

Electrochemistry - applications

ENERGY STORAGE

- Batteries
- Fuel Cells
- Photoelectrochemistry
- Photovoltaic and Solar Cells

MATERIALS ANALYSIS

- Ceramics
- Dielectrics
- Display Technologies
- Ferroelectric Materials
- Energy Devices and Ionic Conductors
- MEMs and NEMs
- Nanomaterials
- Organic Electronics
- Piezoelectric Materials
- Semiconductors and OFET

CORROSION

- Bare Metals
- Coatings
- Galvanic Corrosion
- Hydrogen Embrittlement
- Tribocorrosion
- Corrosion in Air

SIGNAL ANALYSIS

- Electronic Measurement
- Frequency Response Analyzer
- Magnetic Measurement
- Mechanical Testing
- Optical Engineering
- TOF-MS Time-of-Flight Mass Spectrometry
- Scanning Electrochemical Workstation

GENERAL AND PHYSICAL ELCHEM

- Electrochemical Sensors
- Nanotechnology
- Fundamental Electrochemistry Research
- Electroanalysis
- Electrosynthesis
- Electrodeposition
- extraction of metals, refining of metals
- Electroplating, electrocleaning
- production of chemicals

Electrochemistry

- Thermodynamics – kinetics – catalysis
- Faradaic/non-Faradaic processes, Ohmic drop, AC-DC
- Tafel – Faradaic/Non Faradaic – Nernst – Pourbaix
- Butler-Volmer, Gibbs

- 1.-2.-3. current distribution
- ELECTROCHEMICAL METHODS
- Electrochemistry is blind -> Raman in-situ as eyes
- Electrode pretreatment-roughness-crystallographic planes/catalysis
- Orders of magnitude aA-amol-aM, ml-mm³, detection limit-linear range

Difference Between Electronegativity and Electron Affinity

July 9, 2017 · by Madhusa · 7 min read



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Main Difference – Electronegativity vs Electron Affinity

An **electron** is a subatomic particle of an **atom**. Electrons are found everywhere since every matter is made up of atoms. However, electrons are very important in some chemical reactions because the exchange of electrons is the only difference between reactants and products in these reactions. Electronegativity and electron affinity are two terms

that explain the behavior of elements due to the presence of electrons. The main difference between electronegativity and electron affinity is that **electronegativity is the ability of an atom to attract electrons from outside** whereas **electron affinity is the amount of energy released when an atom gains an electron**.

1.3.1 Electrochemical Cells—Types and Definitions

VOLTAIC CELL
Energy is *released* from a spontaneous redox reaction.

System does work on surroundings.

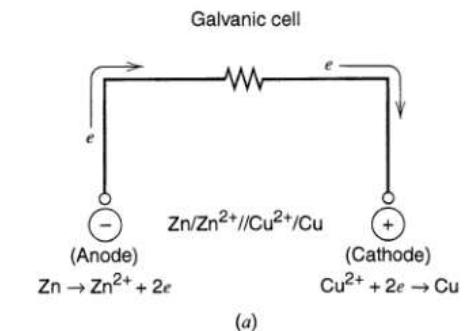
Anode (oxidation) \rightarrow Surroundings (Load) \rightarrow Cathode (reduction)

Electrolyte X^+ Electrolyte Y^+

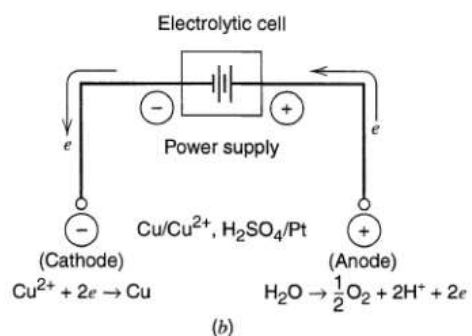
Oxidation half-reaction
 $X \rightarrow X^+ + e^-$

Reduction half-reaction
 $e^- + Y^+ \rightarrow Y$

Overall (cell) reaction
 $X + Y^+ \rightarrow X^+ + Y; \Delta G < 0$



Luigi Galvani
Alessandro Volta



ELECTROLYTIC CELL
Energy is *absorbed* to drive a nonspontaneous redox reaction.

Surroundings (power supply) do work on system (cell).

Anode (oxidation) \leftarrow Power supply \leftarrow Cathode (reduction)

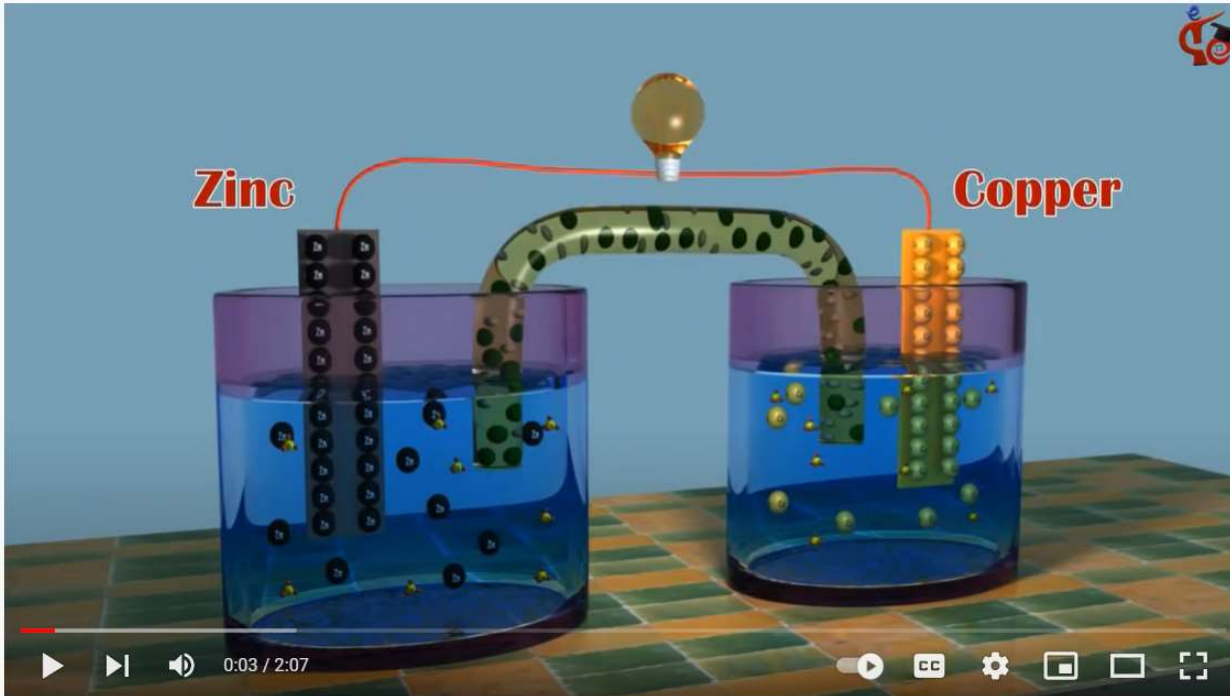
Electrolyte with A^- and B^+

Oxidation half-reaction
 $A^- \rightarrow A + e^-$

Reduction half-reaction
 $e^- + B^+ \rightarrow B$

Overall (cell) reaction
 $A^- + B^+ \rightarrow A + B; \Delta G > 0$

https://www.youtube.com/watch?v=C26pH8kC_Wk



0:03 / 2:07

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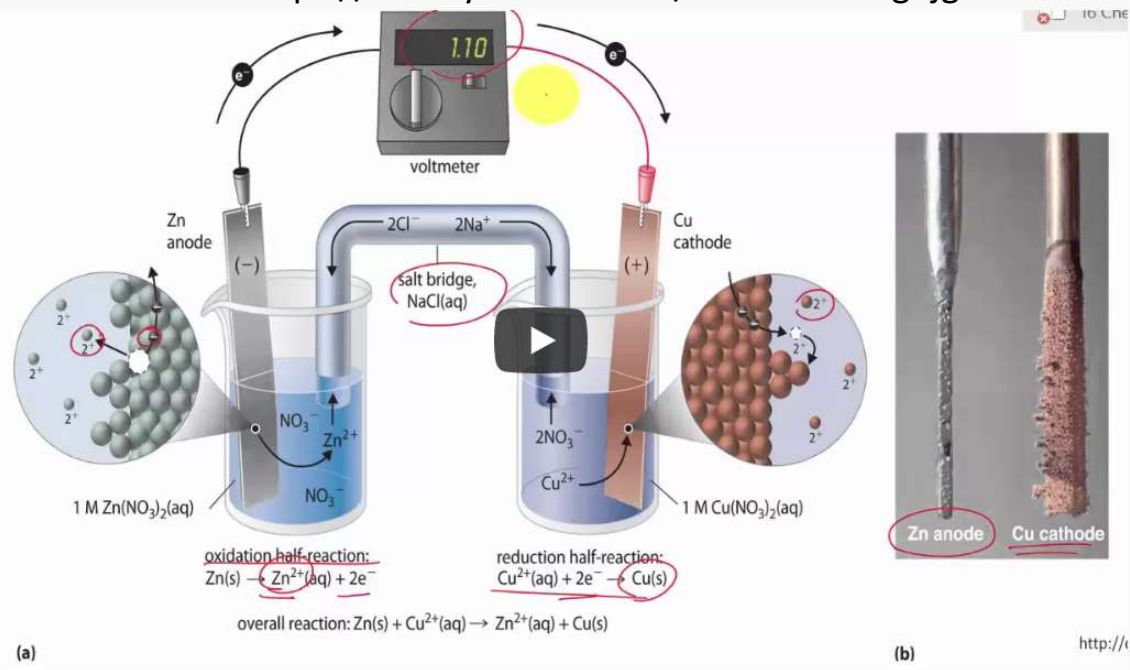
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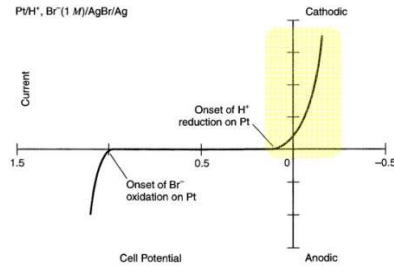
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1.1.2 Faradaic and Nonfaradaic Processes

- Two types of electrochemical processes

1) Faradaic process

- charges (e.g., electrons) are transferred across the metal-solution interface.
- Electron transfer causes oxidation or reduction to occur.
- Since these reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called faradaic processes.

