LECTURE 3 –

CHARGED INTERFACES

- RESOURCES:

  - PHYS. & CHEM. OF I.F. [BUTT ET AL.] CHAPTER 4 ← 3RD EDITION (2013)

- CHARGED MERCURY/WATER INTERFACE & THE LIPPMANN EQUATION

RELATIONS ENTRE LES PHÉNOMÈNES ÉLECTRIQUES ET CAPILLAIRES;

PAR M. GABRIEL LIPPMANN,
Ancien élève de l'École Normale supérieure.

ANN. CHIM. PHYS. 5e t. $\overline{V}$ 1875, p. 494

- L'étude des forces électromotrices de contact a fourni jusqu'à présent un chapitre entièrement distinct de l'étude du phénomène capillaire ...

- On eût sans doute pensé à rapprocher l'une de l'autre ces deux propriétés physiques des surfaces de contact, la force électromotrice et la tension superficielle, et à chercher une relation constante entre elles, ...

- To STUDY THE RELATIONSHIP BETWEEN ELECTRICITY & SURFACE TENSION, FRENCH SCIENTIST[*] GABRIEL LIPPMANN (1845-1921) USED THE FOLLOWING APPARATUS:
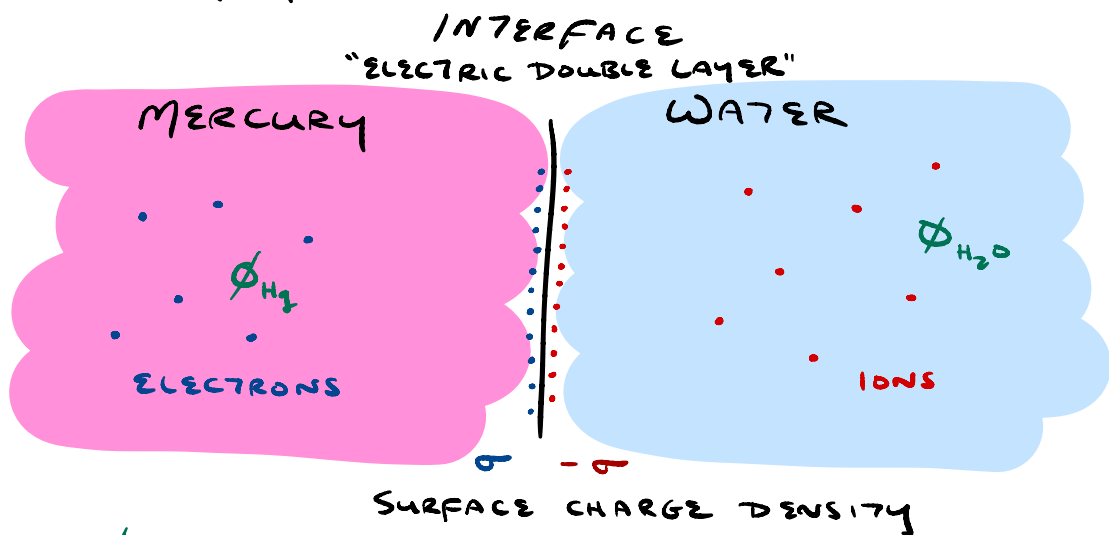
Fig. 1.
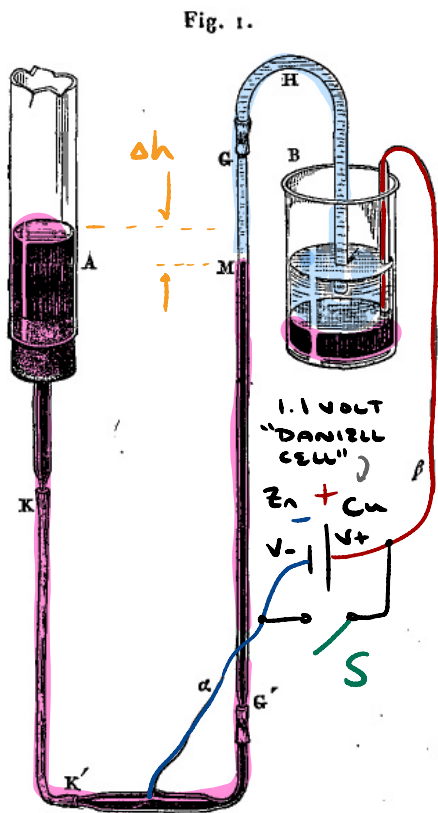
● LIQUID MERCURY

