC DOUBLE LAYER & DEBYE SCREENING

METAL

ELECTRO-LYTE

SURFACE CHARGE DENSITY σ

z

DIFFUSE ION DISTRIBUTION

- CAN WE SAY MORE ABOUT THE CHARGED INTERFACE, I.E. "ELECTRIC DOUBLE LAYER" INTRODUCED IN THE PREVIOUS SECTION?

- E.G. CAN WE PREDICT THE CAPACITANCE $c = a\dfrac{d^2 \gamma}{d\Delta V^2}$ OF THE DOUBLE LAYER FROM THE PHYSICAL PROPERTIES OF THE ELECTROLYTE?

- DISTRIBUTION OF IONIC SPECIES NEAR THE INTERFACE CAN BE MODELLED AS AN INTERPLAY BETWEEN TWO EFFECTS:

- ATTRACTION / REPULSION TO / FROM THE CHARGE @ THE INTERFACE.

- DIFFUSION FROM REGIONS OF HIGH CONCENTRATION TO REGIONS OF LOW ".

- FORMALLY THIS INTERPLAY IS CAPTURED BY THE REQUIREMENT OF CONSTANT ELECTROCHEMICAL POTENTIAL AT ALL DISTANCES FROM THE SURFACE.

- CONSIDER AN ELECTROLYTE CONTAINING A SINGLE MONOVALENT SALT :

DIFFUSION   ATTRACTION/REPULSION

$$\pm \text{ ION}: \quad \mu_{\pm}(z) = \mu^{o}_{\pm} + RT \ln c_{\pm}(z) \pm F\phi(z)$$

CONCENTRATION   ELECTRIC POTENTIAL

- FOR FLAT INTERFACE, THE DIFF. FORM OF GAUSS' LAW GIVES :

$$\varepsilon_r \varepsilon_0 \frac{d}{dz} E(z) = \rho(z) = Fc_+(z) - Fc_-(z) = F\left[c_+(z) - c_-(z)\right]$$

- FROM $\vec{E} = -\vec{\nabla}\phi$ WE THUS HAVE :

$$-\varepsilon_r \varepsilon_0 \frac{d^2}{dz^2}\phi(z) = F\left[c_+(z) - c_-(z)\right]$$

- IF WE ASSUME ONLY WEAKLY CHARGED INTERFACES, THEN:

  - $\ln c_\pm = \ln \left(c_0 + \Delta c_\pm (z) \right)$

    $= \ln \left[c_0 \left[1 + \dfrac{\Delta c_\pm (z)}{c_0} \right] \right]$

    $\simeq \ln c_0 + \dfrac{\Delta c_\pm (z)}{c_0}$

SO: $\mu_\pm (z) = \mu_\pm^0 + RT \left[\ln c_0 + \dfrac{\Delta c_\pm (z)}{c_0} \right]$

$$\pm F \phi (z)$$

THEN: $\dfrac{d^2}{dz^2} \mu_\pm (z) = 0$ $\leftarrow$ $\left[\begin{array}{l} \mu_\pm (z) \text{ MUST BE} \\ \underline{\text{CONSTANT}} \text{ w) } z \\ @ \text{ EQUILIBRIUM} \end{array} \right]$

$= \dfrac{RT}{c_0} \dfrac{d^2}{dz^2} \Delta c_\pm \pm F \dfrac{d^2 \phi}{dz^2}$

$= \dfrac{RT}{c_0} \Delta c_\pm'' \mp \dfrac{F^2}{\varepsilon_r \varepsilon_0} \left[\underbrace{\Delta c_+ - \Delta c_-}_{\equiv \Delta c} \right]$

THEN $\mu_+'' - \mu_-'' = 0 - 0 = 0$

$= \dfrac{RT}{c_0} \Delta c'' - \dfrac{2F^2}{\varepsilon_0 \varepsilon_r} \Delta c$

$\implies \Delta c'' = \dfrac{2F^2 c_0}{\varepsilon_0 \varepsilon_r RT} \Delta c$ "POISSON–BOLTZMANN EQUATION"

$$\implies \left[\Delta C = \Delta C_0 \exp\left(-z/\lambda_D \right) \right] \quad \text{* FOR } \Delta C_0 \ll C_0$$

$$\text{WHERE } \lambda_D = \left[\frac{\varepsilon_r \varepsilon_0 RT}{2 F^2 C_0} \right]^{1/2}$$