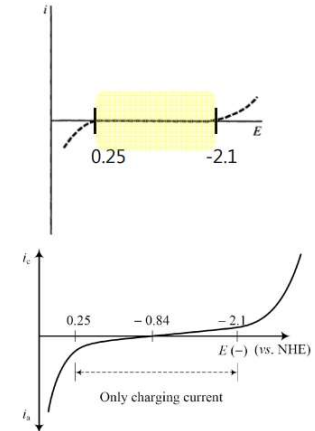


1.1.2 Faradaic and Nonfaradaic Processes

2) Nonfaradaic process

- In a specific range of potentials
- : charge-transfer reactions are thermodynamically or kinetically unfavorable
- no charge-transfer reactions occur
- However, processes such as adsorption and desorption can occur on the surface of electrodes
- Although charge does not cross the interface, external currents can flow (at least transiently) when the potential or solution composition changes.

- Nonfaradaic current: dependent on the surface area of electrodes and concentration of electrolytes
- Both faradaic and nonfaradaic processes can simultaneously occur when electrode reactions take place



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A Practical Beginner's Guide to Cyclic Voltammetry

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Supporting Information

ABSTRACT: Despite the growing popularity of cyclic voltammetry, many students do not receive formalized training in this technique as part of their coursework. Confronted with self-instruction, students can be left wondering where to start. Here, a short introduction to cyclic voltammetry is provided to help the reader with data acquisition and interpretation. Tips and common pitfalls are provided, and the reader is encouraged to apply what is learned in short, simple training modules provided in the Supporting Information. Armed with the basics, the motivated aspiring electrochemist will find existing resources more accessible and will progress much faster in the understanding of cyclic voltammetry.



KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Inorganic Chemistry, Analytical Chemistry, Distance Learning/Self Instruction, Inquiry-Based/Discovery Learning, Textbooks/Reference Books, Electrochemistry

INTRODUCTION

Motivation

Electron transfer processes are at the center of the reactivity of inorganic complexes. Molecular electrochemistry has become a

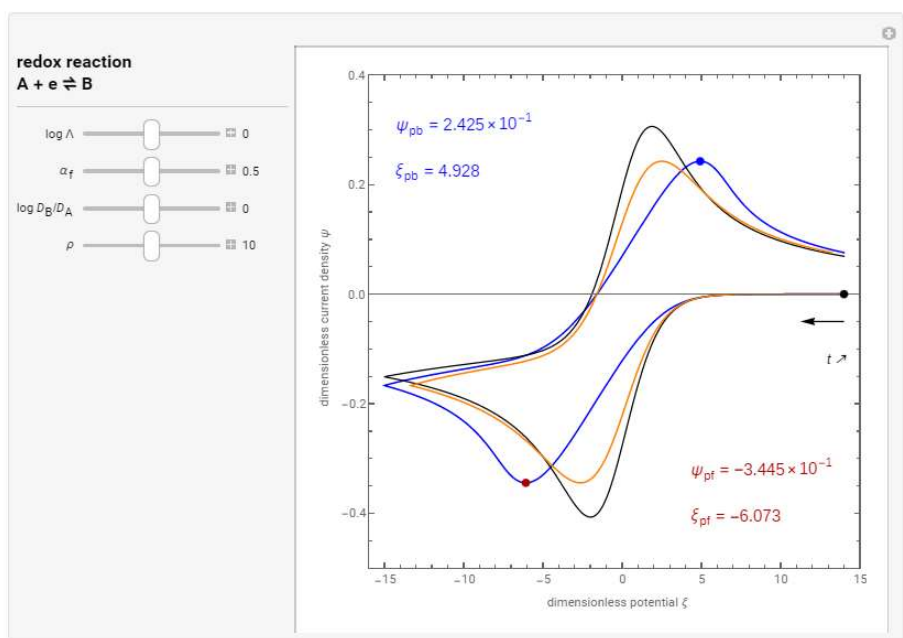
- At an electrode: $\text{Fc}^+ + e^- \rightleftharpoons \text{Fc}$

Why does $[\text{Co}(\text{Cp}^*)_2]$ (Cp^* = pentamethylcyclopentadienyl) reduce Fc^+ ? In the simplest explanation, an electron transfers from $[\text{Co}(\text{Cp}^*)_2]$ to Fc^+ because the lowest unoccupied molec-

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Cyclic Voltammetry Corrupted by Ohmic Drop BETA



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Instrumentation

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Cyclic Voltammetry - Data Analysis

The important parameters for a cyclic voltammogram are the peak potentials E_p and peak currents i_p (Fig1), which are measured using the Peak Parameters operation.

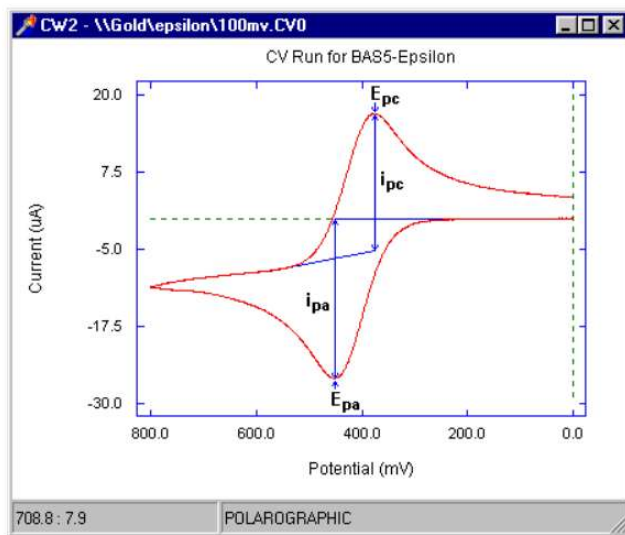


Figure 1. A typical cyclic voltammogram showing the important peak parameters.

If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be *reversible* (equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst equation). The following parameter values are used to characterize the cyclic voltammogram of a reversible process:

- the peak potential separation $\Delta E_p (= E_{pc} - E_{pa}) = 59.2/n$ mV at all scan rates at 25 °C.
- the peak current ratio = $i_{pa}/i_{pc} = 1$ at all scan rates
- the peak current function $i_p/v^{1/2}$ (v = scan rate) is independent of v (see equation for peak current)

The peak current is given by the equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2}$$

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Linear Sweep and Cyclic Voltametry: The Principles

- Department of Chemical Engineering and Biotechnology
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 - Electrode Kinetics
 - Mass Transport
 - Potential Step Voltammetry
 - Linear Sweep and Cyclic Voltametry: The Principles
 - Cyclic Voltametry: The Investigation

In this section two closely related forms of voltametry are introduced

- Linear Sweep Voltammetry
- Cyclic Voltametry

We shall see how these measurements can be employed to study the electron transfer kinetics and transport properties of electrolysis reactions.

Linear Sweep Voltammetry

In linear sweep voltammetry (LSV) a fixed potential range is employed much like potential step measurements. However in LSV the voltage is scanned from a lower limit to an upper limit as shown below.




<https://www.ceb.cam.ac.uk/research/groups/rg-eme/Edu/linear-sweep-and-cyclic-voltametry-the-principles>

CHE 729
Electrochemistry
Lecture 2
Voltammetry

Dr. Wujian Miao
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Reference Books



2

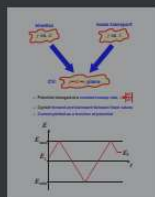
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1



2



3



CYCLIC Voltammetry

⇒ read more:


- C.M.A. Brett & A.M.O. Brett, “Electrochemistry”, Oxford University Press, Oxford, 1993 → **chapter 9**

- E. Gileadi, “Electrode Kinetics for Chemists, Chemical Engineers and Materials Scientists”, VCH, Weinheim, 1993 → **chapter 25**

<http://www.sfu.ca/~aroudgar/Tutorials/lecture27-31.pdf>

7.5: Voltammetric Methods

 Last updated: Jun 9, 2020

 Thomas Wenzel
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Voltammetry refers to electrochemical methods in which a specific voltage profile is applied to a working electrode as a function of time and the current produced by the system is measured. This is commonly done with an instrument called a potentiostat, which for these measurements is capable of applying variable potentials to the working electrode relative to a reference electrode (like Ag/AgCl) while measuring the current that flows as a result of the electrode reaction. Depending on the particular method, it is possible to apply reducing and/or oxidizing potentials. When a reduction occurs, the current is called a cathodic current. When an oxidation occurs, the current is called an anodic current. Different voltammetric methods involve different voltage profiles. Voltammetric methods are among some of the most common electrochemical methods in use today. There are a variety of voltammetric methods. This unit will only explore three of these methods: anodic stripping voltammetry (ASV), linear sweep voltammetry, and cyclic voltammetry (CV).

Voltammetric methods typically involve the use of microelectrodes that frequently have areas on the order of 0.3-10 cm². Originally it was common to use mercury electrodes often as a hanging mercury drop (HMDE) or as drops through a glass capillary (DME) for voltammetric methods. Mercury had several desirable properties in electrode applications. One advantage of mercury is that it has a high overvoltage toward the reduction of H⁺ so it can be used at high reducing potentials in water without leading to the electrochemical splitting of water into hydrogen and oxygen gas. A second advantage of mercury electrodes is that metals dissolve in mercury by forming amalgams, which improves the measurement of low concentrations of analytes. A concern with electrodes is that mercury can become fouled or the surface of a solid electrode can become poisoned, which significantly alters their properties. This can occur if species in the matrix adsorb to the surface of the electrode. Solid electrodes usually are put through a prescribed polishing procedure before used for measurement purposes, while mercury drops can easily be replaced through a glass capillary.



Introduction.

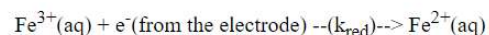
This experiment is offered as an alternative [Lab #4](#). If you find this experiment more interesting and at least another student who shares your choice, you should **discuss it with the instructor on the last day of your Lab #1 or #2** whichever comes last. No switching will be allowed after that.

Objective: In this lab you will study the **cyclic voltammetry** technique and measure redox potentials of a few compounds.

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of **redox potentials** of the electroactive species, and convenient evaluation of the effect of media upon the redox process.

