4B6
Solid State Devices and Chemical/Biological Sensors

Chemical Sensors

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The earliest chemical sensor in human history:

Canary in a Coal Mine

Modern Competitions

PHOTO: SYLVAIN PIRAUX

Mine-sniffing rats head to Asia

This African Giant Pouched Rat is a hero. Belgian innovator Bart Weetjens has trained rats, which have a powerful sense of smell, to detect lethal buried landmines in Mozambique. He calls them HeroRATS.

Their next frontier is the Thai-Cambodia border, where hidden landmines have caused immense loss of human life and limbs.

Mr Weetjens is a winner of Singapore's inaugural Lien i3 Challenge, a global contest to encourage innovative non-profit ideas for the good of Asia.

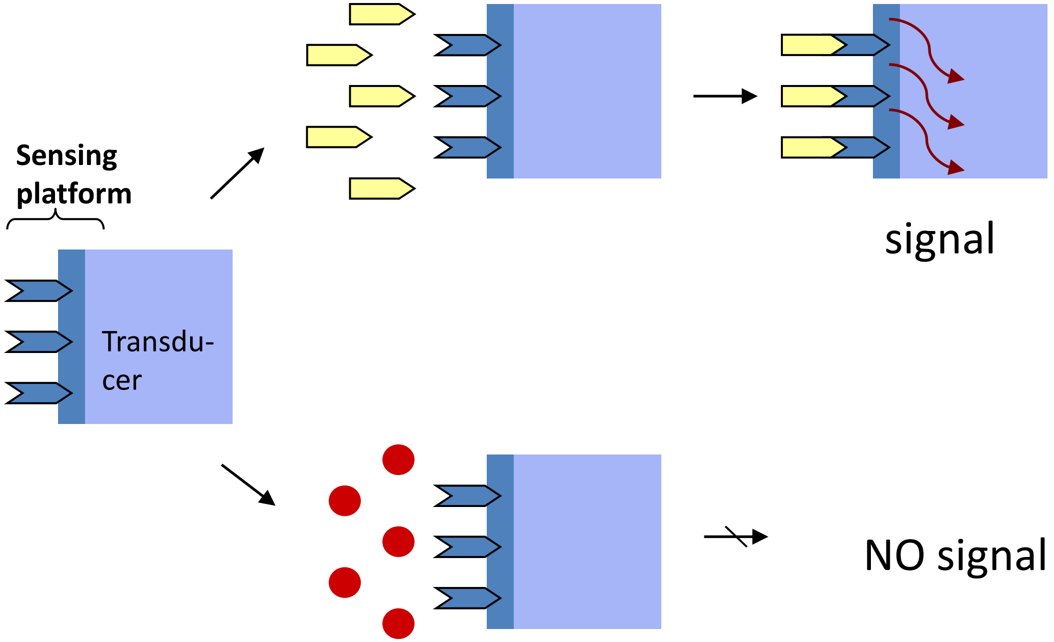
■ SEE SATURDAY SPECIAL REPORT, PAGES D1-9

Singapore Strait Times, Oct 24, 2009

Inscentinel.co

What is Biosensor / Chemical Sensor

- Research (medical, biochemical, biotechnological)
- Monitoring
- Pharmaceutics & Drug Discovery
- Environment
- Food control
- Biodefense
- Forensics
- Diagnostics



Overview

Chemical sensors

1 Under dry condition: Gas sensor

1.1 Hydrogen chemical field effect transistor (ChemFET)

2 Solution based chemical sensor

2.1 Basic concepts of electrochemistry

2.2 Electrochemical double layer

2.3 Example – Ion Sensitive Field Effect Transistor (ISFET)

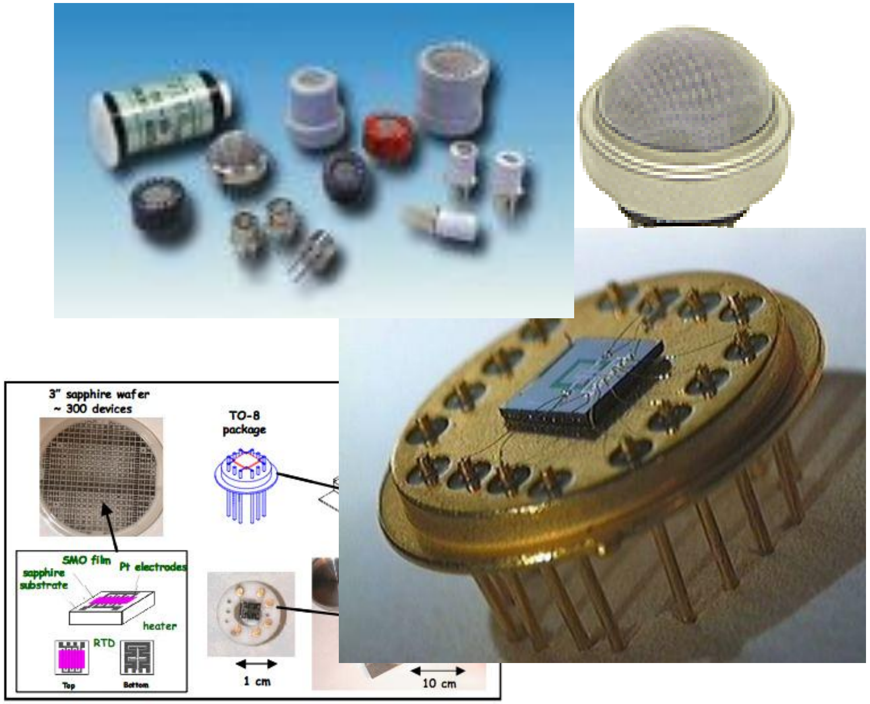
Gas sensor

Gas sensors are sensing devices that interact with various gases and then provide the output to an instrument for displaying the measurements. Their applications are in ***toxic*** and ***combustible gas detection***.

Global market for gas sensor reached $1.24 billion for 2008, and is projected to reach $1.4 billion by 2012

The major gas sensor types are:

- Electrochemical
- Semiconductor
- Catalytic
- Infrared



Gas sensor – conventional vs. solid state

Conventional gas sensor:

- Catalytic bead sensors, explosimeter, infrared point sensor, etc.

Semiconductor gas sensor:

- Sensitive, ultra-small in size, low cost, easily integratable, mass manufacturing…

	Type of solid state devices	Physical changes
1	Field effect gas sensor: Diode, transistors, capacitors	Work function (electrical polarisation)
2	Piezoelectric sensors: Quartz crystal microbalances (QCM), surface acoustic wave (SAW), microcantilevers	Mass
3	Optical sensors: fibre optic or thin film	Optical parameters: surface plasmon resonance (SPR), reflection, absorption, fluorescence, refractive index

Gas sensor – Recap on MOSFET

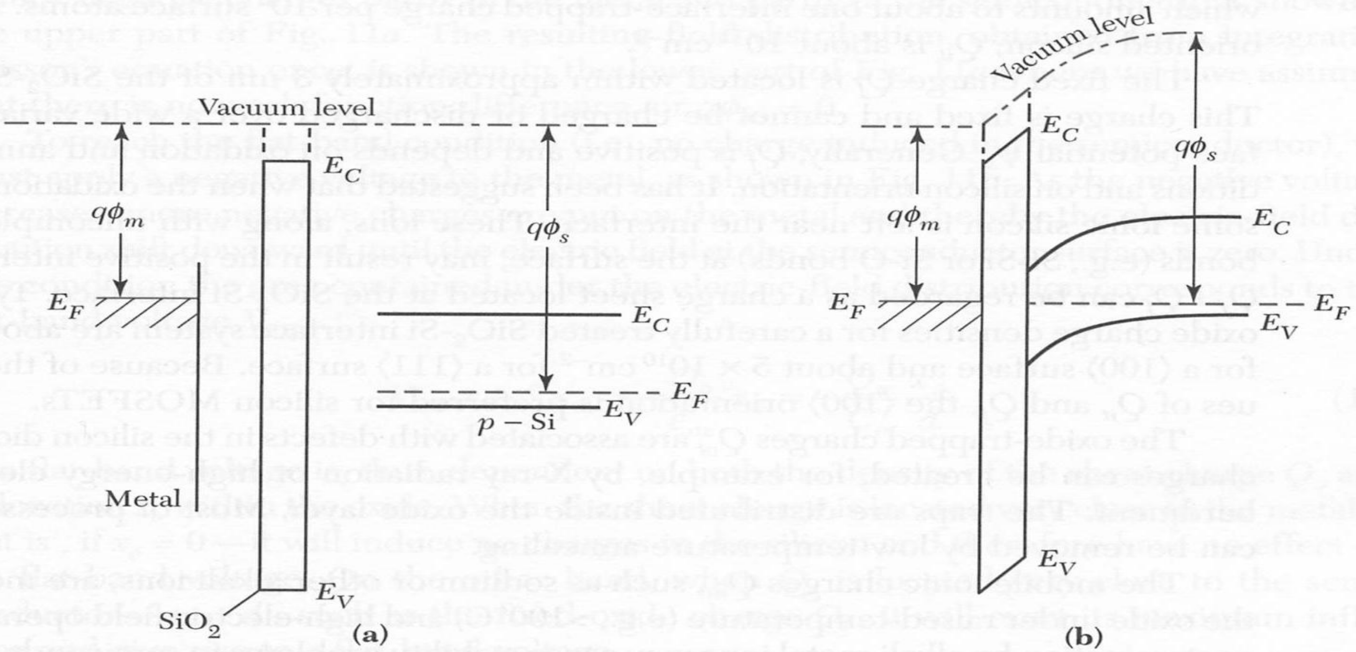
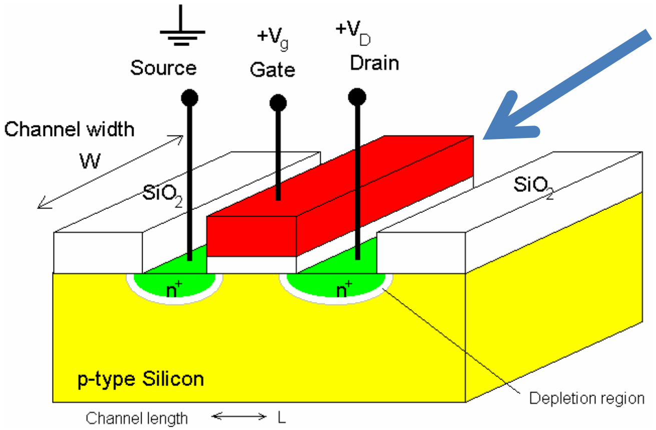