● DILUTE ACID

- W/ THE SWITCH S CLOSED, THE CAPILLARY FALL IS $\Delta h = 14.0$ mm

- QUIZ: IF THE RADIUS OF THE CAPILLARY IS $R = 0.32$ mm, THEN WHAT IS THE IMPLIED SURFACE TENSION @ THE MERCURY/WATER INTERFACE?[*]

- WHEN LIPPMANN OPENS THE SWITCH S, THE MENISCUS IS OBSERVED TO FALL ANOTHER 4.9 mm TO $\Delta h = 18.9$ mm!

[*] THE SLIGHTLY ACIDIC AQUEOUS SOLUTION ENSURES A CONTACT ANGLE $\theta = 0°$

- A $\approx 1V$ POTENTIAL APPLIED BETWEEN THE TWO VOLUMES OF MERCURY ARE ENOUGH TO CREATE A 35% INCREASE IN THE SURFACE TENSION!

- THERMODYNAMIC ANALYSIS :

INTERFACE
"ELECTRIC DOUBLE LAYER"

MERCURY   WATER

ϕ_{Hg} ϕ_{H_2O}

ELECTRONS   IONS

σ $-\sigma$

SURFACE CHARGE DENSITY

ϕ : ELETRIC POTENTIAL

- WE START W/ THE GIBBS ISO-THERM :

$$d\gamma = -\Gamma_{ION}\, d\mu^s_{ION} - \Gamma_{ELEC}\, d\mu^s_{ELEC}$$

- IN EQUILIBRIUM, THE CHEMICAL POT. μ^s OF THE ELECTRONS AND IONS @ THE INTERFACE ARE EQUAL TO THE CORRES-

PONDING CHEM. POTS μ^{BULK} OF THE BULK
PHASES.

- BECAUSE WE DEAL NOW W/ CHARGED
PARTICLES, WE MUST INCLUDE THE
ELECTRIC POTENTIAL ϕ IN THE CHEMICAL
POTENTIAL:

$$\left[F = eN_A = 9.6 \, C/_{mol} \right]$$
"FARADAY CONSTANT"

$$\mu^{BULK}_{ELEC} = \mu^{0}_{ELEC} - F\phi_{Hg}$$

$$\mu^{BULK}_{ION} = \mu^{0}_{ION} + Fz\,\phi_{H_2O}$$

ION CHARGE

- IF WE CONSIDER ONLY CHANGES DUE
TO THE APPLIED VOLTAGE $V_+ - V_-$, THEN
WE CAN IGNORE μ^{0}_{ELEC} & μ^{0}_{ION}:

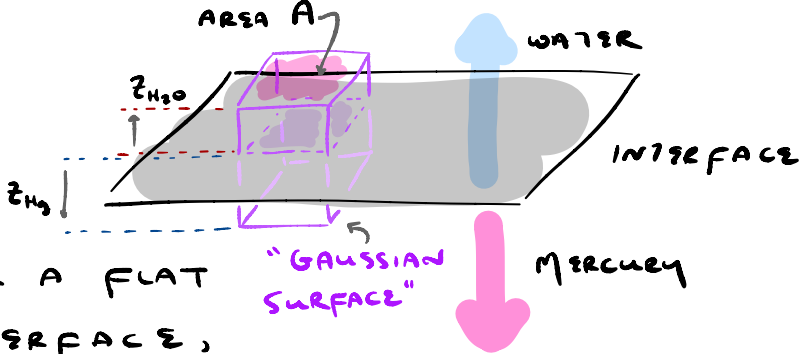$$d\mu^{S}_{ELEC} = d\mu^{BULK}_{ELEC} = -F\,d\phi_{Hg}$$

$$d\mu^{S}_{ION} = +Fz\,d\phi_{H_2O}$$

- "ELECTRONEUTRALITY":

  - BOTH MERCURY AND THE WEAK
    ACID SOLUTION ARE ELECTRICAL
    CONDUCTORS.