Potential Step Voltammetry

Let us begin by discussing what happens near an **electrode** in a polar solution (water or other highly polar solvent) with high concentration of a **background electrolyte** (an electrochemically inert salt such as NaCl or tetra butylammonium perchlorate, TBAP; usually added in high concentration $\sim 0.1\text{M}$ to allow the current to pass). If an **analyte or reactant**, say $\text{Fe}^{3+}(\text{aq})$, is present at a low concentration (*ca.* 10^{-3}M), its distribution near the electrode surface is initially uniform (see picture to the right). If at time zero a voltage sufficient to initiate electrochemical reaction is applied, a current starts flowing due to the reaction:



The concentration of $\text{Fe}^{3+}(\text{aq})$ near the electrode will gradually decline and thus the current will decrease in time as well (see Figure to the right).

$$\delta[\text{Fe}^{3+}]\delta t = D\delta^2[\text{Fe}^{3+}]\delta t^2 \quad (1)$$

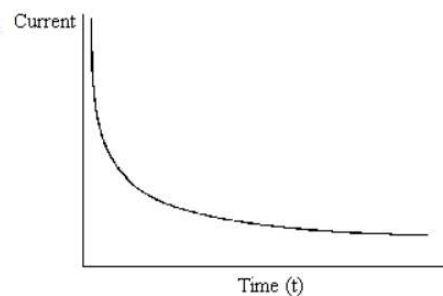
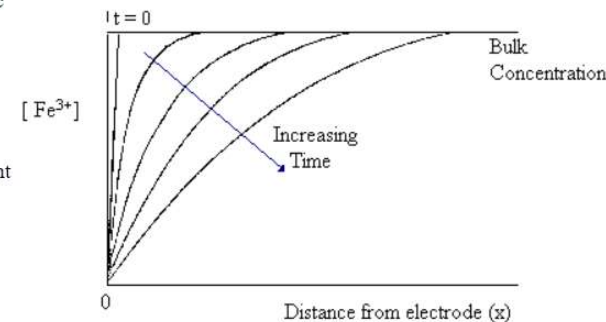
$$i_c = -nFAk_{\text{red}}[\text{Fe}^{3+}]_{\text{surface}} \quad (2)$$

$$|i_c| = nFAk_{\text{red}}[\text{Reactant}]_{\text{bulk}}(D/\pi t)^{1/2} \quad (3)$$

Linear Sweep Voltammetry (LSV)

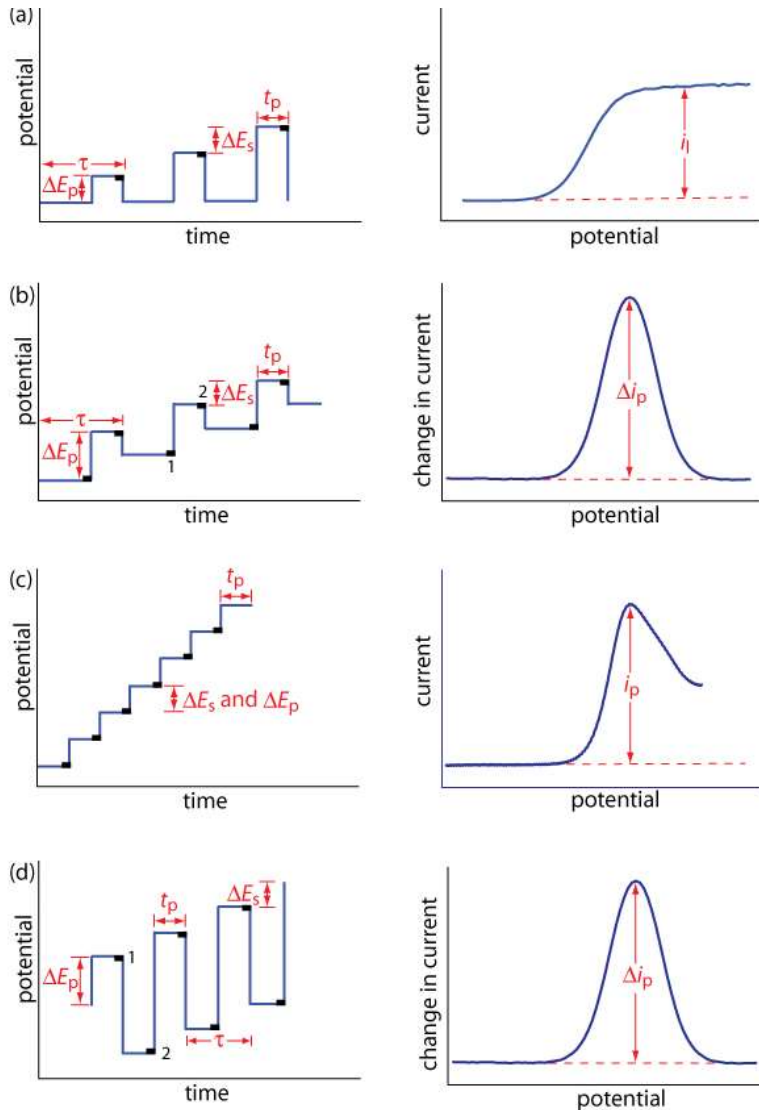
Voltage

Now let us assume that the voltage is changed from value V_1 (where electrochemical reaction of interest is thermodynamically unfavorable) to a value V_2 linearly increasing in time (see



<https://web.nmsu.edu/~snsnsm/classes/chem435/Lab13/intro.html>

Various elchem techniques

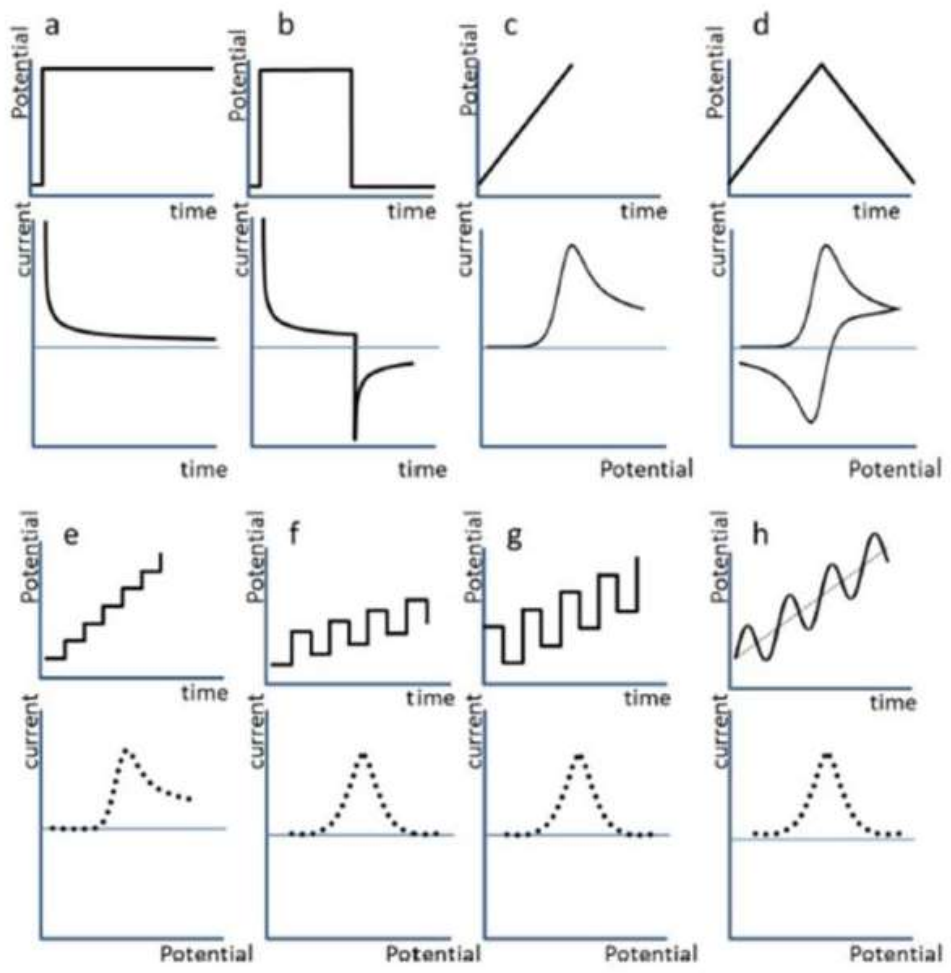


Normal pulse polarography (a), for example, uses a series of potential pulses characterized by a cycle of time of τ , a pulse-time of t_p , a pulse potential of ΔE_p , and a change in potential per cycle of ΔE_s . Typical experimental conditions for normal pulse polarography are $\tau \approx 1$ s, $t_p \approx 50$ ms, and $\Delta E_s \approx 2$ mV. The initial value of ΔE_p is ≈ 2 mV, and it increases by ≈ 2 mV with each pulse. The current is sampled at the end of each potential pulse for approximately 17 ms before returning the potential to its initial value. The shape of the resulting voltammogram is similar to that of normal polarography, but without the current oscillations. Because we apply the potential for only a small portion of the drop's lifetime, there is less time for the analyte to undergo oxidation or reduction and a smaller diffusion layer. As a result, the faradaic current in normal pulse polarography is greater than in the polarography, resulting in better sensitivity and smaller detection limits.