Fig. 9 (*a*) Energy band diagram of an isolated metal and an isolated semiconductor with an oxide layer between them. (*b*) Energy band diagram of an MOS diode in thermal equilibrium.

$$V_{FB} = \frac{\phi_m - \phi_s}{q}$$

$$V_T = V_{FB} + 2\psi_B + \frac{d}{\varepsilon_i}\left[2\varepsilon_s q N_A (2\psi_B)\right]^{\frac{1}{2}}$$

Gas sensor – Hydrogen ChemFET



Palladium:
functional material

- A Hydrogen ChemFET is made by using Palladium (Pd) as a metal gate
- H_2 diffuses trough the Pd gate changing the metal work function
- V_T changes and the I_D-V_{GS} characteristic shifts
- Palladium is the functional material which provides specificity!

Gas sensor – Hydrogen ChemFET

Hydrogen adsorb on palladium surface to form palladium hydride and generate positive charge at the metal – gas interface.

A dipole layer is formed

$$V_{FB} = -\psi_{\mathrm{int}}$$

$$\phi_m = \phi_s$$

$$V_{FB} = \frac{\phi_m - \phi_s}{q} - \psi_{\mathrm{int}}$$

$$\phi_m \neq \phi_s$$

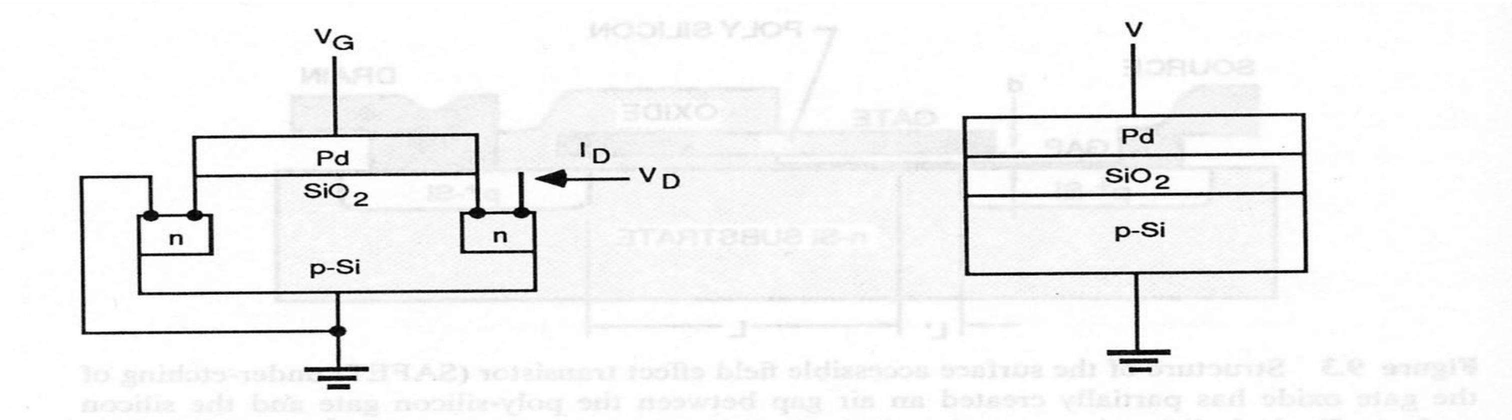
Alternative explanation:

Remember:

ϕ_m = work done to extract an electron from the metal

This work is done against the surface dipole

Gas sensor – Hydrogen ChemFET



Schematic diagrams of hydrogen-sensitive MOS structures (a) a Pd MOS transistor and its $I_D(V_G)$ curve (b) a Pd MOS capacitor and its C-V curve

Other gases can be detected by this principle: H_2S, NH_3, CO etc.

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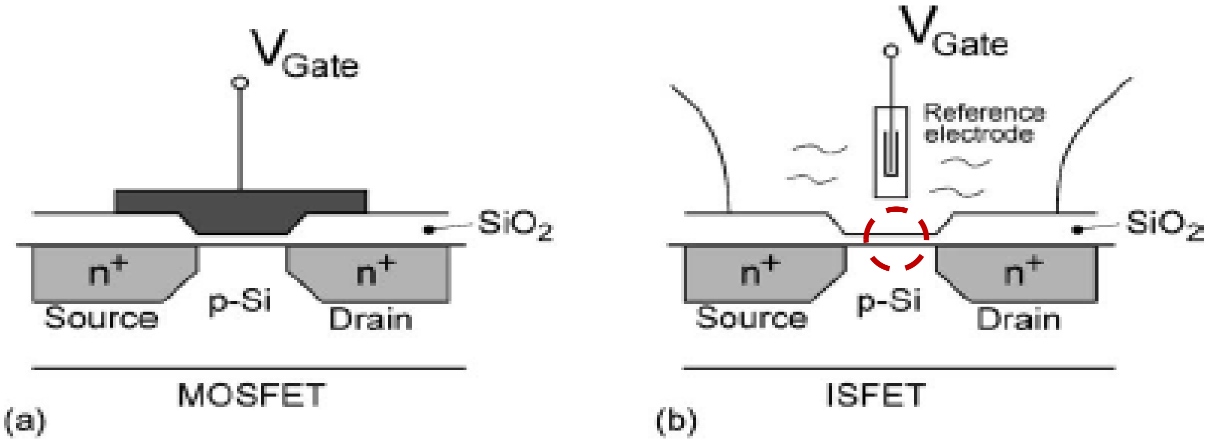
- Helmholtz model
- Gouy-Chapman model
- Gouy-Chapman-Stern model

2.3 Example - ISFET

Solution Based Chemical Sensors

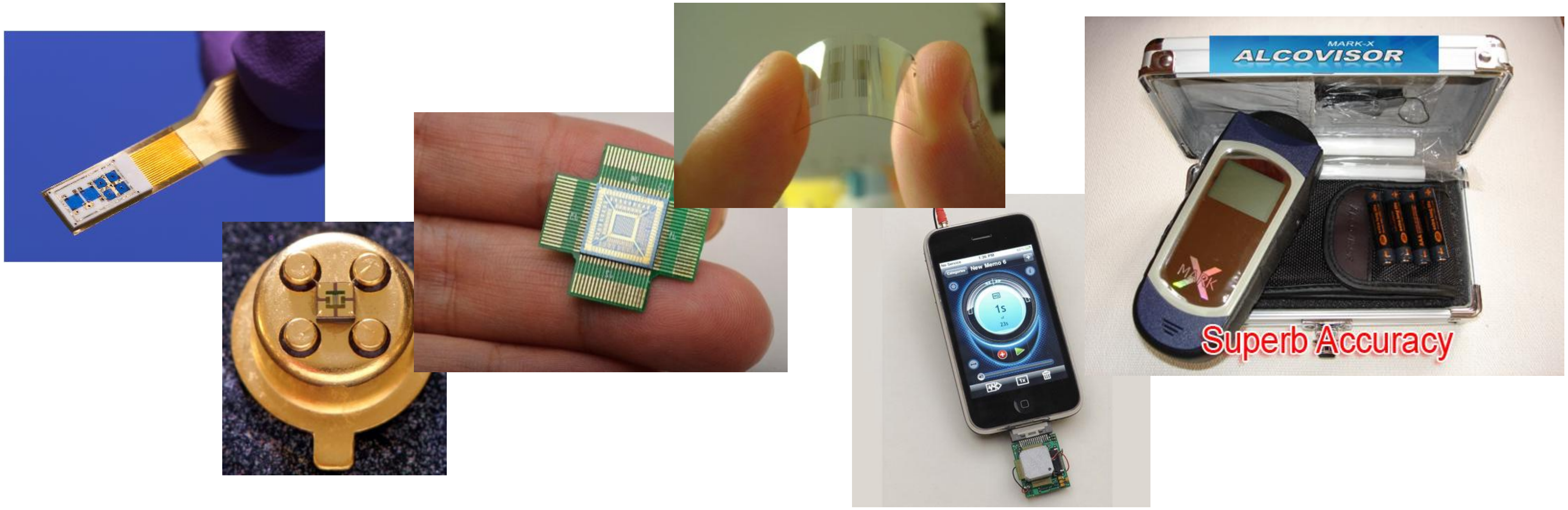
Solid state sensor device in contact with a solution, which contains the chemical to measure. Properties of liquid solution, and liquid-solid interface have to be considered in this type of sensors.