    - THEREFORE IN THE BULK
      PHASES WE REQUIRE THE
      ELECTRIC FIELD $\vec{E} = 0$.

AREA A

z_{H_2O}

z_{Hg}

WATER

INTERFACE

"GAUSSIAN SURFACE"

MERCURY

- FOR A FLAT
  INTERFACE,
  WE HAVE FROM
  GAUSS' LAW:

$$\oint \vec{D} \cdot d\vec{A} = \int dV \rho = Q_{ENC}$$

$$\left[\vec{D}(z) = \varepsilon_r(z)\, \varepsilon_0\, \vec{E}(z) \right]$$

"DISPLACEMENT FIELD"

$$\varepsilon_r^{Hg}\, \varepsilon_0\, A\, E_z(z_{Hg}) + \varepsilon_r^{H_2O}\, \varepsilon_0\, A\, E(z_{H_2O}) = A\, \sigma_{ELEC} + A\, \sigma_{ION}$$

$$\implies \sigma_{ELEC} = -\sigma_{ION}$$
$$\equiv \sigma$$

"ELECTRO-NEUTRALITY"

- BuT: $\sigma_{ELEC} = -F \, \Gamma_{ELEC}$

  $\sigma_{ION} = +zF \, \Gamma_{ION}$

$$\implies d\gamma = -\Gamma_{ELEC} \times \left(-F \, d\phi_{Hg}\right)$$

$$-\Gamma_{ION}\left[+Fz \, d\phi_{H_2O}\right]$$

$$= +\sigma \, d\left[\phi_{H_2O} - \phi_{Hg}\right]$$

- NOW WE CAN MODEL Lippmann's EXPERIMENT AS THE FOLLOWING CIRCUIT:
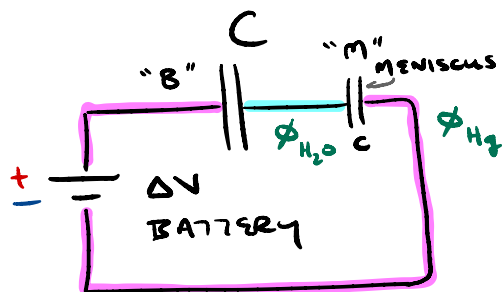
- BOTH MERCURY/WATER INTERFACES "B" + "M" WILL ACT LIKE CAPACITORS W/ IDENTICAL CAPACITANCES PER UNIT AREA.

- BECAUSE THE MENISCUS IS MUCH SMALL-ER, IT'S CAPACITANCE c WILL BE MUCH SMALLER THAN THE INTERFACE @ "B" CAPACITANCE C.

- THE CHARGE ON THE MENISCUS IS $\pm \sigma a$, (surf. area of menisc.) AND THIS MUST ALSO BE THE CHARGE ON THE LARGER INTERFACE.