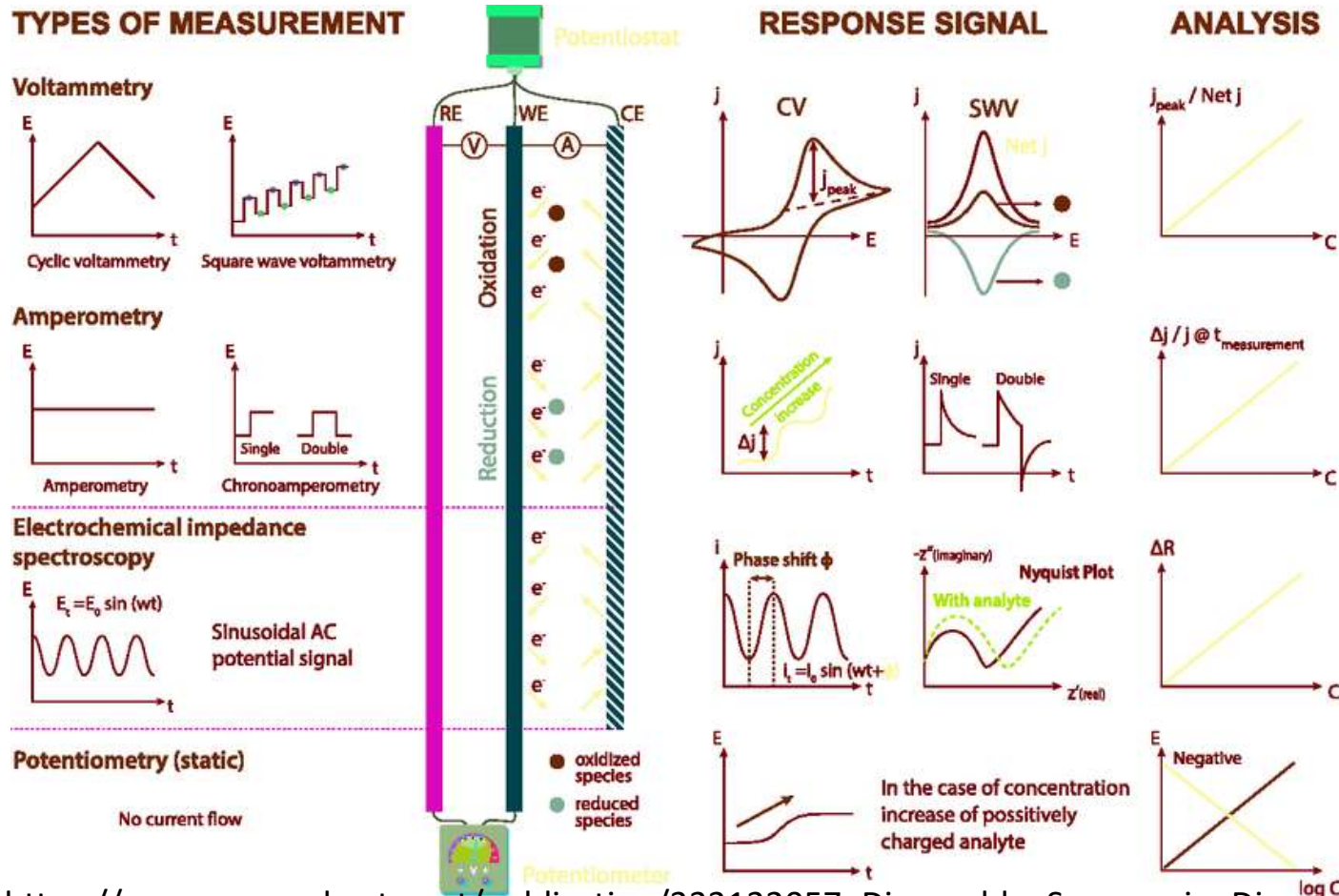
In differential pulse polarography (b) the current is measured twice per cycle: for approximately 17 ms before applying the pulse and for approximately 17 ms at the end of the cycle. The difference in the two currents gives rise to the peak-shaped voltammogram. Typical experimental conditions for differential pulse polarography are $\tau \approx 1$ s, $t_p \approx 50$ ms, $\Delta E_p \approx 50$ mV, and $\Delta E_s \approx 2$ mV.

Various elchem techniques

| Technique | Imposed function | Recorded function | Conc. range (mole L) |
|---|------------------|-------------------|----------------------|
| Linear sweep voltammetry (LSV) (cyclic voltammetry dotted line) | | | $10^{-2} - 10^{-6}$ |
| Differential pulse voltammetry (DPV) | | | $10^{-4} - 10^{-7}$ |
| Square wave voltammetry (SWV) | | | $10^{-4} - 10^{-8}$ |
| Anodic Stripping Voltammetry (ASV) with linear scan (full line) or modulations (e.g. DP → DPASV or SW → SWASV; dotted line) | | | $10^{-6} - 10^{-11}$ |
| Adsorptive stripping voltammetry (AdSV) (with or without modulation) | | | $10^{-6} - 10^{-12}$ |
| Stripping Chronopotentiometry (SCP) | | | $10^{-5} - 10^{-9}$ |



Various elchem techniques



Electrochemical signal transduction. There are four main types of electrochemical methods of analysis: voltammetry, amperometry, electrochemical impedance spectroscopy (EIS), and potentiometry. In voltammetry, a potential sweep (linear, cyclic, i.e., cyclic voltammetry (CV), or pulsed, e.g., square-wave voltammetry (SWV)) with respect to the reference electrode (RE) is applied by a potentiostat (an electronic instrument) between the working (WE) and counter (CE) electrodes and the current generated is measured as the analytical signal. In amperometry, a constant or stepped (chronoamperometry) potential is employed instead. In potentiometry, the open-circuit voltage between the WE and RE is measured as the analytical signal which can increase or decrease depending on concentration of the analyte. In EIS, a sinusoidal potential over a frequency range is applied to an electrochemical cell. By measuring the current response, the impedance (resistance, capacitance etc.) of the system can be estimated, allowing the study of the surface and material properties.

https://www.researchgate.net/publication/333132057_Disposable_Sensors_in_Diagnostics_Food_and_Environmental_Monitoring/figures?lo=1

Various elchem techniques

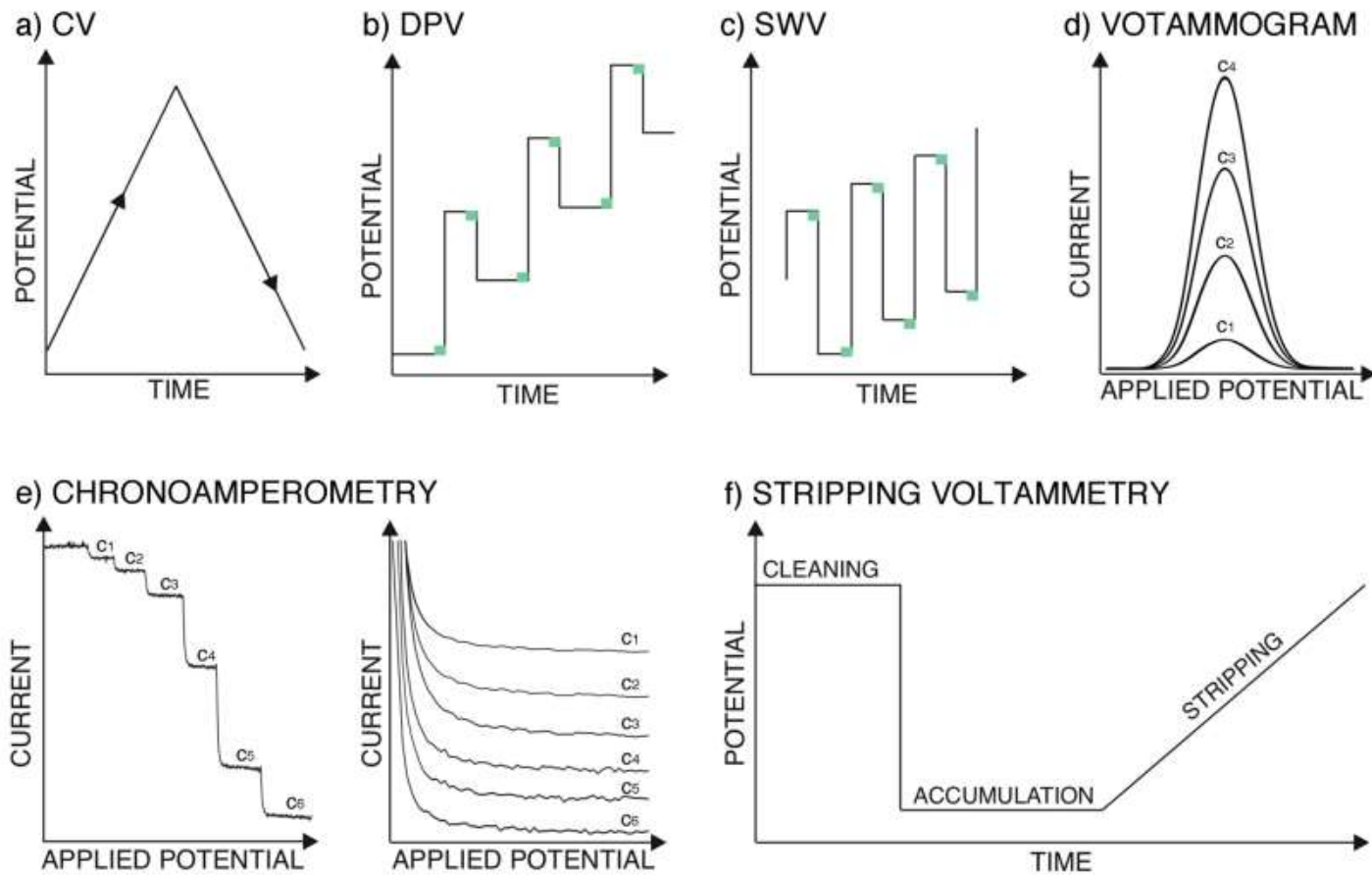
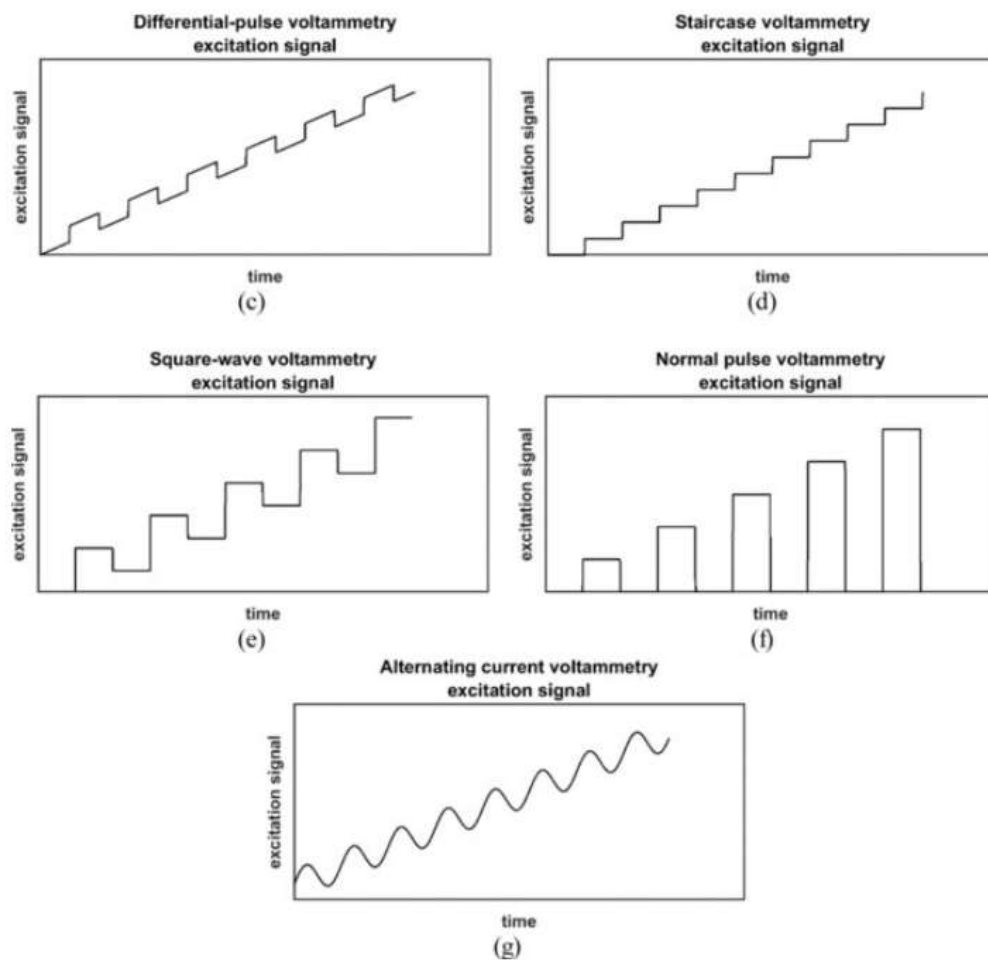