Example:
Ion-Sensitive-Field-Effect Transistor (ISFET)



Solution Based Chemical Sensor

- $4 billion annual US market including biosensors
- Annual growth rate between 7-8%
- Including optical, electrochemical, semiconductor and others
- Medical diagnostic remains the largest sector



Basic Concepts of Electrochemistry

Definitions:

- *Solution: a* liquid, normally *water,* referred to as the *solvent,* containing other species, normally a *salt,* like sodium chloride, *NaCl,* referred to as the *solute.*

- *Mole* of a monoatomic substance*: the atomic weight expressed in grams (g=10^{-3} Kg)*

Example: Al (atomic weight =27) 1 mole = 27 g
Au (atomic weight = 197) 1 mole = 197 g

- *Mole* of a molecular substance*: the molecular weight expressed in grams*

Example: H_2O (molecular weight 2+16=18) 1 mole = 18 g

Basic Concepts of Electrochemistry

Important property: whatever the substance, 1mole contains the same number N_A of "particles":

$N_A = 6 \times 10^{23}$ Avogadro's number

- *Concentration of a solution* :

$$\frac{\text{moles of solute}}{\text{moles of solvent}}$$

abbrev. : **mol/l = Molar**

- *pH of a solution :*

$$\mathbf{pH} = -\log_{10}\left[\mathbf{H}^{+}\right]$$

$$\left[\mathbf{H}^{+}\right] = \textbf{concentration of hydrogen ions in mol / l}$$

pH < 7 *acidic* solution
pH > 7 *basic* solution

Basic Concepts of Electrochemistry

- ***Electrolyte****:* a solution which is also an ionic conductor. For NaCl in water, for instance, due to the high relative permittivity of water (ε_r= 80), the electrostatic force keeping the Na^+ and Cl^- together is much lower than in air. The two ions separate and can move under the action of an electric field. Like in a semiconductor there are positive and negative charge carriers, but in this case they are ions, not electrons and holes!

- ***Redox***: reduction-oxidation reaction, describes all chemical reactions in which atoms have their oxidation state changed. Oxidation is the loss of electron or increase in oxidation state by a molecule, atom or ion. Reduction is the gain of a electron.

Discussion: what is ionic conductor and what's the difference between ionic conductor and electronic conductor?

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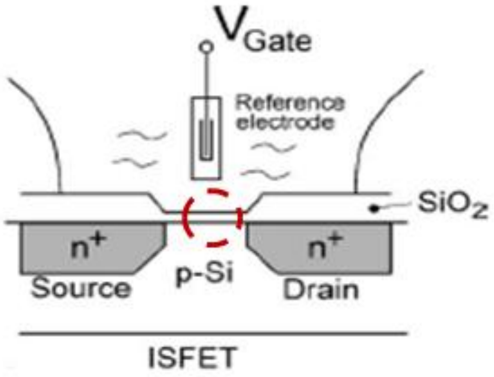
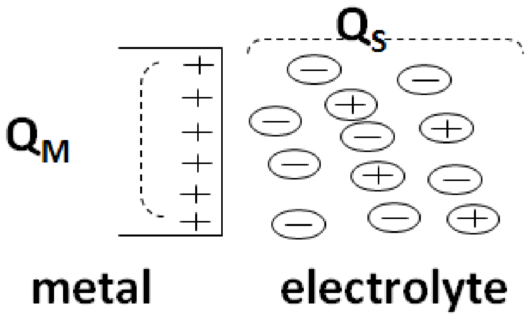
- 2.1 Basic concepts of electrochemistry
- 2.2 Metal-electrolyte interface
  - Helmholtz model
  - Gouy-Chapman model
  - Gouy-Chapman-Stern model
- 2.3 Example - ISFET



Metal-Electrolyte Interface

Electrochemistry is the study of structures and processes at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte)

We start from an ideal case: a planar metal electrode in contact with an electrolyte with no chemical reactions occurring between the electrolyte and the metal.



Like in the case of a metal-semiconductor junction, charge neutrality requires:

$$Q_M = -Q_S$$

Q_M charge on metal, all the surface
Q_S charge in electrolyte; distributed in a volume next to the interface

The resulting charge distribution – two regions of equal and opposite charge – is known as the **electrical double layer**. It can also be viewed as a capacitor.

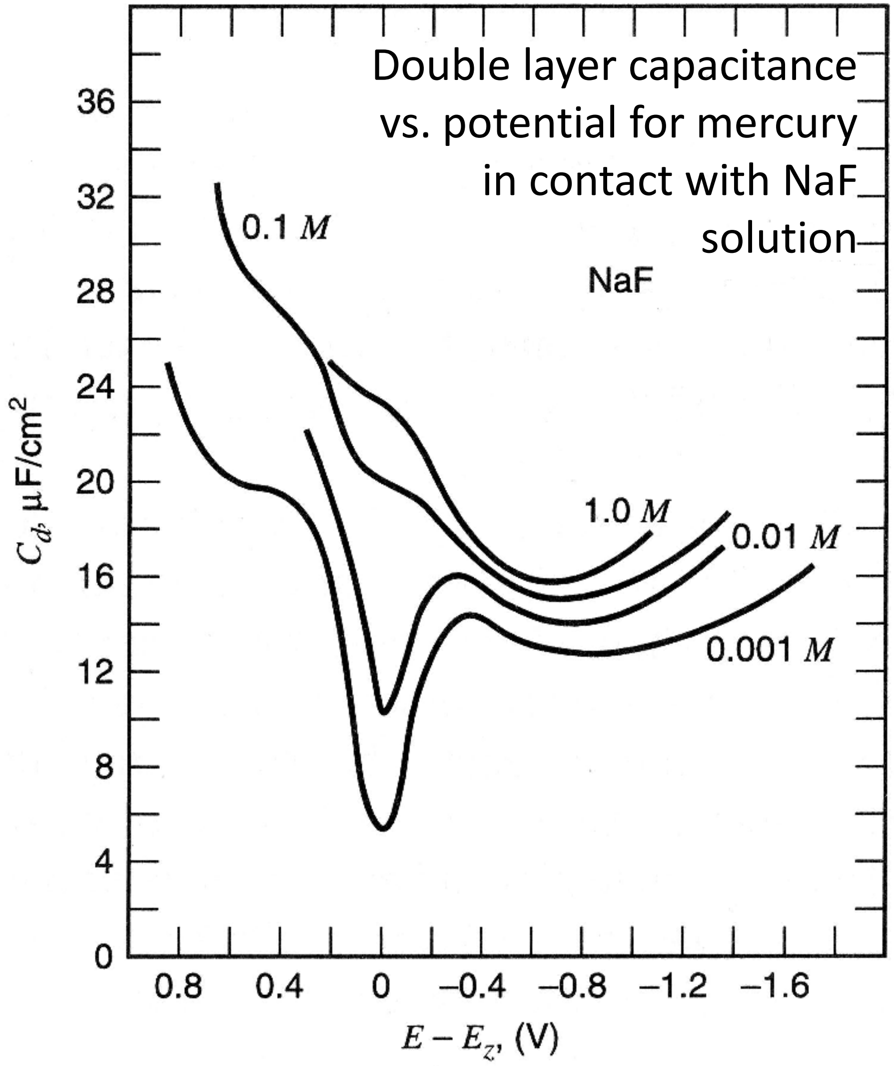
Metal-Electrolyte Interface

The double layer capacitance depends on:

- applied potential
- electrolyte ionic strength

Three models frequently used to describe the metal/electrolyte interface:

- Helmholtz model
- Gouy-Chapman model
- Gouy-Chapman-Stern model



Double layer capacitance vs. potential for mercury in contact with NaF solution

E_z : potential of zero charge

Helmholtz Model

The earliest model presented for the double layer:

- Opposite charge in solution resides at the surface of the charged electrode;

- Two sheets of charge, having opposite polarity, separated by a distance of molecular order, *d.*

=> The double layer was first considered as a parallel plate capacitor:

$$C_D = \frac{\varepsilon\varepsilon_o}{d}$$

Like an ordinary capacitor where its capacitance is independent of the potential

Problem: In practice, the double layer capacitance is **NOT independent of the potential applied**, and it is also a function of the **electrolyte concentration**!

Gouy-Chapman Model

A simple but surprisingly accurate theory was proposed independently by Gouy and Chapman in 1910. The basic ideas are the following:

•The solution is modeled as point ions embedded in a dielectric continuum representing the solvent;

•The metal electrode is considered as a perfect conductor;

•The distribution of the ions near the interface is calculated from electrostatics and statistical mechanics.