"DEBYE LENGTH" E.G. $\lambda_D^{H_2O} = \dfrac{3.0 \, \mathring{A}}{[C_0]^{1/2}}$

$\Delta C_0 = \Delta C (z = 0)$ $\hookleftarrow$ IN MOLAR

- FOR A GENERAL ELECTROLYTE WE

HAVE : $\lambda_D^{*} = \left[\dfrac{\varepsilon_r \varepsilon_0 RT}{2 F^2 \sum\limits_i^N z_i c_i^0} \right]^{1/2}$

- i.e. N SALTS W/ VALENCIES z_i AND BULK CONCENTRATIONS c_i^0.

- BALANCE SHEET $\left[\ll \text{BILAN} \gg \right]$:

  - TEMPERATURE T :
    - ENCOURAGES DIFFUSION
    - INCREASES λ_D

  - C_0
    - MORE CHARGE CARRIERS
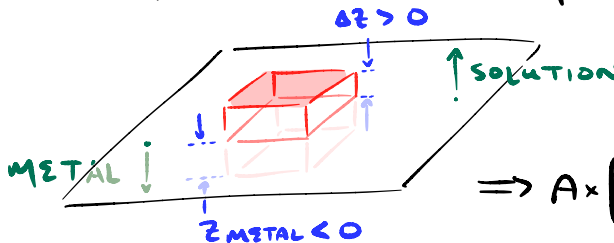   - DECREASES λ_D

  - ε_r ~ POLARIZABILITY
    - DECREASES ELECTROSTATIC INTERACTION $\rightarrow$ INCREASES λ_D

- # CAPACITANCE OF DIFFUSE DOUBLE LAYER

  - IF WE HAVE A SURFACE CHARGE σ @ THE INTERFACE $\left(\text{I.E. } z = 0\right)$, THEN AGAIN FROM GAUSS' LAW @ ASSUMING $|E| = 0$ IN THE METAL, WE HAVE:

$$\oint \vec{E} \cdot d\vec{A} = \frac{Q_{ENC}}{\varepsilon_r \varepsilon_0}$$

$$\Rightarrow A \times \left[E(z_{METAL}) + E(\Delta z > 0) \right]$$

$$= \frac{A}{\varepsilon_r \varepsilon_0} \times \left[\sigma + \int_{z_{METAL}}^{0} dz \, \rho(z) \,^{[\rho_{IN \, METAL}]} + \int_{0}^{\Delta z} dz \, \rho(z) \right]$$

BUT $\lim\limits_{\Delta z \to 0} \int_{0}^{\Delta z} \rho(z) \, dz = 0$, SO: $E(z=0) = \frac{\sigma}{\varepsilon_r \varepsilon_0}$

BUT $E(z=0) = -\phi'(z=0)$

$$= +\frac{\Delta \phi}{\lambda_D} ^{*} \Longrightarrow \boxed{\frac{c}{a} = \frac{\sigma}{\Delta \phi} = \frac{\varepsilon_r \varepsilon_0}{\lambda_D}} ^{*}$$

  - DIFFUSE LAYER IS LIKE A PARALLEL PLATE CAPACITOR W/ DIELECTRIC ε_r @ PLATE SEPARATION λ_D !

* SINCE $\phi \propto \Delta c'' \propto \Delta c$, $\phi \propto e^{-z/\lambda_D}$

* FOR $\Delta C_0 \ll C_0$

- SO WE SEE WHY Gouy OBSERVED A DECREASING "LONGEUR" / INCREASING CAPACITANCE W7 INCREASING ION CONCENTRATION:
  - INCREASING C_0 INCREASES CONDUCTIVITY OF SOLUTION, WHICH INCREASES ITS "SCREENING" ABILITY, WHICH REDUCES THE THICKNESS λ_D OF THE DIFFUSE LAYER, THUS INCREASING THE DOUBLE LAYER CAPACITANCE.