Fig. 2. Schemes for the applied potential in (a) cyclic voltammetry (CV), (b) differential pulse voltammetry (DPV) and (c) square-wave voltammetry (SWV). (d) Voltammetric peak increasing with the analyte concentration. (e) Time traces for the current in chronoamperometry upon subsequent (left) and isolated (right) concentration additions of the analyte. (f) Example of the variation of the applied potential in stripping voltammetry.

Various elchem techniques



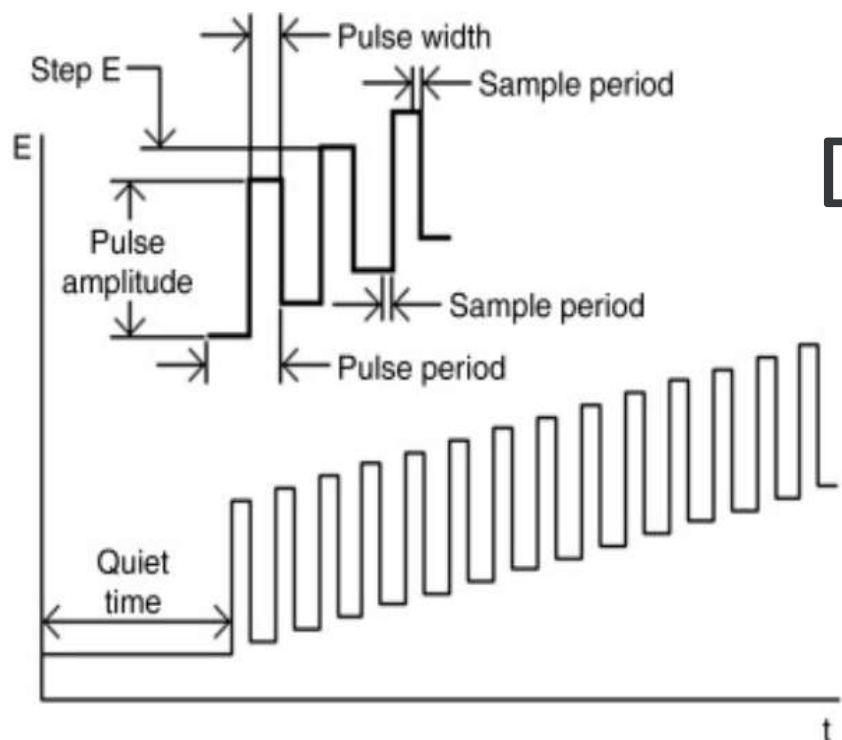
Figure

Caption

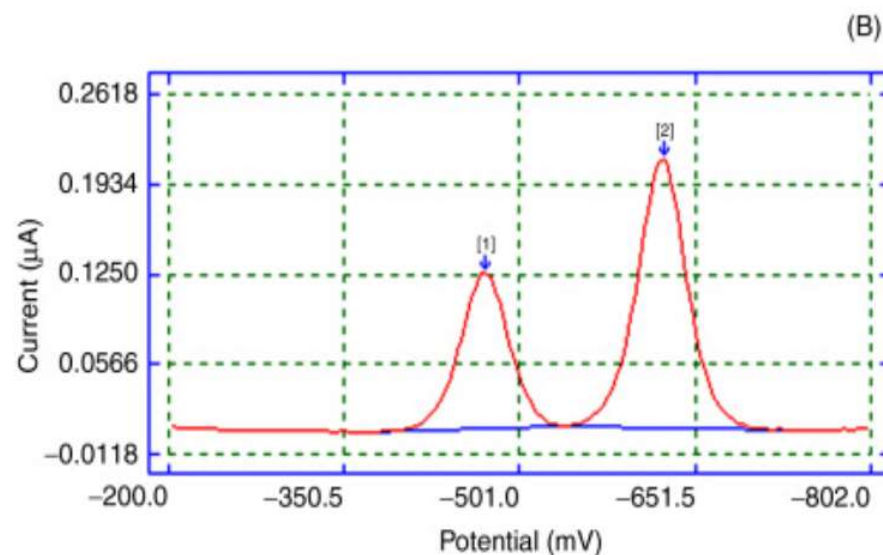
Fig. 5. Comparing excitation signals of all types of voltammetry techniques. (a) Linear sweep, Rotated Electrode, and Polarography voltammetry, (b) Cyclic voltammetry, (c) Differential-pulse voltammetry, (d) Staircase voltammetry, (e) Square-wave voltammetry, (f) Normal pulse voltammetry, (g) Alternating current voltammetry.