  - THE VOLTAGE ACROSS THE MENISCUS IS THUS $V_M = \dfrac{\sigma a}{c}$

  - AND ACROSS THE OTHER:
    $$V_B = \frac{\sigma a}{C}$$

  - SO $\dfrac{V_M}{V_B} = \dfrac{C}{c} \gg 1$

  - SO:
    $$d\left[\phi_{H_2O} - \phi_{Hg} \right] = dV_m \simeq d\Delta V$$

    ($\simeq$ BATTERY VOLTAGE)

    $$\implies d\gamma = \sigma \, d\Delta V$$

    $$\implies \boxed{\frac{d\gamma}{d\Delta V} = \sigma} \quad \left[\text{WHERE } \Delta V = V_{H_2O} - V_{Hg} \right]$$
    "LIPPMANN EQN"

    $\Delta V = V_{H_2O}$ " " V_{Hg}
    VOLTAGE APPLIED TO H_2O - SIDE OF MENISCUS
    VOLTAGE APPLIED TO H_g - SIDE OF MENISCUS

- BUT WE ALSO HAVE:
  * $Q = -a\sigma$

  $$\implies \boxed{C_A \equiv -\frac{1}{a}\frac{dQ}{d\Delta V} = -\frac{\cancel{a}}{\cancel{a}}\frac{d\sigma}{d\Delta V} = -\frac{d^2\gamma}{d\Delta V^2}}$$

  "DIFFERENTIAL CAPACITANCE PER UNIT AREA"

  * Q HERE REFERS TO CHARGE ON AQUEOUS SIDE OF THE INTERFACE.

- **SURFACE CHARGE AND γ vs. ΔV CURVES.**

  - ANOTHER FRENCH PHYCISIST L.G. Gouy [1854 - 1926] PERFORMED CAREFUL MEASUREMENTS OF γ vs. ΔV FOR THE MERCURY/AQUEOUS INTERFACE FOR A LARGE NUMBER OF SOLUTIONS + CONCENTRATIONS:

Gouy

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

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 $\dfrac{d^2\theta}{d\Delta^2}$ 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.

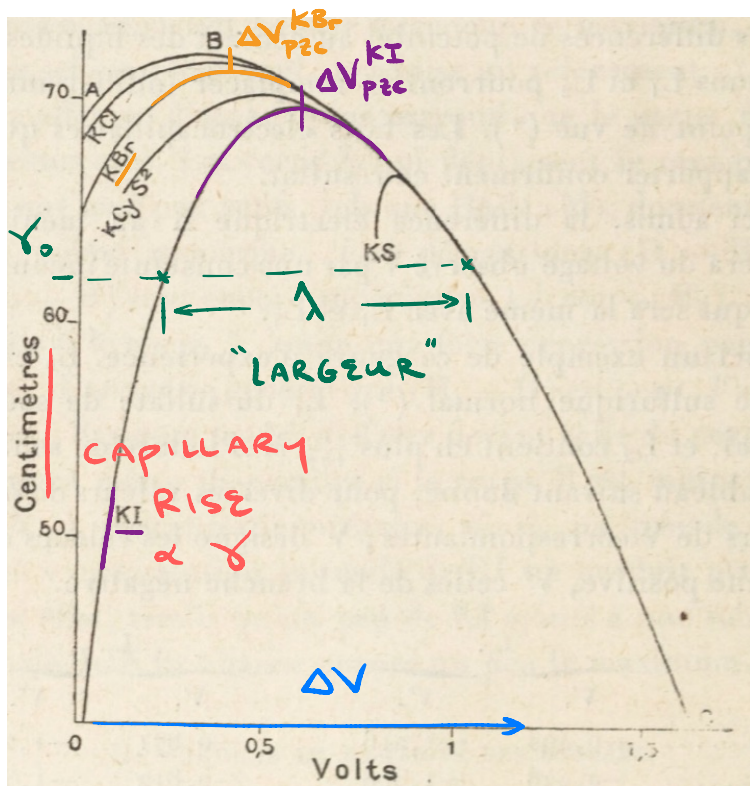$$[\ \theta = \gamma\ ,\ \Delta = \Delta V\ ]$$

- FOR EXAMPLE, HE MEASURED
γ vs. ΔV FOR SEVERAL POTASSIUM
SALTS:

- WHAT WE MIGHT FIRST NOTE:
  - THE PEAKS OF THE CURVES
    DIFFER FOR DIFFERENT ANIONS

- E.G. $\dfrac{d\gamma^{KI}}{d\Delta V}(\Delta V = 0.5V) = 0$

WHILE $\dfrac{d\gamma}{d\Delta V}(\Delta V = 0.3V) \ne 0$

BUT: $\dfrac{d\gamma}{d\Delta V} = \sigma^{*}$

* RECALL: SURFACE CHARGE IS DEFINED TO BE THAT OF THE <u>METAL</u> SIDE OF THE INTERFACE.