Gouy-Chapman Model

We consider a planar electrode in contact with a solution of a z - z electrolyte, i.e. cations of positive charge +zq and anions of negative charge number –zq, q = 1.6 x 10^{-19} coulomb, the electronic charge.

The electrode surface is situated in the plane at x = 0.

The treatment is similar to that of the depletion region of a Schottky barrier in semiconductors. The electrostatic potential $\psi(x)$ obeys **Poisson's equation**:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho(x)}{\varepsilon\varepsilon_0} \tag{1}$$

$\rho(x)$	charge density in the electrolyte
ε	dielectric constant of the solvent
ε_0	permittivity of the vacuum

Gouy-Chapman Model

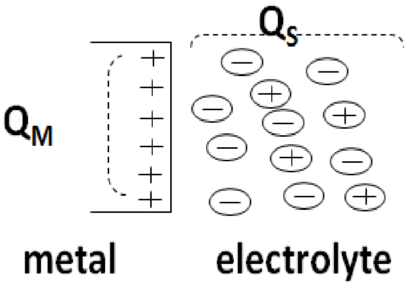
Assign **$n_+(x)$** and **$n_-(x)$** as densities of cations and anions in the solutoin

in the bulk: (2)

near the interface there is a net charge:

(3)

The ionic densities depend on the potential. We choose $\psi(\infty) = 0$ as our reference, and apply **Boltzmann statistics**:



(4)

Gouy-Chapman Model

Substituting Eqn. (3) and (4) into Eqn. (1) :

Poisson-Boltzmann Equation

$$\frac{d^2\psi}{dx^2} = -\frac{zqn_0}{\varepsilon\varepsilon_0}[\exp(-\frac{zq\psi(x)}{kT}) - \exp(\frac{zq\psi(x)}{kT})] \qquad (5)$$

Simple case: $\frac{zq\psi(x)}{kT} << 1$

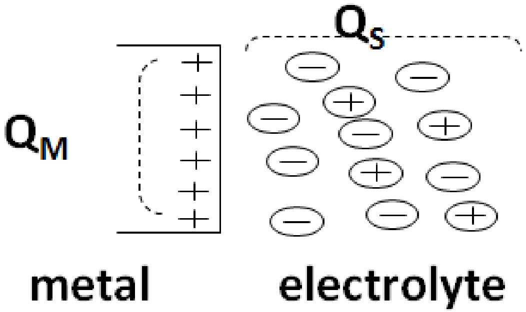
$$\frac{d^2\psi}{dx^2} = k_D^2\psi(\mathrm{x}) \qquad (6)$$

where:

(7)

and $L_D = 1/k_D$ is the **Debye length**

Gouy-Chapman Model



Solution: $\psi(x) = \psi(0)\ \exp(-k_D \mathrm{x})$

To find $\psi(0)$ **:** Charge neutrality:

$$\int_0^\infty \rho(x)dx = -Q_M \qquad (9)$$

Q$_M$ charge /unit surface on electrode surface

From Eqn. (1) and (6): $\psi(x) = -\dfrac{\rho(x)}{\varepsilon\varepsilon_0 k_D^2} \Rightarrow \rho(x) = -\varepsilon\varepsilon_0 k_D^2 \psi(x)$

From Eqn. (8) and (9):

$$\psi(0) = \frac{Q_M}{\varepsilon\varepsilon_0 k_D} \qquad (10)$$

Therefore: $\psi(x) = \dfrac{Q_M}{\varepsilon\varepsilon_0 k_D} \exp(-k_D \mathrm{x})$ (11)

Gouy-Chapman Model

What determines the charge and therefore the potential of the electrode?

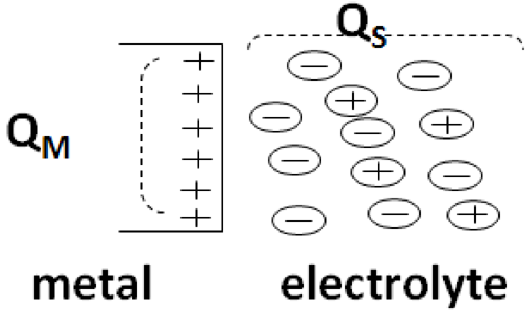
Answer: **The chemistry at the electrode-solution interface**.

That's how a battery works: place two different metals in a solution and you can measure a potential difference between the two metals

If the potential of one electrode is fixed (reference electrode) and the potential of the other is varied through an external voltage source, for a certain voltage V_{pzc} we shall have:

$$\psi(0) = 0 \qquad\qquad Q_M = 0$$

V_z potential of zero charge



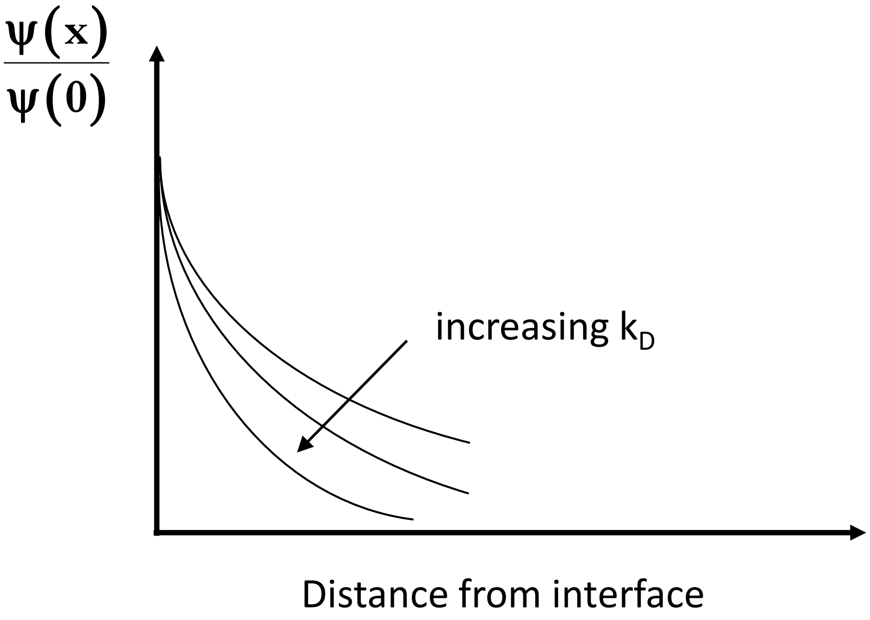
Gouy-Chapman Model

Double layer potential profile:

$$\psi(x)=\psi(0)\exp(-k_D x)$$ where $$\psi(0)=\frac{Q_M}{\varepsilon_0\varepsilon k_D}$$

Note: $\psi(0)$ *is* related monotonically *to* Q_M

$$k_D=\left(\frac{2(zq)^2 n_0}{\varepsilon\varepsilon_0 kT}\right)^{1/2}$$



Concentration **n_0** mol / l	10^{-4}	10^{-3}	10^{-2}	10^{-1}
Debye length=1/k_D Å	304	96	30.4	9.6

Potential exponentially decays through the diffuse layer from the interface, in Gouy-Chapman model.

Gouy-Chapman Model

Double layer capacitance:

The assumption made between Eqn. (5) and (6),

$$\frac{zq\psi(x)}{kT} << 1$$

oversimplified the model.

Remove this simplification results Grahame equation:

$$Q_M = (8kT\varepsilon\varepsilon_0 n_0)^{1/2} \sinh\left(\frac{zq\psi(0)}{2kT}\right) \qquad (12)$$

Note the potential is still related monotonically to the state of charge on the electrode.