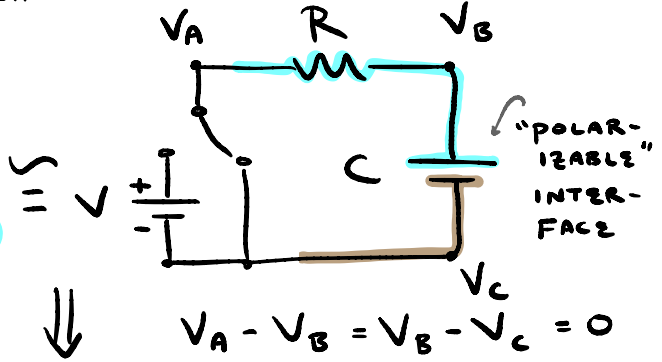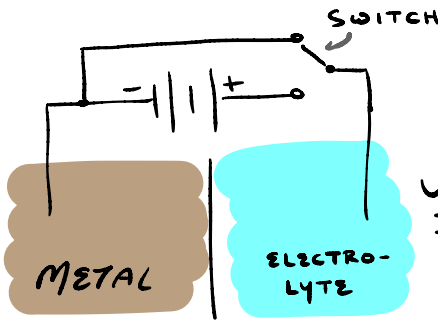- # $Ag\,I$ / AQUEOUS INTERFACE : REVERSIBLE ELECTRODE

- IN THE MERCURY / ELECTROLYTE SYSTEMS CONSIDERED SO FAR, WE NEGLECTED THE POSSIBILITY OF CHARGE TRANSFER ACROSS THE INTERFACE, ADMITTING ONLY THE POSSIBILITY OF CHARGING (I.E. "POLARIZATION") OF THE INTERFACE:
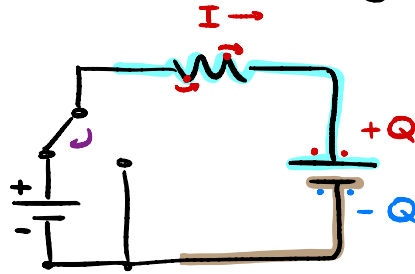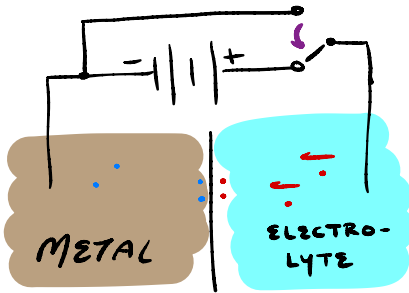
• CHARGING of POLARIZABLE INTERFACE:

[SIMPLIFIED PICTURE WHERE $\Delta V_{PZC} = 0$]

UNCHARGED: $t = 0$:

SWITCH

V_A R V_B

"POLAR- IZABLE" INTER- FACE

C

V_C

$V_A - V_B = V_B - V_C = 0$

CHARGING: $t > 0$

    "$I \cdot R$"   "Q/C"
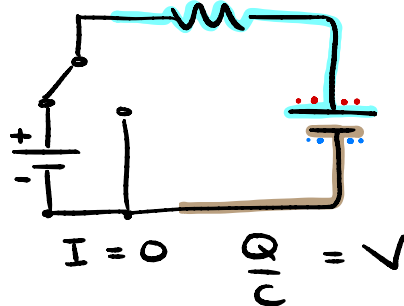

$I \rightarrow$

$+Q$

$-Q$

$0 < IR < V$

$0 < Q/C < V$

$IR + Q/C = V$

CHARGED: $t \rightarrow \infty$

$I = 0$ $\dfrac{Q}{C} = V$
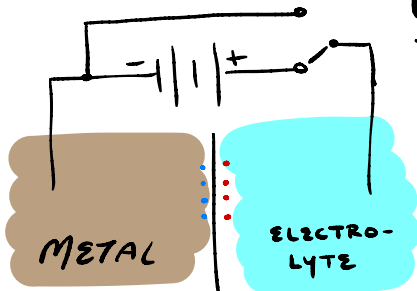
- To SUMMARIZE THE DIAGRAM ABOVE:

  - ON APPLICATION OF AN ELECTRIC POTENTIAL, CHARGE ACCUMULATES AT A POLAR-IZABLE INTERFACE @ A RATE DETERMINED BY THE CONDUC-TIVITY OF THE ELECTROLYTE UNTIL $Q = CV$.