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(A) DPV

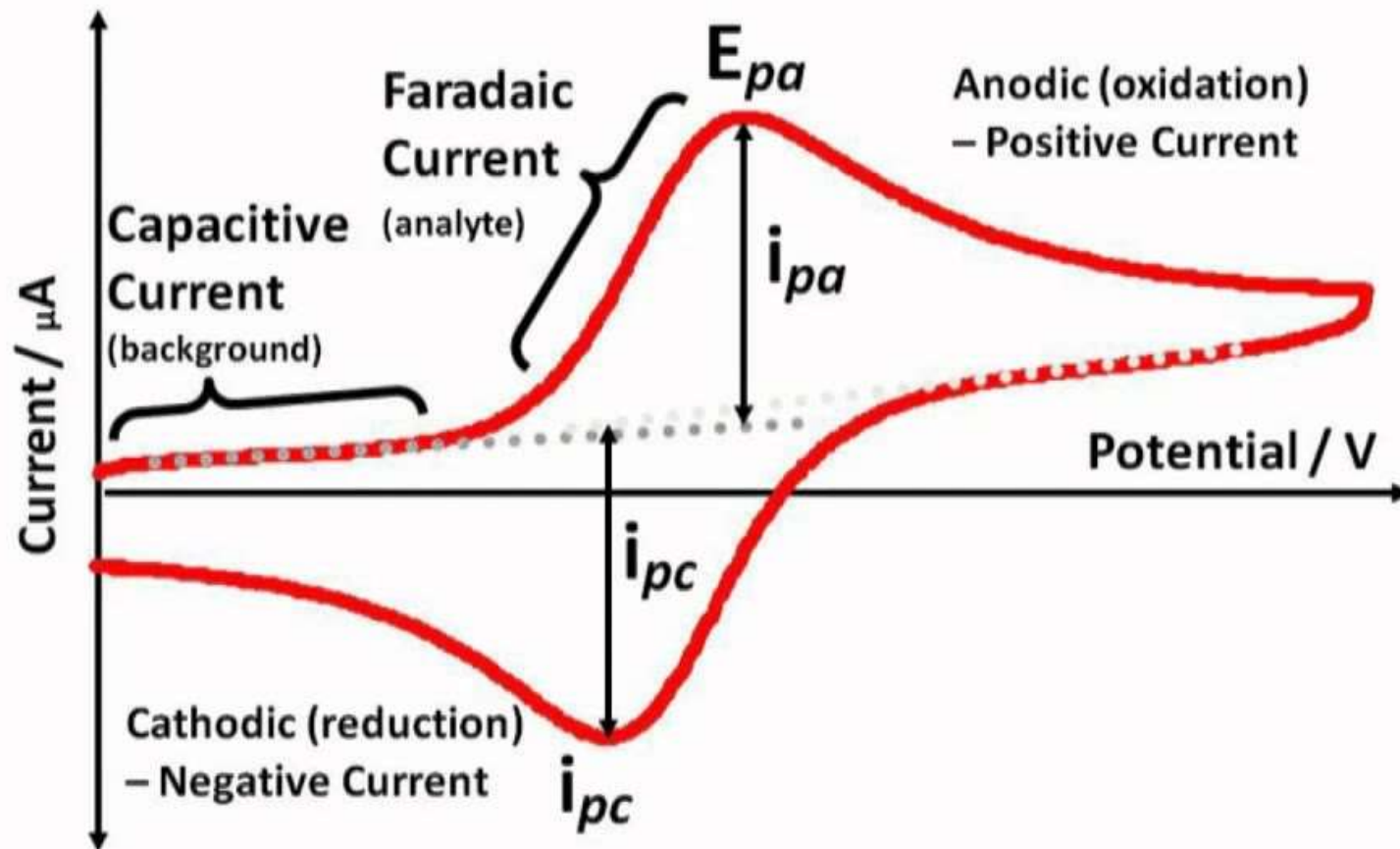


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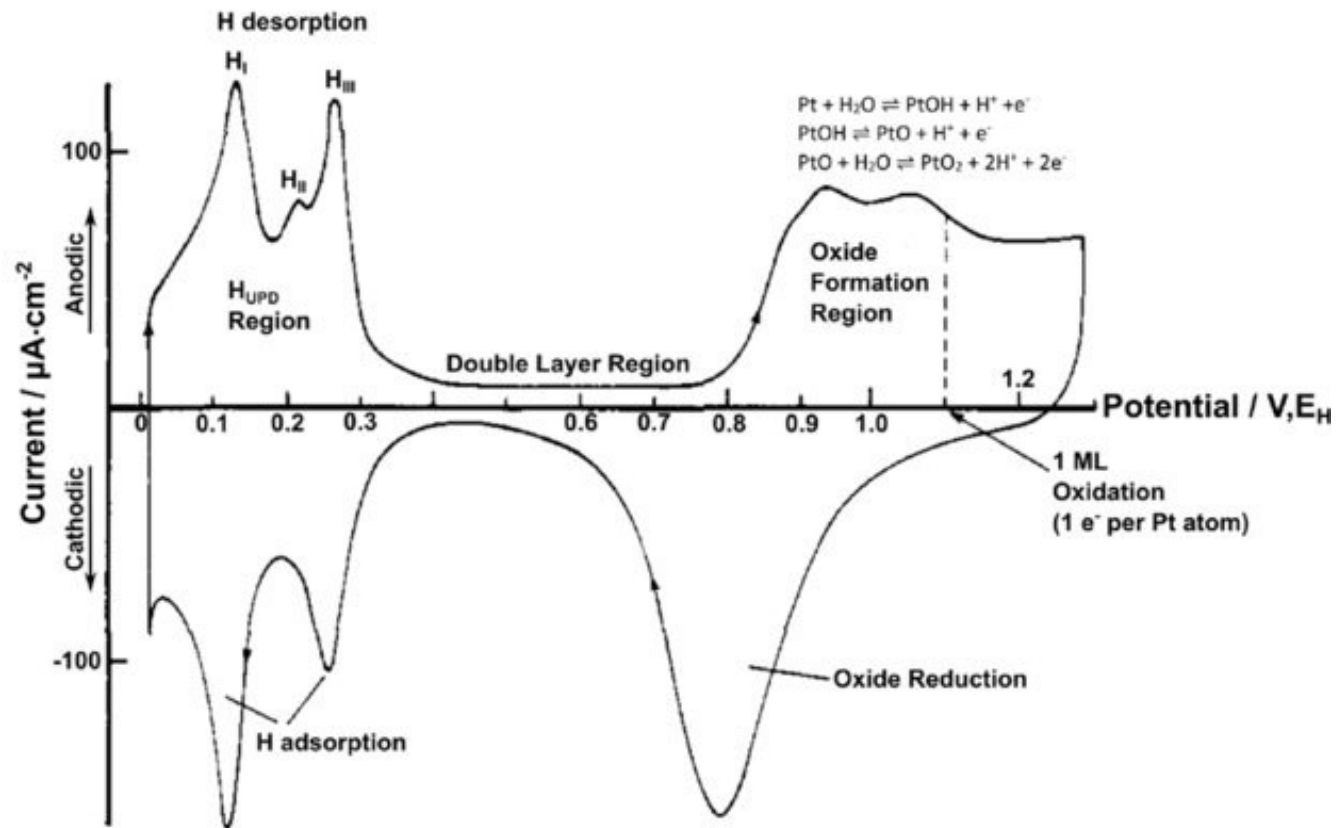
Figure 28.9. (A) Potential wave form for differential pulse voltammetry. (B) A typical differential pulse voltammogram.

In differential pulse voltammetry (DPV), small amplitude, short pulses are superimposed on a linear ramp. Current is measured before the application of the pulse and at the end of each pulse, and the difference between the currents is calculated. This procedure effectively reduces the background current due to the DC ramp, and thus this procedure results in a Faradaic current free of most capacitive current. The major advantage of [DPV](#) is low capacitive current, which leads to high sensitivity. The small step sizes in DPV also lead to narrower voltammetric peaks and thus DPV is often used to discriminate analytes that have similar [oxidation](#) potentials.