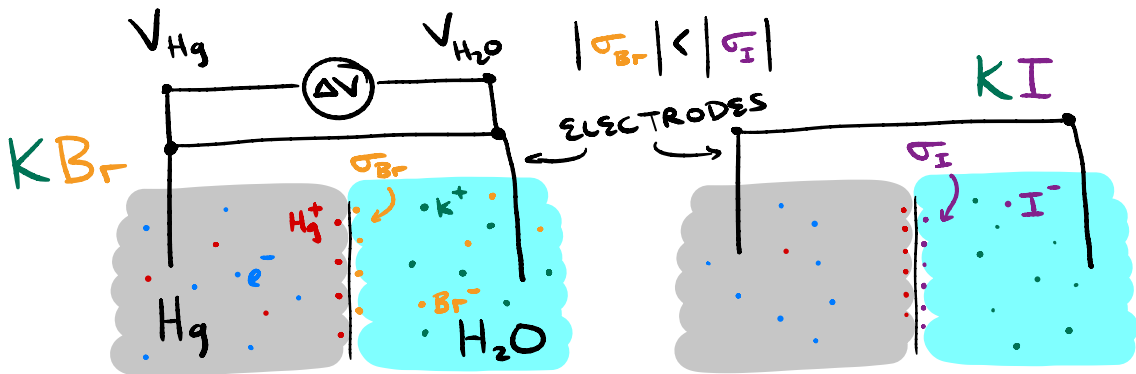SO: · IONS SPONTANEOUSLY ADSORB ONTO MERCURY / AQUEOUS INTER-FACE.

"SPECIFIC ADSORPTION"