Gouy-Chapman Model

The differential capacitance is defined as

$$C_D = \frac{d\sigma}{d\psi(0)} \tag{13}$$

Substitute σ with Q_M from Eqn. (12), hence

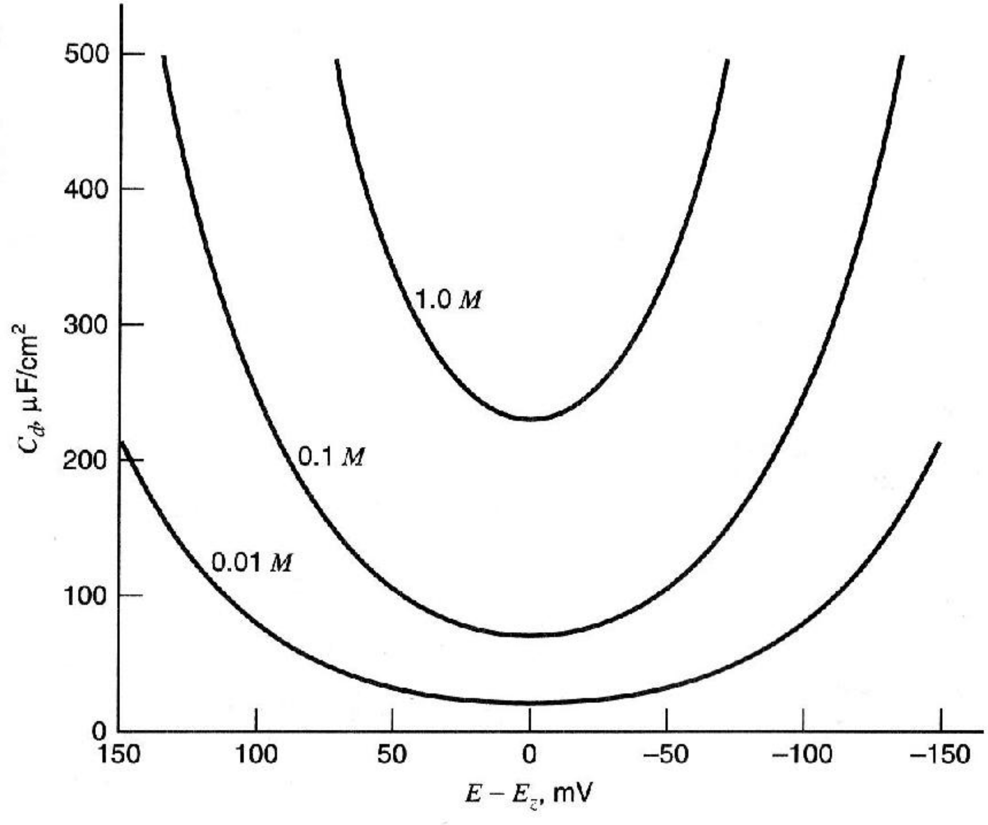
$$C_D = \frac{dQ_M}{d\psi(0)} = \left(\frac{2z^2q^2\varepsilon\varepsilon_0 n_0}{kT}\right)^{\frac{1}{2}} \cosh\left[\frac{zq\psi(0)}{2kT}\right] \tag{14}$$

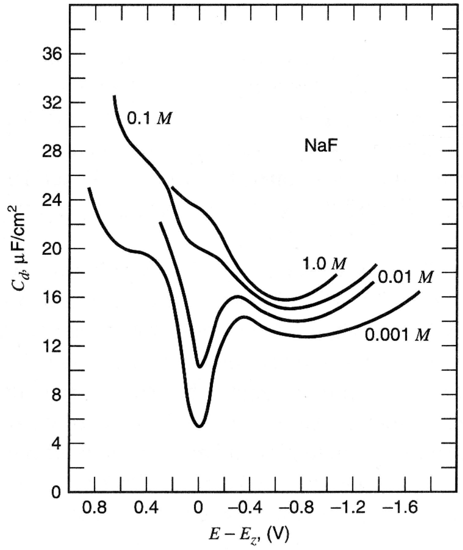
For dilute aqueous solution at room temperature, (14) can be written

$$C_D = 228qC^{*1/2}\cosh[19.5q\psi(0)] \tag{15}$$

where C* is the **concentration** of the electrolyte

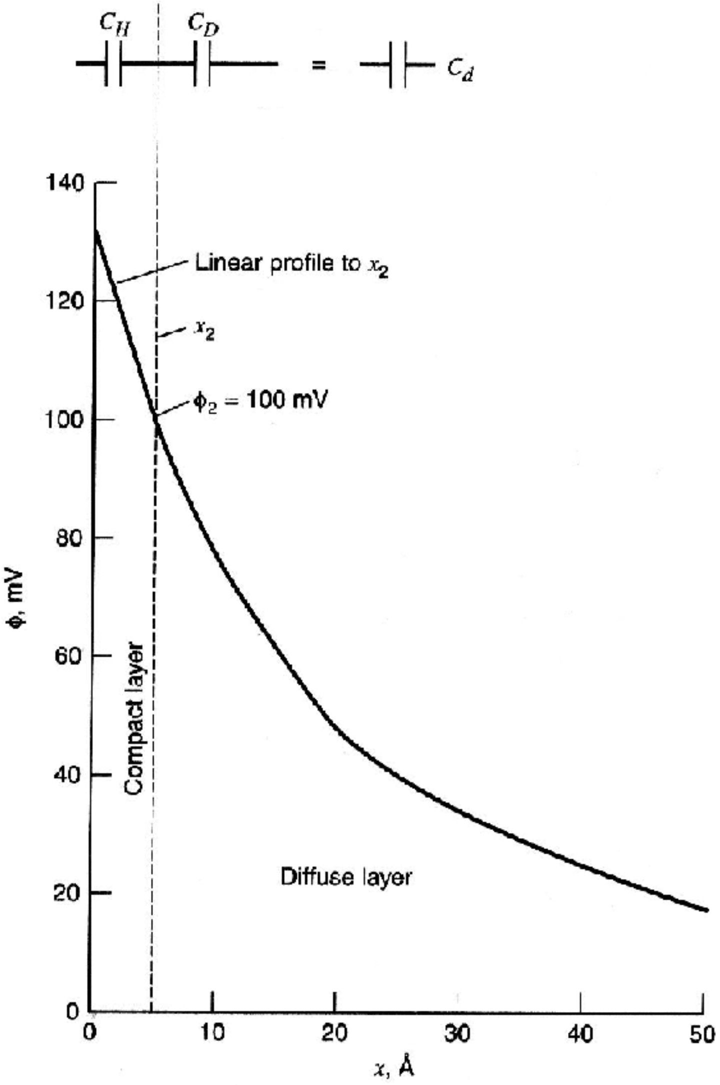
Gouy-Chapman Model





Double layer capacitance calculated from Eqn. (15) for the indicated concentrations of a 1:1 electrolyte in water at 25°C

Gouy-Chapman-Stern Model



- The double layer capacitance calculated from Gouy-Chapman model increase unlimitedly with potential.

- Ions have a finite size and cannot approach the surface any closer than its only radius.

- Define a plane of closest approach for the centre of the ions at distance x_2

- The plan at x_2 is called outer Helmholtz plan (OHP)

- Total capacitance is serial connection of diffuse layer capacitance and OHP capacitance.

Gouy-Chapman-Stern Model

The total double layer capacitance now is

(16)

Since there is no charge between the OHP and the interface

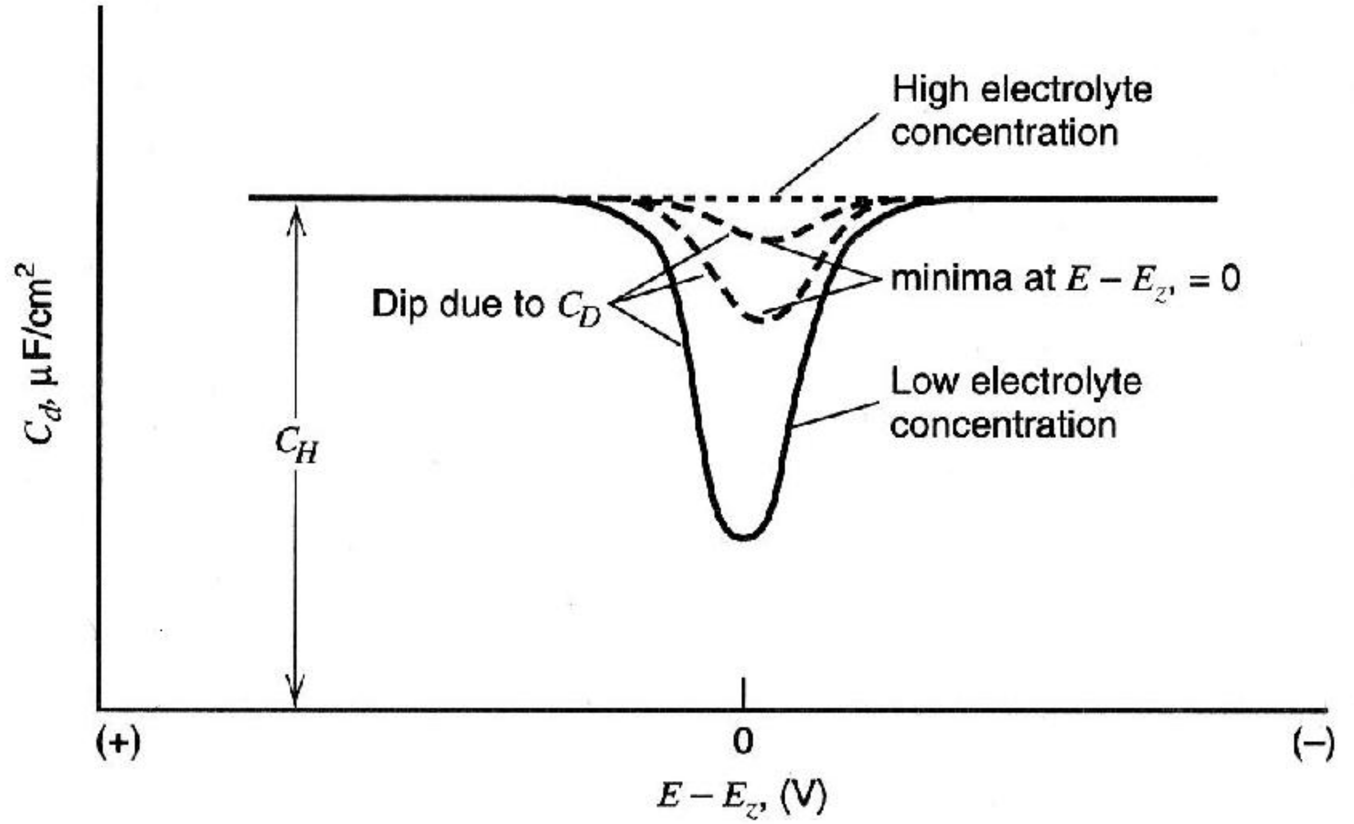
$$C_H = \frac{\varepsilon\varepsilon_0}{x_2} \tag{17}$$