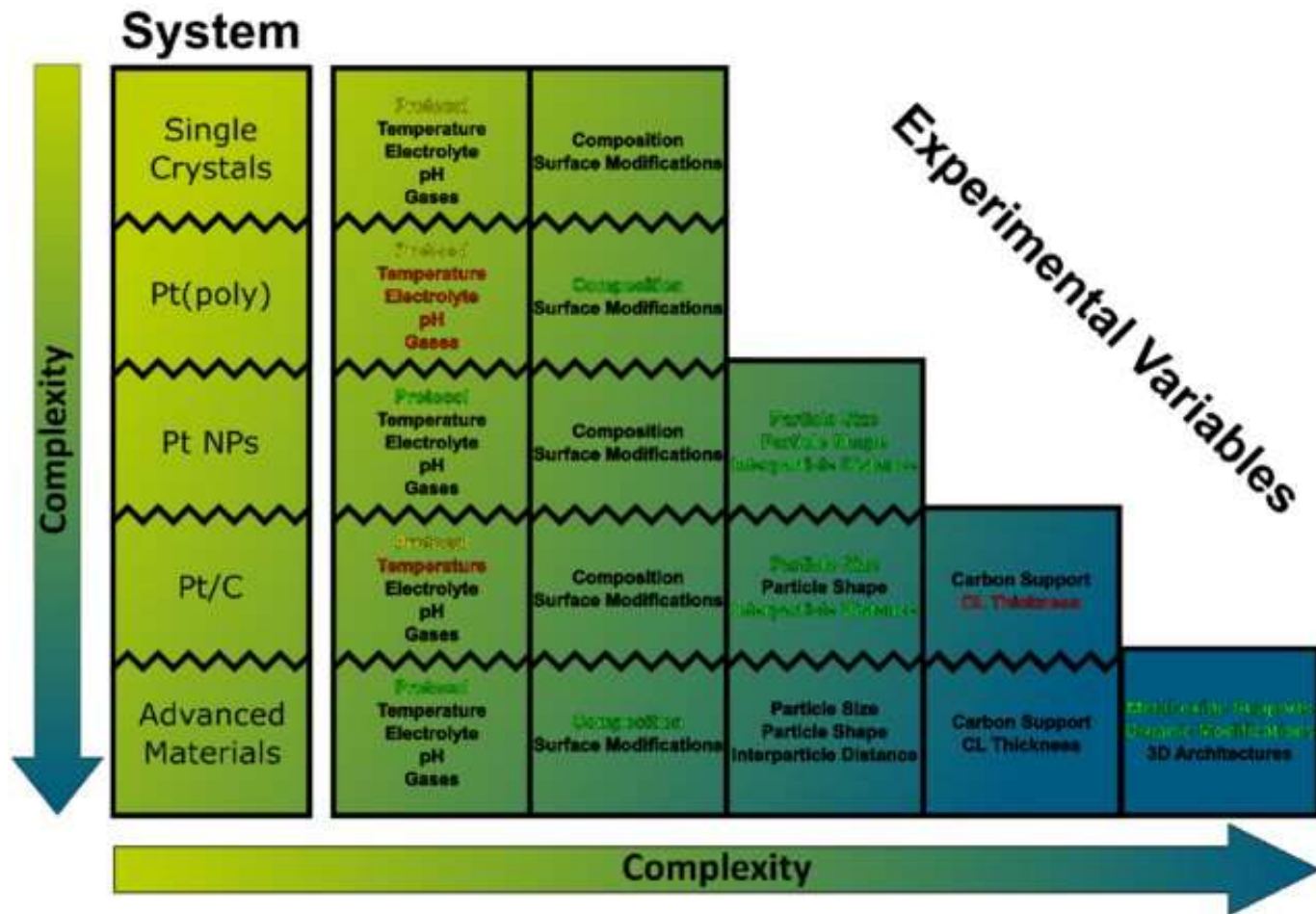
Cyclic Voltammogram



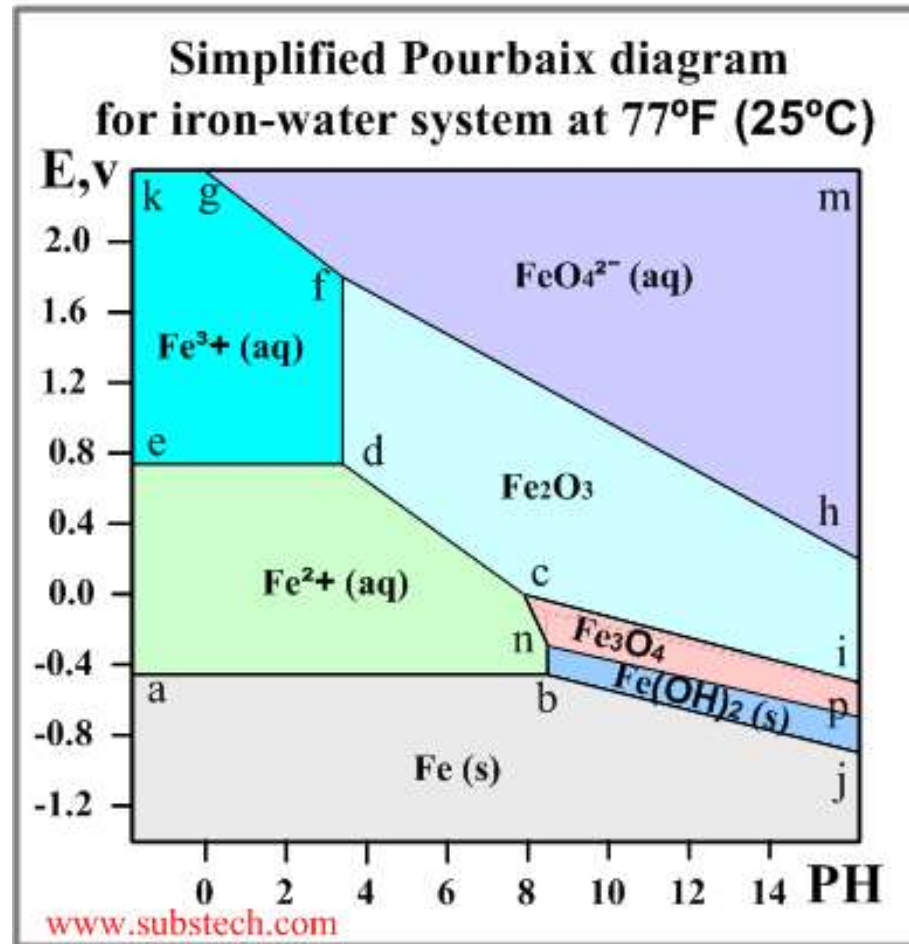
Pt CV in acid



System complexity



Pourbaix diagram



Possible reactions in the Fe-H₂O system

1. $2 e^- + 2H^+ = 1H_2$
2. $4 e^- + 1O_2 + 4H^+ = 2H_2O$
3. $2 e^- + 1Fe(OH)_2 + 2H^+ = 1Fe + 2H_2O$
4. $2 e^- + 1Fe^{2+} = 1Fe$
5. $2 e^- + 1Fe(OH)_3 + 3H^+ = 1Fe + 3H_2O$
6. $1 e^- + 1Fe(OH)_3 + 1H^+ = 1Fe(OH)_2 + 1H_2O$
7. $1 e^- + 1Fe(OH)_3 + 3H^+ = 1Fe^{2+} + 3H_2O$
8. $1Fe(OH)_3 + 1H^+ = 1Fe(OH)_2 + 1H_2O$
9. $1 e^- + 1Fe(OH)_3 = 1Fe(OH)_3^-$
10. $1Fe^{3+} + 3H_2O = 1Fe(OH)_3 + 3H^+$
11. $1Fe^{2+} + 2H_2O = 1Fe(OH)_2 + 2H^+$
12. $1 e^- + 1Fe^{3+} = 1Fe^{2+}$
13. $1Fe^{2+} + 1H_2O = 1FeOH^+ + 1H^+$
14. $1FeOH^+ + 1H_2O = 1Fe(OH)_2(sln) + 1H^+$
15. $1Fe(OH)_2(sln) + 1H_2O = 1Fe(OH)_3^- + 1H^+$
16. $1Fe^{3+} + 1H_2O = 1FeOH^{2+} + 1H^+$
17. $1FeOH^{2+} + 1H_2O = 1Fe(OH)_2^+ + 1H^+$
18. $1Fe(OH)_2^+ + 1H_2O = 1Fe(OH)_3(sln) + 1H^+$
19. $1FeOH^{2+} + 1H^+ = 1Fe^{2+} + 1H_2O$
20. $1 e^- + 1Fe(OH)_2^+ + 2H^+ = 1Fe^{2+} + 2H_2O$
21. $1 e^- + 1Fe(OH)_3(sln) + 1H^+ = 1Fe(OH)_2(sln) + 1H_2O$
22. $1 e^- + 1Fe(OH)_3(sln) + 2H^+ = 1FeOH^+ + 2H_2O$
23. $1 e^- + 1Fe(OH)_3(sln) + 3H^+ = 1Fe^{2+} + 3H_2O$

Lecture Note By: Dr.S.P

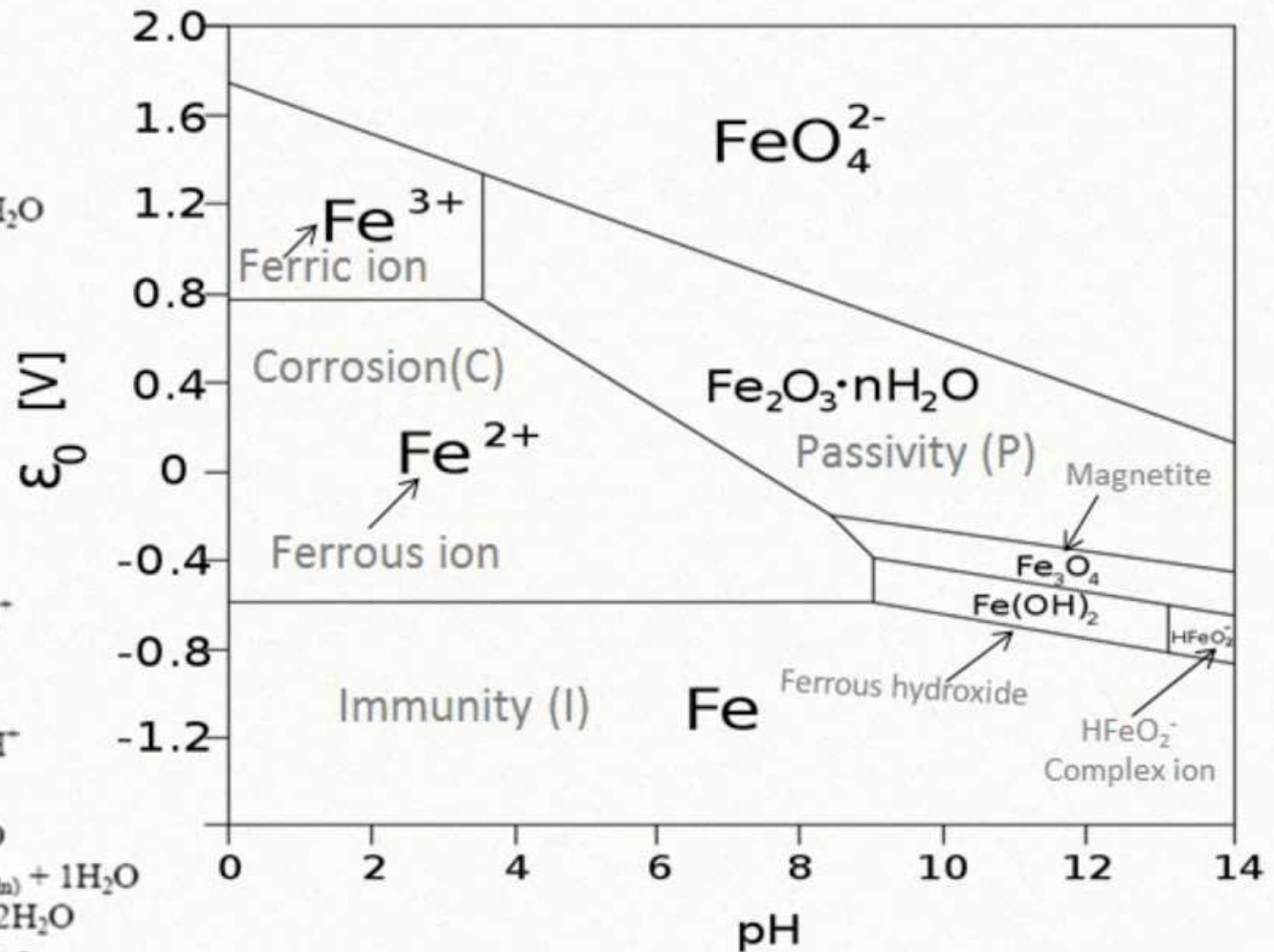


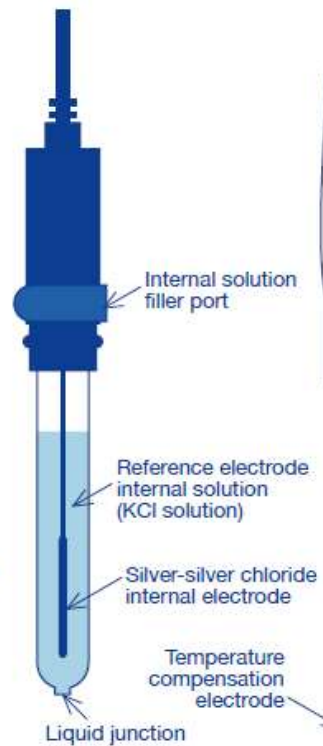
Fig: Potential pH diagram for iron at 25°C