· I.E. THE "POINT OF ZERO CHARGE" [PZC] ΔV_{PZC} WHERE $\dfrac{d\gamma}{d\Delta V}(\Delta V_{PZC}) = 0$
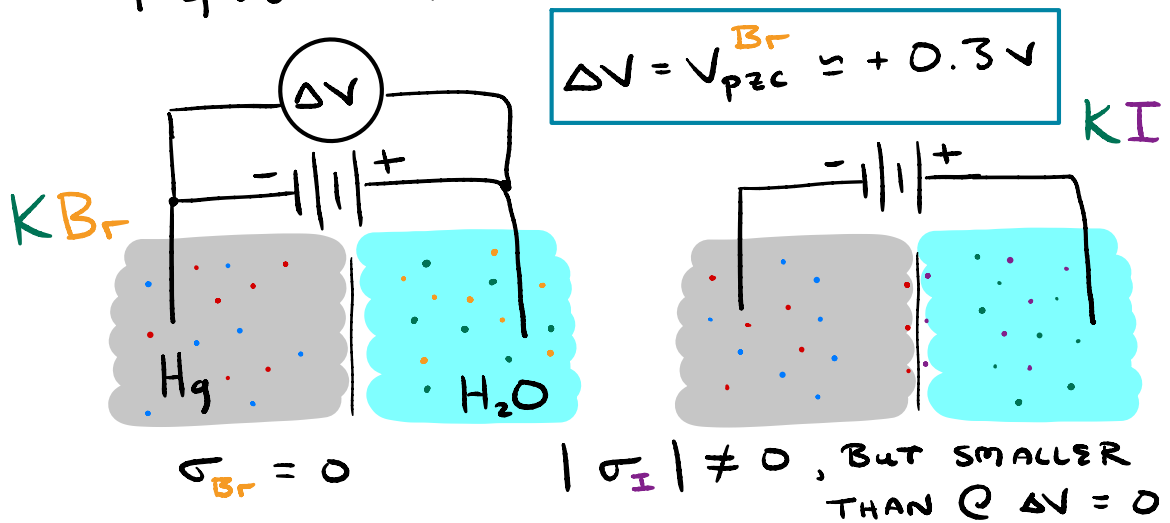
$$\boxed{\Delta V = V_{H_2O} - V_{Hg} = 0}$$
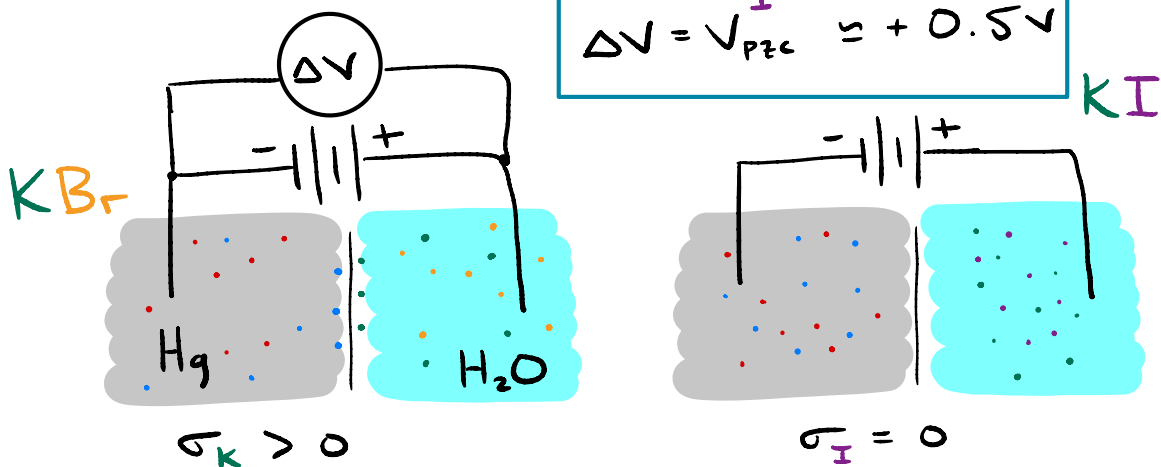
DEPENDS ON THE SOLUTION:

V_{Hg} ΔV V_{H_2O} $|\sigma_{Br}| < |\sigma_{I}|$ KI

KBr σ_{Br} ← ELECTRODES → σ_I

Hg_2^{+} k^{+} I⁻

Hg   Br⁻ H_2O

- @ $\Delta V = 0$: $-\dfrac{d\gamma^{KI}}{d\Delta V} = \sigma_I < \sigma_{Br} < 0$

- TO <u>DEPLETE</u> THIS NEGATIVE SURFACE CHARGE, WE APPLY A <u>POSITIVE</u> VOLTAGE $\Delta V = V_{H_2O} - V_{Hg}$ BETWEEN THE AQUEOUS SOLUTION & THE MERCURY.

- THE POSITIVE CHARGE ON THE AQUEOUS ELECTRODE <u>ATTRACTS</u> THE ANIONS AWAY FROM THE INTERFACE, LIKEWISE THE NEGATIVE CHARGE ON THE MERCURY ELECTRODE REPELS THE ANIONS :

$$\boxed{\Delta V = V_{pzc}^{Br} \simeq + 0.3 \, V}$$

KI

KBr

ΔV

$-|||+$

Hg H_2O

$\sigma_{Br} = 0$

$|\sigma_I| \neq 0$, BUT SMALLER THAN @ $\Delta V = 0$

- WHY DO ANIONS BIND TO MERCURY [AND OTHER METALS (Au, Pt, Ag)] MORE THAN CATIONS?