- IF HOWEVER CHARGE TRANSFER ACROSS THE INTERFACE BECOMES POSSIBLE, WE MUST ACCOUNT IN A SENSE FOR THE FINITE CONDUCTIVITY ACROSS THE INTER-FACE:

POLARIZABLE

"NON-POLARIZABLE"

R_1 C R_2

CONDUCTION ACROSS INTERFACE
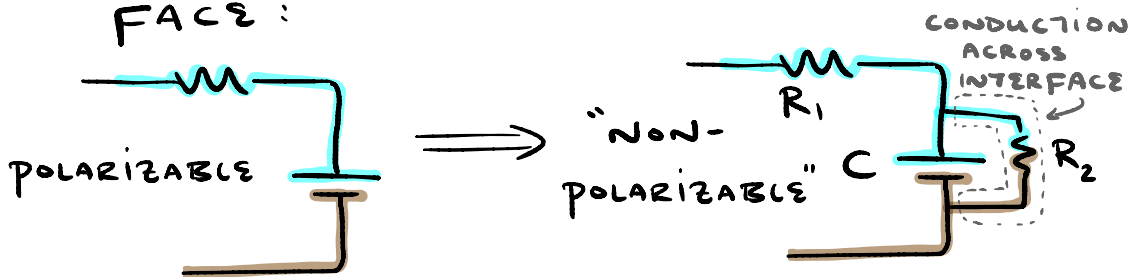
- IF, FOR EXAMPLE, THE AQUEOUS SOLUTION CONTAINED A REDOX PAIR, I.E. Fe^{2+} & Fe^{3+}, THE FOLLOWING REACTION BECOMES POSSIBLE:

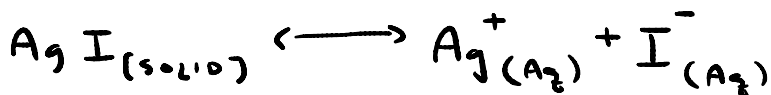$$Fe^{3+}_{(Aq)} + e^{-}_{(Hg)} \longleftrightarrow Fe^{2+}_{(Aq)}$$
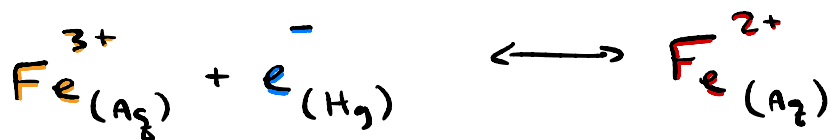
- WE NOW HAVE A MECHANISM FOR ELECTRONS TO HOP BACK & FORTH ACROSS THE INTERFACE, SO THAT THE MERCURY / AQUEOUS INTERFACE IS NO LONGER COMPLETELY POLARIZABLE:

$IR_1 > 0$

$\Rightarrow \underline{Q/_C < V}$
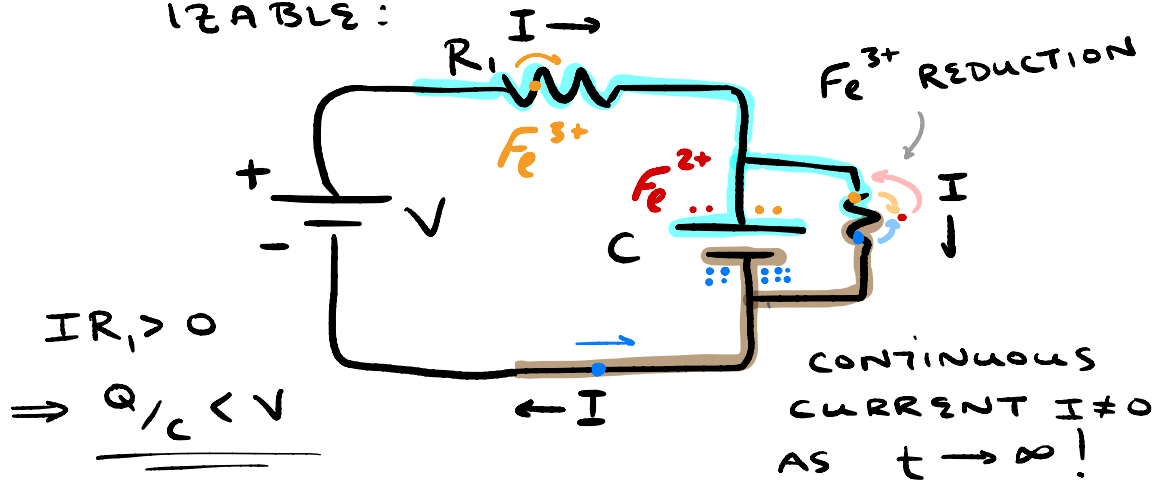
- ANOTHER EXAMPLE OF A NON-POLARIZABLE INTERFACE IS THE SILVER IODIDE (AgI) ELECTRODE IN AQUEOUS SOLUTION.