Substituting Eqn. (14) and (17) into Eqn. (16)

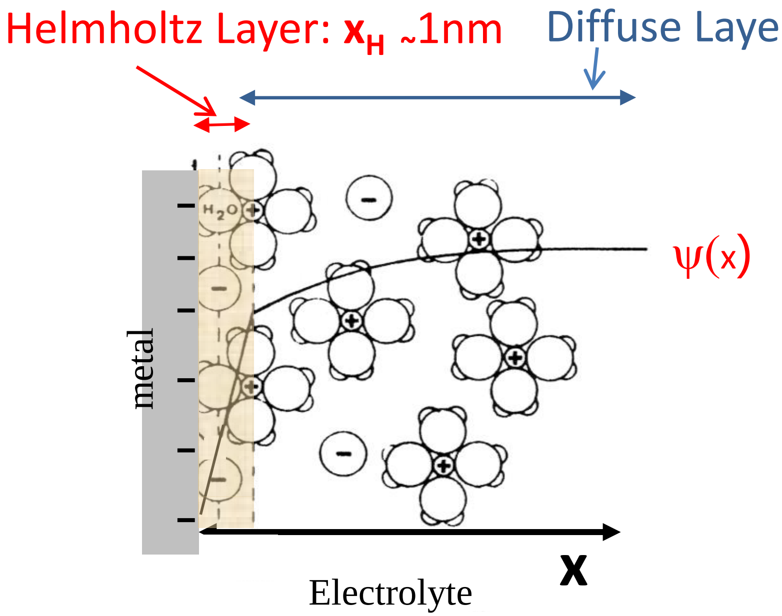
$$\frac{1}{C_d} = \frac{1}{\left(\frac{2z^2q^2\varepsilon\varepsilon_0 n_0}{kT}\right)^{1/2} \cosh\left[\frac{zq\psi(0)}{2kT}\right]} + \frac{x_2}{\varepsilon\varepsilon_0} \tag{18}$$

Gouy-Chapman-Stern Model

From Eqn. (18), the expected behaviour of double layer capacitance is



Realistic Model of Metal/Electrolyte Interface



Helmholtz Layer: $\mathbf{x_H}$
dielectric with constant capacitance **C_H**

$$C_H = \frac{\varepsilon\varepsilon_0}{x_H}$$

For $\frac{zq\psi(x)}{kT}$ not $<< 1$

$$\psi(0) = \frac{Q_M}{C_H} + \frac{2kT}{ze}\sinh^{-1}\left[\frac{Q_M}{\left(8kT\varepsilon\varepsilon_0 n_0\right)^{1/2}}\right]$$

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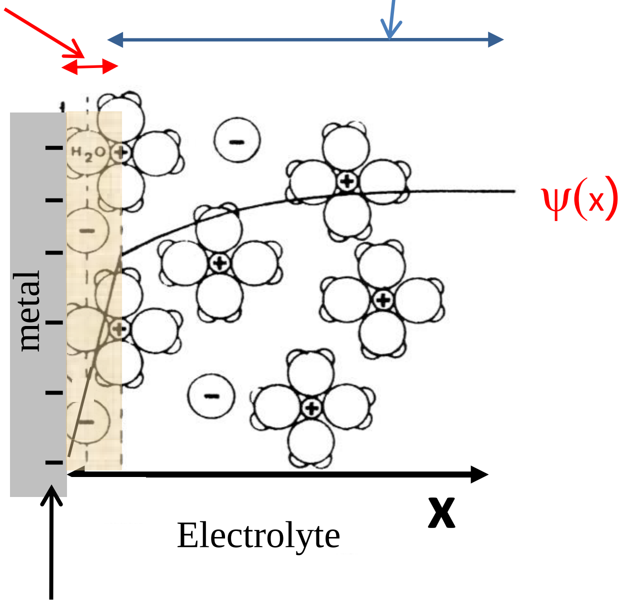
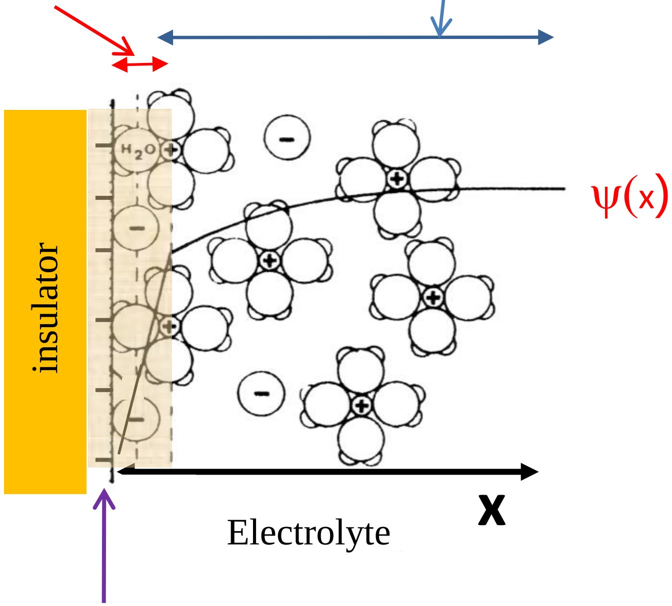
2.3 Example - ISFET

Ion-Sensitive-Field-Effect Transistor (ISFET)



Helmholtz Layer: $\mathbf{x_H}$ Diffuse Layer

Free electron charge

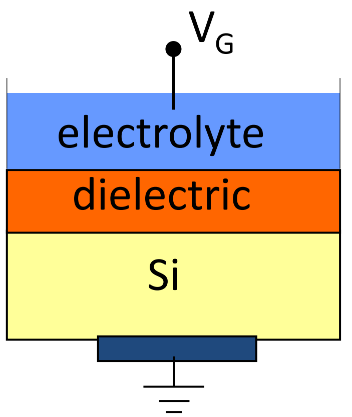


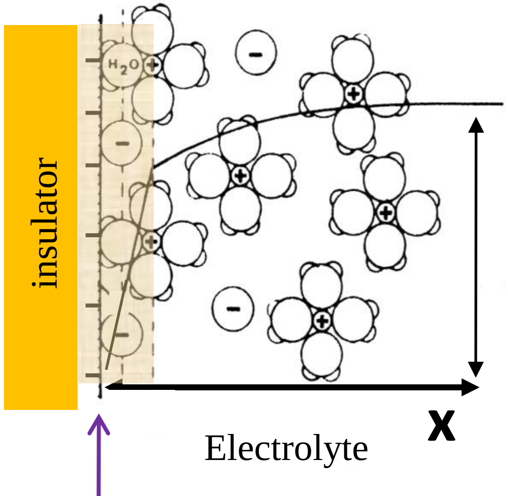
Helmholtz Layer: $\mathbf{x_H}$ Diffuse Layer

Fixed interface charge due to surface reactions

Ion-Sensitive-Field-Effect Transistor (ISFET)