- ACCORDING TO P.C.I.: IT'S COMPLICATED. BUT PART OF THE ANSWER LIES IN THE STRONGER "HYDRATION" OF CATIONS:

    - THE COST OF "SHEDDING" THE ORDERED SHELL OF H_2O MOLECULES IN ORDER TO BIND TO METAL SURFACE IS TOO HIGH.

DOUBLE LAYER CAPACITANCE.

- Gouy ALSO STUDIED THE VOLTAGE DIFFERENCE ["LARGEUR"] λ BETWEEN TWO POINTS ON A γ VS. ΔV CURVE OF EQUAL REFERENCE SURFACE TENSION γ_0 [SEE EXAMPLE CURVE ABOVE].

- BELOW WE SHOW THE RESULTS FOR λ FOR DIFFERENT γ_0 FOR SOLUTIONS OF POTASSIUM NITRATE FOR DIFFERENT CONCENTRATIONS:

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

[handwritten, blue] CONCENTRATION $1M \equiv \frac{1g}{liter}$

TABLEAU V.

[handwritten, teal] γ₀

h.	940.		900.		860.		820.	
	λ.	δλ.	λ.	δλ.	λ.	δλ.	λ.	δ
K Az O³ $(\frac{1}{100}$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	

[handwritten, purple]

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

[handwritten, black]

· SO GOUY MEASURES A SYSTEMATIC DECREASE IN λ W/ INCREASING "KA_zO^3" CONCENTRATION.

$\equiv KNO_3$
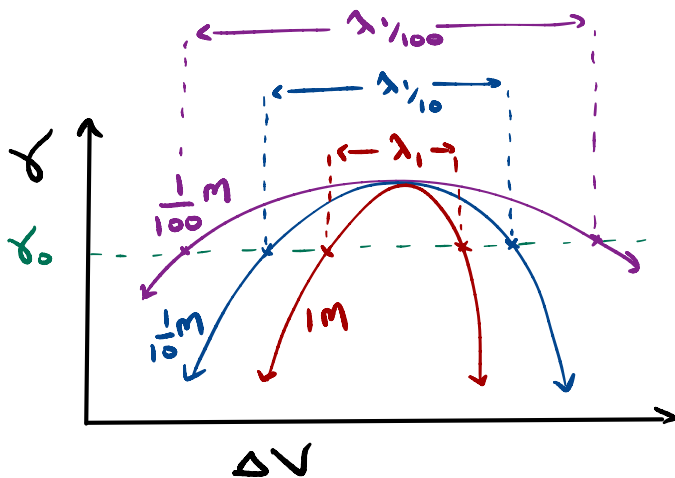
· WHAT DOES THIS IMPLY?

· NEAR MAXIMUM OF γ VS. ΔV CURVE, WE HAVE:

✳ APPROX. CONST. W/ CONCENTRATION

$$\gamma(\Delta V_{zpc} + \delta V) \simeq \gamma(\Delta V_{pzc}) + \frac{1}{2} \frac{d^2\gamma}{d\Delta V^2}(\Delta V_{pzc}) \, \delta V^2$$

[TAYLOR EXPANSION OF γ(ΔV) ABOUT ΔV_{pzc}. NOTE THAT $d\gamma/d\Delta V \,(\Delta V_{pzc}) = 0$]

- A SMALLER λ WE SEE THEN CORRESPONDS TO A LARGER CURVATURE OF THE PARABOLA, I.E. A LARGER $\left| \dfrac{d^2 \gamma}{d \Delta V^2} \right|$.

- BUT WE KNOW $-\dfrac{d^2 \gamma}{d \Delta V^2} = C_A$

- SO INCREASING SOLUTE CONCENTRATION INCREASES THE CAPACITANCE OF THE DOUBLE LAYER!

- WHY?
  - GOUY ALONG W/ ENGLISH CHEMIST D.L. CHAPMAN [1869-1958] WORKED OUT THE THEORY OF THE DIFFUSE LAYER TO EXPLAIN THESE [& OTHER] OBSERVATIONS.