. AgI IS PARTIALLY SOLUBLE IN WATER:

$$Ag I_{(SOLID)} \longrightarrow Ag^+_{(Aq)} + I^-_{(Aq)}$$

⤳ A SOLUBILITY PRODUCT:

$$\left[Ag^+_{(Aq)} \right]\left[I^-_{(Aq)} \right] \simeq 10^{-16} MOLAR^2$$

- SINCE THIS REACTION INVOLVES NO NET CHARGE TRANSFER, THIS SOL. PRODUCT IS INDEPENDENT OF THE ELECTRIC POTENTIAL ACROSS THE INTERFACE.

- HOWEVER, IT IS ALSO POSSIBLE THAT A SILVER ATOM DISSOLVES BY ITSELF:
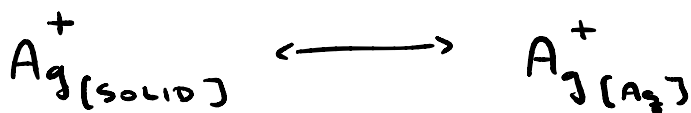
$$Ag^+_{(SOLID)} \longrightarrow Ag^+_{(Aq)}$$

- EQUILIBRIUM IS ACHIEVED WHEN THE CHEMICAL POTENTIALS OF THE IONS IN THE SOLID ARE EQUAL TO THOSE OF THE IONS IN SOLUTION:

$$\mu_{A_g^+}^{SOLID} = \mu_{A_g^+}^{Liquid} \quad , \quad \mu_{I^-}^{SOLID} = \mu_{I^-}^{LIQUID}$$

- ION TRANSFER ACROSS THE SOLID / LIQUID INTERFACE WILL OCCUR UNTIL THE ABOVE CONDITIONS ARE MET.

- IN THE SOLID WE HAVE:

$$\mu_{A_g^+}^{SOLID} = \mu_{A_g^+}^{o,s} + F\phi^s \quad , \quad \underbrace{\qquad}_{\substack{ELECTRIC\ POT.\\ IN\ SOLID.}}$$

- AND IN THE LIQUID, FOR DILUTE SOLUTIONS:

$$\mu_{A_g^+}^{LIQUID} = \mu_{A_g^+}^{o,L} + RT \ln [A_g^+] + F\phi^L \underset{\substack{CONCENTRATION\\ IN\ SOLUTION}}{\overset{}{\nwarrow}} \quad \substack{ELEC.\ POT.\\ IN\ LIQUID}$$

- WE DEFINE A CONCENTRATION $[A_g^+]_{PZC}$:

$$\mu_{A_g^+}^{o,L} = \mu_{A_g^+}^{o,s} - RT \ln [A_g^+]_{PZC}$$

- THEN:

$$\mu_{Ag^+}^{LIQUID} - \mu_{Ag^+}^{SOLID} = RT \ln \frac{[Ag^+]}{[Ag^+]_{PZC}} - F \underbrace{\left(\phi^S - \phi^L \right)}_{\overset{|||}{\Delta\phi}}$$

$$\implies \mu_{Ag^+}^{LIQUID} = \mu_{Ag^+}^{SOLID}$$

$$\boxed{[Ag^+] = [Ag^+]_{PZC} \, e^{\frac{F\Delta\phi}{RT}}}$$

🇩🇪 "NERNST EQUATION"

- SO Ag^+ CONCENTRATION IS DETERMINED BY POTENTIAL DROP ACROSS INTERFACE.

- IS IT REASONABLE?

  - IF, E.G. $\Delta\phi > 0 \implies \phi_S > \phi_L$, SO Ag^+ IONS WILL BE REPELLED BY POSITIVELY CHARGED ELECTRODE CONNECTED TO SOLID AND ATTRACTED TO NEGATIVELY CHARGED ELECTRODE CONNECTED TO LIQUID. VICE VERSA FOR $\Delta\phi < 0$.

$$\implies \text{WE EXPECT } [Ag^+](+\phi) > [Ag^+](-\phi) \quad \begin{array}{c} \text{FOR ANY} \\ \phi > 0 \end{array}$$