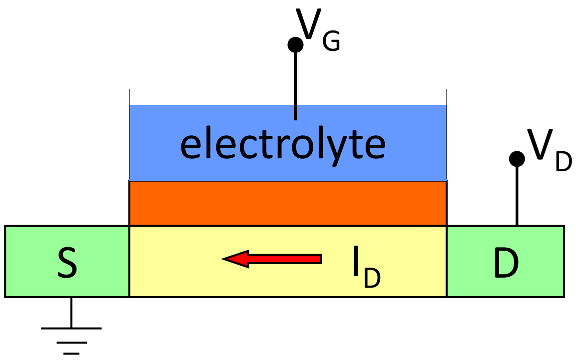
MOS

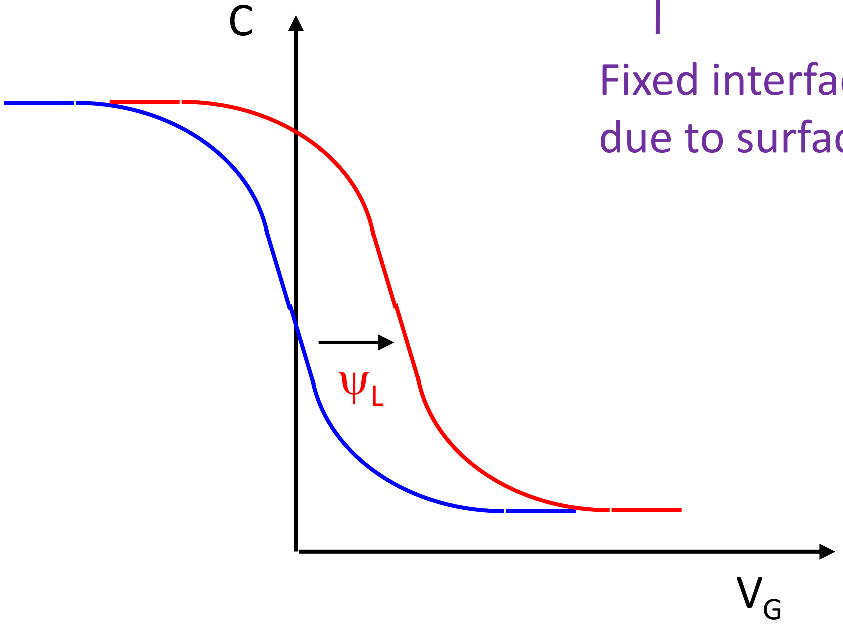


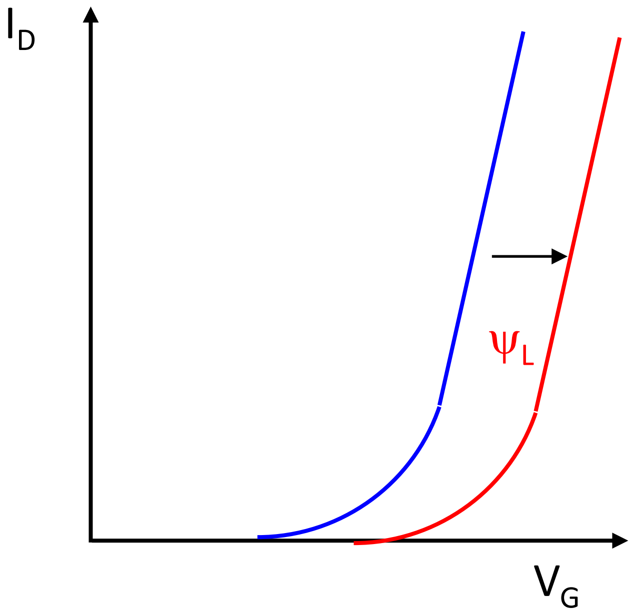


Fixed interface charge due to surface reactions

MOSFET





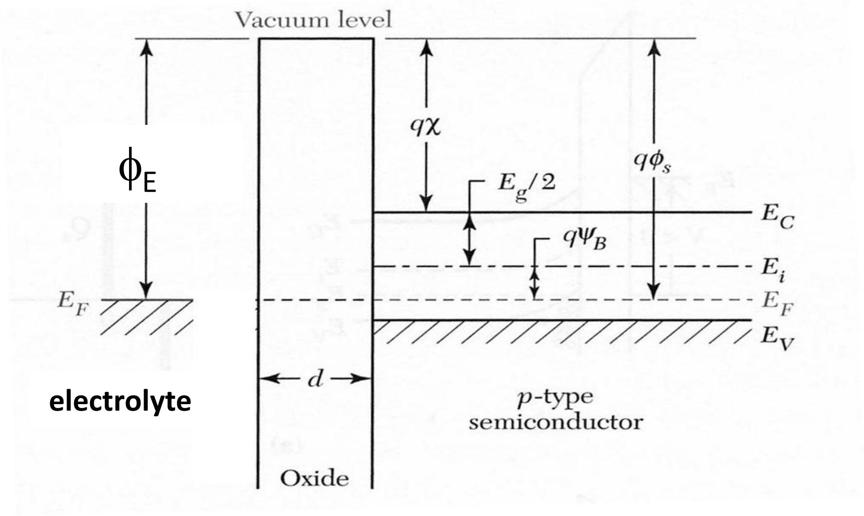


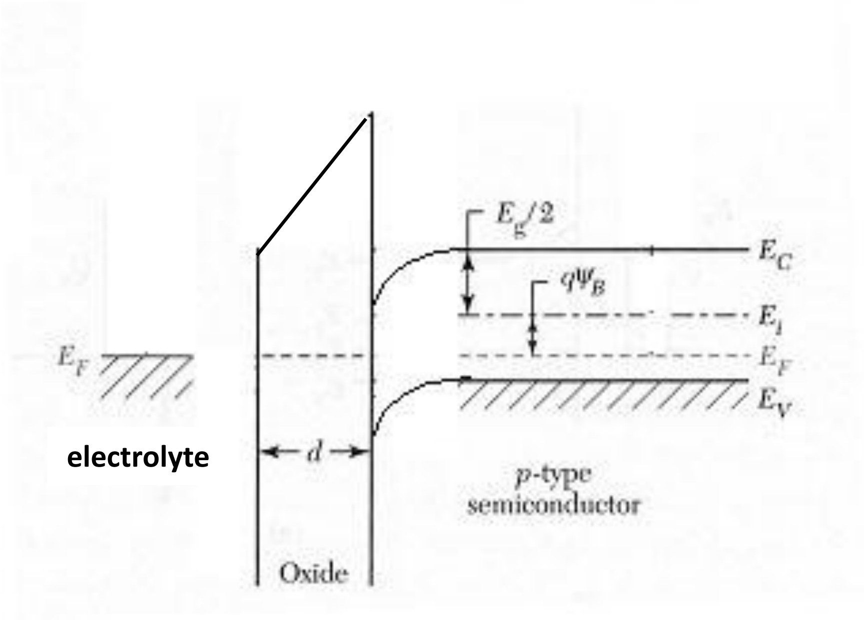
Ion-Sensitive-Field-Effect Transistor (ISFET)

$$\psi_L = \frac{Q_{int}}{C_{dl}}$$

$\mathbf{where:}$ Q_{int} =charge on insulator surface

C_{dl} =capacitance of the electrochemical double layer



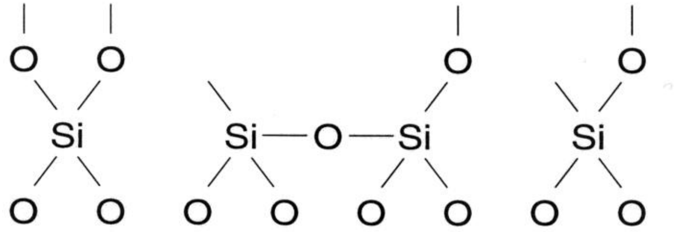


$$V_{FB} = \phi_E - \phi_S - \psi_L$$

Ion-Sensitive-Field-Effect Transistor (ISFET)

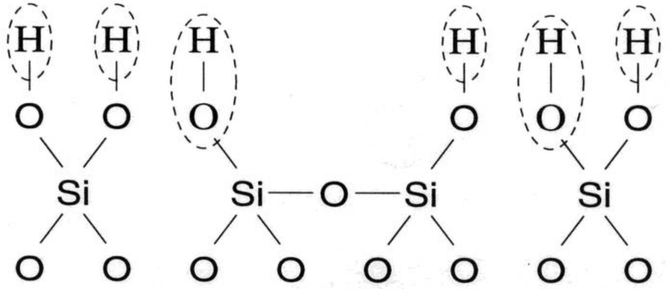
What is Q_{int} due to ? - Surface Adsorption / Desorption for SiO_2