- BUT $[Ag^+](+\phi) \big/ [Ag^+](-\phi) = \exp\left[\frac{+2F\phi}{RT} \right] > 0$ ✅

- THE EQUILIBRIUM I^- CONCENTRATION IS INCIDENTALLY DETERMINED BY $\left(A_g^+\right)$ VIA THE SOLUBILITY PRODUCT:

$$\left[I^-\right] = \frac{10^{-16} \text{ MOLAR}}{\left[A_g^+\right] \text{ IN MOLAR}}$$

- @ $\phi_S = \phi_L$ WE HAVE $\left[A_g^+\right] = \left[A_g^+\right]_{PZC}$

  BUT ALSO: $\sigma = \frac{C}{A} \Delta\phi = 0$,

  SO THAT THE $\underset{\text{INTERFACE CAPACITANCE}}{}$ $\underset{\text{INTERFACIAL AREA}}{}$

  NAME WE GAVE OUR CONSTANT $\left[A_g^+\right]_{PZC}$ IS WELL-DESERVED.

- MEASUREMENTS REVEAL THAT $\left[A_g^+\right]_{PZC} \simeq 10^{-5.5} m$

  SO THAT, FOR AgI IN PURE WATER,

  WHERE $\left[A_g^+\right] = \left[I^-\right] \simeq \left[10^{-16}\right]^{\frac{1}{2}} m = 10^{-8} m$, WE HAVE:

  $$\Delta\phi = \frac{RT}{F} \ln\left[\frac{10^{-8}}{10^{-5.5}}\right] \simeq -140 m_e V \overset{@ \ 300K = T}{,} \text{ SO THAT}$$

  THE AgI SURFACE SPONTANEOUSLY ACQUIRES A NEGATIVE CHARGE, SUGGESTING A PREFERRED AFFINITY FOR BINDING I^- IONS.

- THE NERNST EQUATION REVEALS THE NON-POLARIZABILITY OF THE AgI INTERFACE: I.E. $[Ag^+]$ & $\Delta\phi$ CAN NOT BE VARIED INDEPENDENTLY.

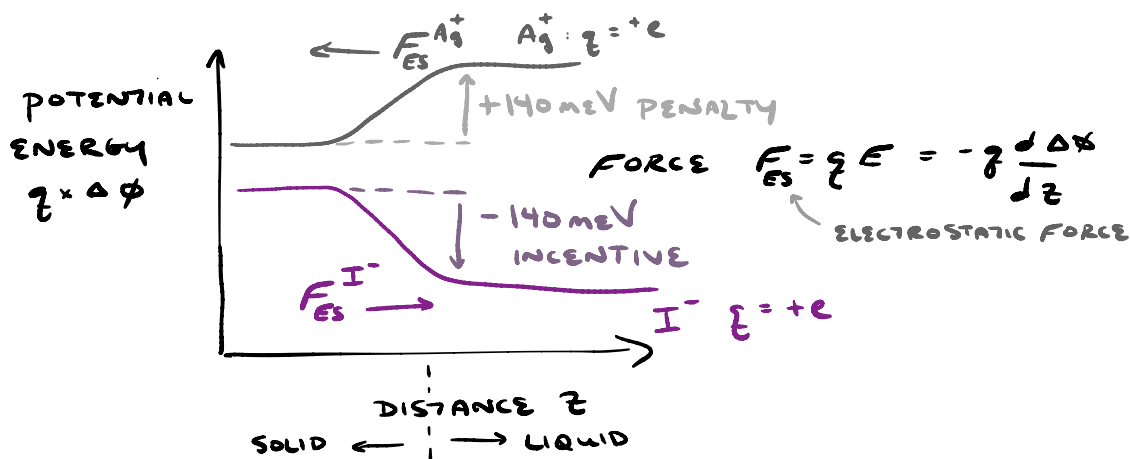 - IF FOR INSTANCE WE PLACE AgI IN PURE WATER, THEN, AS WE JUST ARGUED, THE SOLUTION WILL ACQUIRE A BULK CONCENTRATION $[Ag^+] \simeq 10^{-8}m$ AND THE INTERFACE WILL ACQUIRE A SPONTANEOUS POLARIZATION $\Delta\phi \simeq -140mV$ @ EQUILIBRIUM.

- THIS 140mV DROP IN POTENTIAL GOING FROM LIQUID TO SOLID CAN BE THOUGHT OF AS A 140meV ELECTROSTATIC ENERGY PENALTY & INCENTIVE FOR DISSOCIATION OF Ag^+ & I^- IONS, RESPECTIVELY.

- THIS PENALTY & INCENTIVE ARE REQUIRED TO COMPENSATE THE PREFERENTIAL DISSOCIATION OF SILVER & EQUALIZE THE FORWARD & BACKWARD RXN RATES, ESTABLISHING EQUILIBRIUM.

POTENTIAL ENERGY $z \times \Delta \phi$

$\leftarrow F_{ES}^{Ag^+}$ $\quad Ag^+ : z = {}^+e$

$\uparrow$ +140 meV PENALTY

$\downarrow$ −140 meV INCENTIVE

$F_{ES}^{I^-} \rightarrow$

$I^- \quad z = +e$

FORCE $F_{ES} = z \, \mathcal{E} = -z \dfrac{d \Delta \phi}{dz}$

$\curvearrowleft$ ELECTROSTATIC FORCE

DISTANCE z

SOLID $\leftarrow$ ⋮ $\longrightarrow$ LIQUID

- IF WE THEN TRY TO FURTHER POLARIZE THE INTERFACE BY APPLYING A POSITIVE EXTERNAL POTENTIAL BETWEEN THE SOLID & SOLUTION, THEN:

  - I^- DISSOCIATION IS $\overset{\text{NOW}}{\wedge}$ OVERLY INCENTIVIZED.

  - Ag^+ DISS. IS $\overset{\text{NOW}}{\wedge}$ OVERLY DISCOURAGED.

- THEREFORE:
    - I^- DISSOCIATION WILL PROCEED MORE RAPIDLY THAN THE REVERSE REACTION OF ADSORPTION OF I^- IONS ONTO THE AgI SURFACE.
    - VICE VERSA FOR Ag^+ IONS
    - THEREFORE, W/ TIME:
        - $[I^-]$ INCREASES, WHICH INCREASES THE RATE OF I^- ADSORPTION BACK ONTO AgI
        - VICE VERSA FOR Ag^+.
    - EVENTUALLY THE INCREASE/DECREASE IN I^-/Ag^+ CONCENTRATION WILL BE ENOUGH FOR THE FORWARD & BACKWARDS REACTION RATES TO EQUALIZE, ESTABLISHING A NEW EQUILIBRIUM.
    - THE Ag^+ CONCENTRATION @ WHICH THE OCCURS IS GOVERNED BY THE NERNST EQUATION.

LECTURE 3 summary:

- SURFACE TENSION @ METAL/AQUEOUS INTERFACE IS INFLUENCED BY AN APPLIED POTENTIAL:

    - LIPPMANN EQUATION:

    $$\frac{d\gamma}{d\Delta V} = \sigma \quad : \quad \Delta V = V_{LIQ} - V_{SOL}$$

    σ : SURF. CHARGE DENS. @ SOLID SIDE OF INTERFACE

    - INTERFACE CAPACITANCE

    $$\frac{d^2\gamma}{d\Delta V^2} = C_A$$

    C_A : DIFF. CAP. PER UNIT SURF. AREA

- "SPECIFIC ADSORPTION" & SPONTANEOUS CHARGING OF SURFACE:

    - $$\frac{d\gamma}{d\Delta V}(\Delta V_{PZC}) = 0$$

- CAPACITANCE OF DOUBLE LAYER DEPENDS ON SOLUTE CONCENTRATION

- CAPAC. VS. CONCEN. EXPLAINED BY
  GOUY - CHAPMAN THEORY
  - FOR $\Delta c \ll c_o$: $-z/\lambda_D$ ← DEBYE LENGTH
    $$\Delta c(z) = \Delta c_o \, e$$
    $$\Delta\phi = \Delta\phi_o \, e^{-z/\lambda_D}$$
  - $C_A = \varepsilon_r \varepsilon_o / \lambda_D$
  - $\lambda_D \propto 1/\sqrt{c_o}$

- POLARIZABLE VS. NON-POLARIZABLE
  INTERFACES.
  - AgI, CHEM. EQUIL. ↔ THE
    NERNST EQUATION :
    $$\Delta\phi = RT \ln \frac{[A_g^+]}{[A_g^+]_{pzc}}$$
    $$\Delta\phi : \phi^{SOLID} - \phi^{LIQUID}$$