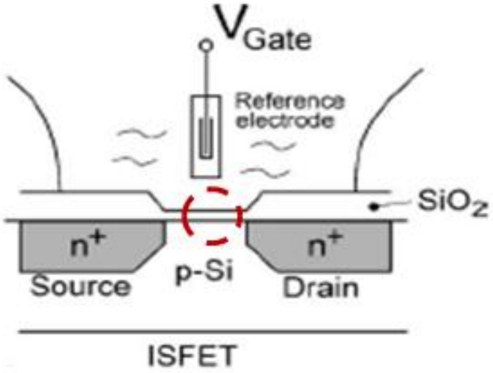
1. Surface Dangling Bonds on SiO_2



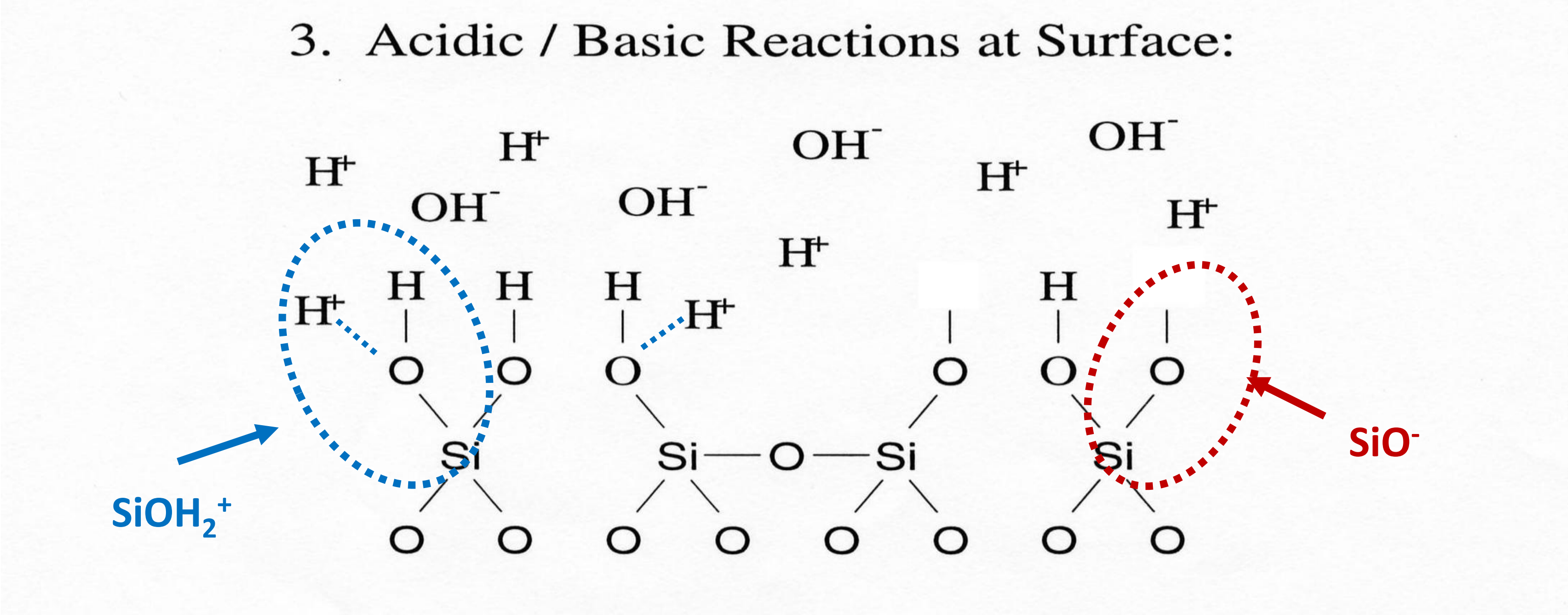
2. Ions in aqueous solution form bonds at surface.

eg. Water: $H_2O \leftrightarrow H^+ + OH^-$





Ion-Sensitive-Field-Effect Transistor (ISFET)



3. Acidic / Basic Reactions at Surface:

$SiOH + H_s^+ \rightarrow SiOH_2^+$

$SiOH \rightarrow SiO^- + H_s^+$

Ion-Sensitive-Field-Effect Transistor (ISFET)

$SiOH + H_s^+ \rightarrow SiOH_2^+$

BASE $$K_b = \frac{[SiOH_2^+]}{[H_S^+][SiOH]}$$

$SiOH \rightarrow SiO^- + H_s^+$

ACID $$K_a = \frac{[H_S^+][SiO^-]}{[SiOH]}$$

$$\frac{\mathbf{K_a}}{\mathbf{K_b}} = \frac{\left[\mathbf{H_S^+}\right]^2\left[\mathbf{SiO^-}\right]}{\left[\mathbf{SiOH_2^+}\right]}$$

$$\therefore [H_S^+] = \sqrt{\frac{K_a}{K_b}\frac{[SiOH_2^+]}{[SiO^-]}}$$

$\left[\mathbf{H_S^+}\right]$ Concentration of H^+ in solution at the surface

$\left[\mathbf{SiO^-}\right]$ Concentration of $\mathbf{SiO^-}$ on the insulator surface

$\left[\mathbf{SiOH_2^+}\right]$ Concentration of $\mathbf{SiOH_2^+}$ on the insulator surface

Ion-Sensitive-Field-Effect Transistor (ISFET)

To find the double layer potential ψ_L :

Boltzman relationship $$\left[H_s^+\right] = \left[H_b^+\right]\exp\left(-\frac{q\psi_L}{kT}\right)$$

where $\left[H_b^+\right]$ Concentration of H+ in the solution bulk

$$-\ln\left[H_b^+\right] + \ln\left(\frac{K_a}{K_b}\right)^{\frac{1}{2}} = -\frac{q\psi_L}{kT} + \ln\left(\frac{\left[SiO^-\right]}{\left[SiOH_2^+\right]}\right)^{\frac{1}{2}}$$

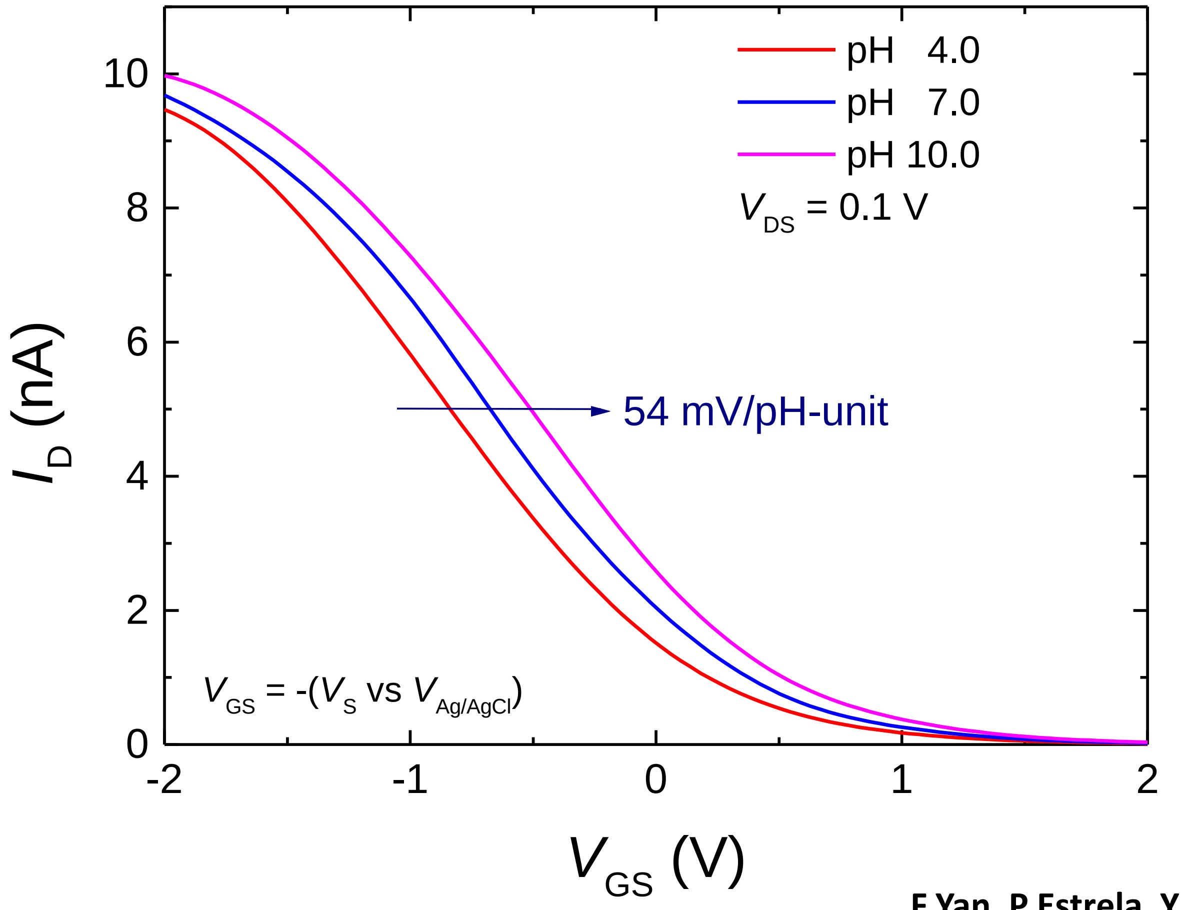
$$-\ln\left[H_b^+\right] + \ln\left(\frac{K_a}{K_b}\right)^{\frac{1}{2}} \approx -\frac{q\psi_L}{kT}$$

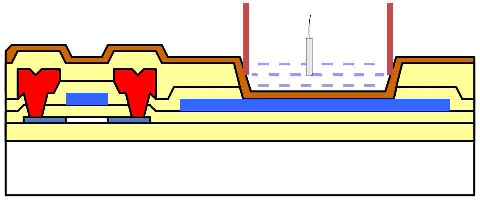
$$pH = -\log_{10}\left[H_b^+\right]$$ and $$pH_{pzc} = -\log_{10}\left(\frac{K_a}{K_b}\right)^{\frac{1}{2}} = \text{constant}$$

$$\boxed{\begin{gathered}\psi_L = 2.303\frac{kT}{q}\left(pH_{pzc} - pH\right) \\ \Delta\psi_L = 59\text{mV}/(\text{pH unit}) \quad \text{at } 300^{\circ}\text{K}\end{gathered}}$$

Ion-Sensitive-Field-Effect Transistor (ISFET)

pH Sensor – Poly-Si TFT with Si_3N_4 gate





W/L = 10 µm / 6 µm
Si_3N_4 pad: 990 x 990 μm^2

F Yan, P Estrela, Y Mo, P Migliorato, H Maeda,
S Inoue, T Shimoda: Appl.Phys.Lett. 86, 053901 (2005)

Ion-Sensitive-Field-Effect Transistor (ISFET)

- An ISFET senses and amplifies the change in
- *Double layer potential* due to the change in pH
- pH measurements are important (blood pH)
- By functionalising the gate insulator organic/bio/inorganic compounds can be detected