pH electrodes

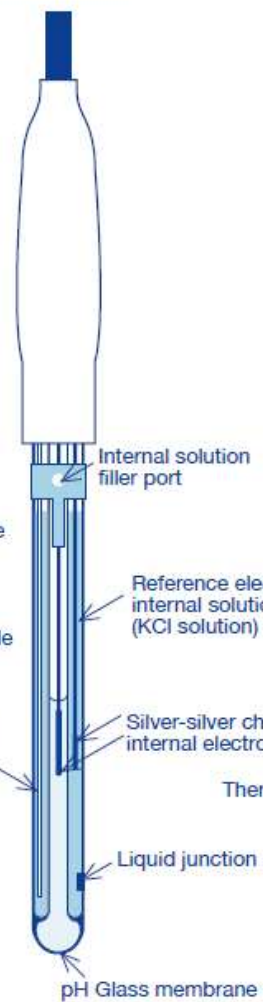
Glass Electrode



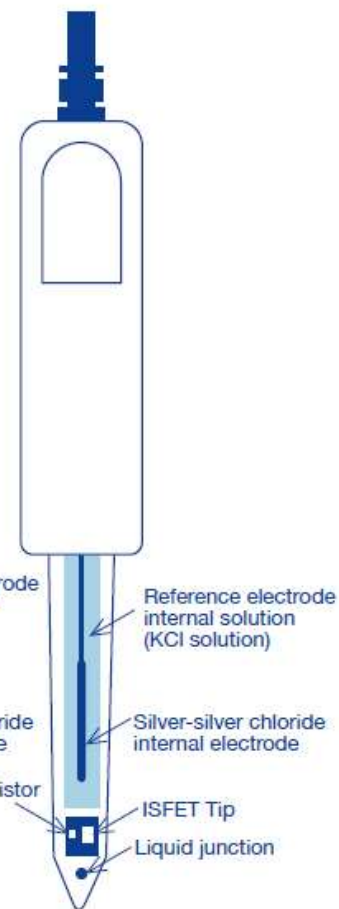
Reference Electrode



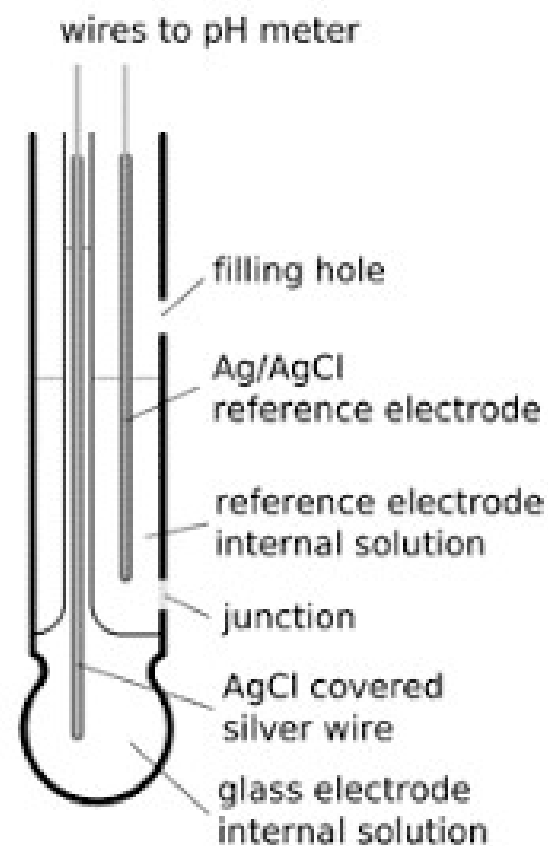
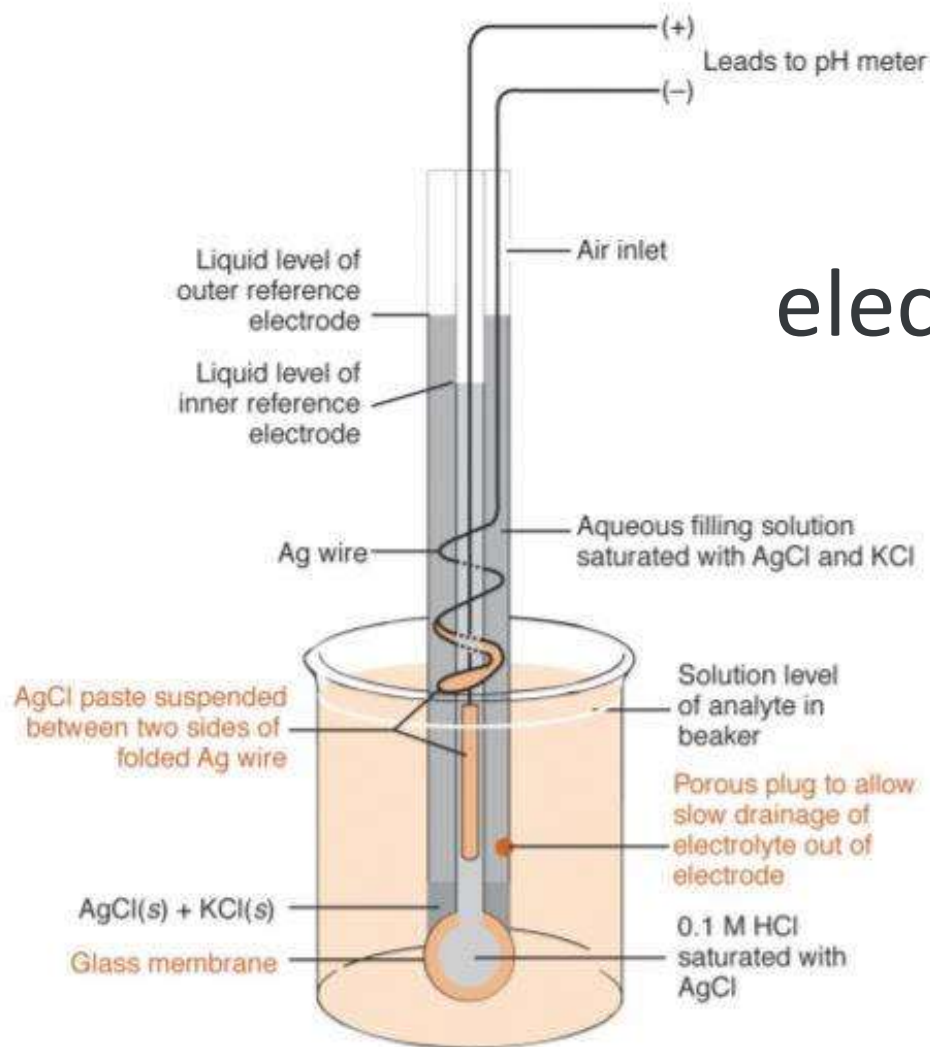
Combination Electrode



ISFET



pH electrodes



Chemical kinetics vs Thermodynamic

| Chemical Kinetics vs Thermodynamics | | |
|-------------------------------------|---|--|
| | More Information Online WWW.DIFFERENCEBETWEEN.COM | |
| | Chemical Kinetics | Thermodynamics |
| DEFINITION | Chemical kinetics is the branch of physical chemistry that deals with the rates of chemical reactions | Thermodynamics is the branch of physical science that deals with the relations between heat and other forms of energy such as mechanical, electrical, or chemical energy |
| DESCRIPTION | Describes the chemical reaction rate | Describes the direction of chemical reaction |
| USE | To determine the characteristics of the reaction | To predict the relations between heat and other forms of energy such as mechanical, electrical, or chemical energy |

What is Chemical Kinetics?

The term chemical kinetics refers to the branch of physical chemistry that deals with the rates of chemical reactions. It is also known as **reaction kinetics**. This term is described in contrast to thermodynamics. (Thermodynamics deal with the direction in which a process occurs).

What is Thermodynamics?

Thermodynamics can be described as the branch of physical science that deals with the relations between heat and other forms of energy such as mechanical, electrical, or chemical energy. This phenomenon explains the relationship between all energy forms. The main idea of thermodynamics is the association of heat with work done by or on a system.

<https://web.stanford.edu/~kaleeg/chem32/kinT/>

Thermodynamic

Thermodynamics should be called "thermostatics." Thermodynamics is not about things moving and changing but instead about how stable they are in one state versus another, while kinetics is about how quickly or slowly species react. It is dangerously easy to confuse thermodynamic quantities like free energy with kinetic ones like activation energy.

There are several important terms in thermodynamics, as listed below.

1. Enthalpy – the total energy content of a thermodynamic system
2. Entropy – a thermodynamic expression explaining the inability of a thermodynamic system to convert its thermal energy into mechanical energy
3. Thermodynamic state – the state of a system at a given temperature
4. Thermodynamic equilibrium – the state of a thermodynamic system being in equilibrium with one or more other thermodynamic systems
5. Work – the amount of energy that is transferred to the surrounding from a thermodynamic system.
6. Internal energy – the total energy of a thermodynamic system that is caused by the motion of molecules or atoms in the system.

Furthermore, thermodynamics includes a set of laws.

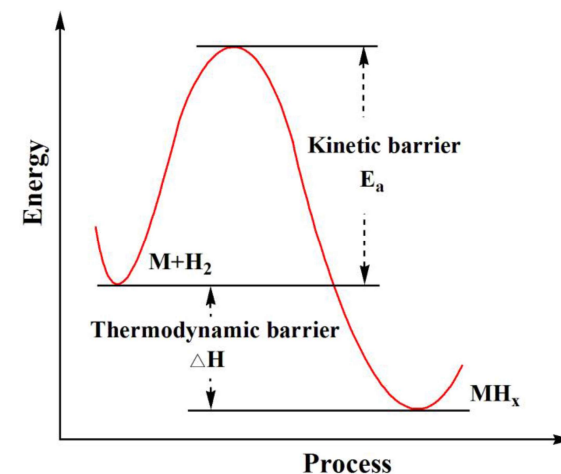
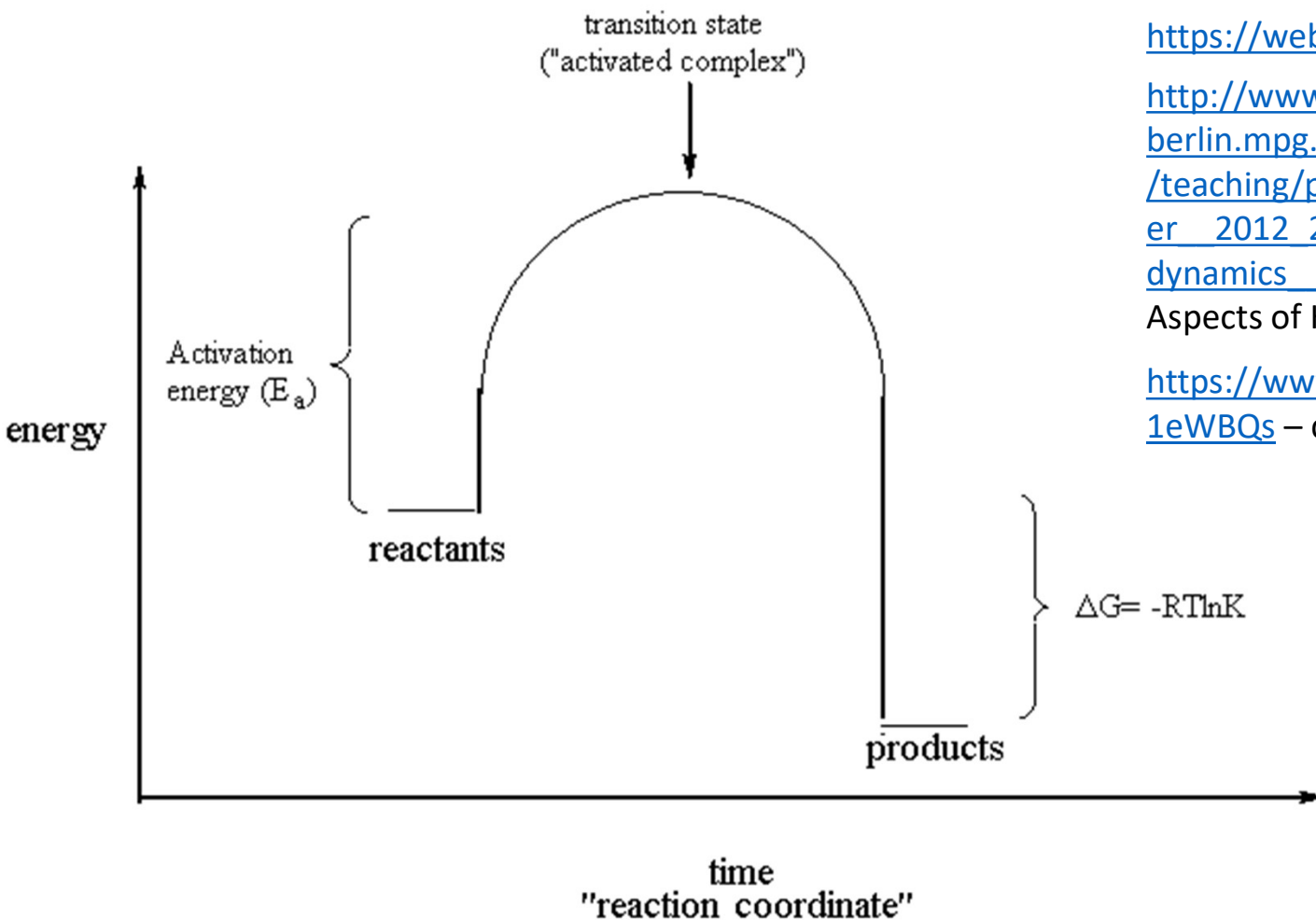
1. Zeroth Law of Thermodynamics – When two thermodynamic systems are in thermal equilibrium with a third thermodynamic system, all three systems are in thermal equilibrium with each other.
2. First Law of Thermodynamics – The internal energy of a system is the difference between the energy it absorbs from the surroundings and the work done by the system on the surrounding.
3. Second Law of Thermodynamics – Heat cannot flow from a colder location to a hotter area spontaneously.
4. Third Law of Thermodynamics – As a system approach absolute zero, all processes cease, and the entropy of the system becomes minimum.

Energy of the reaction

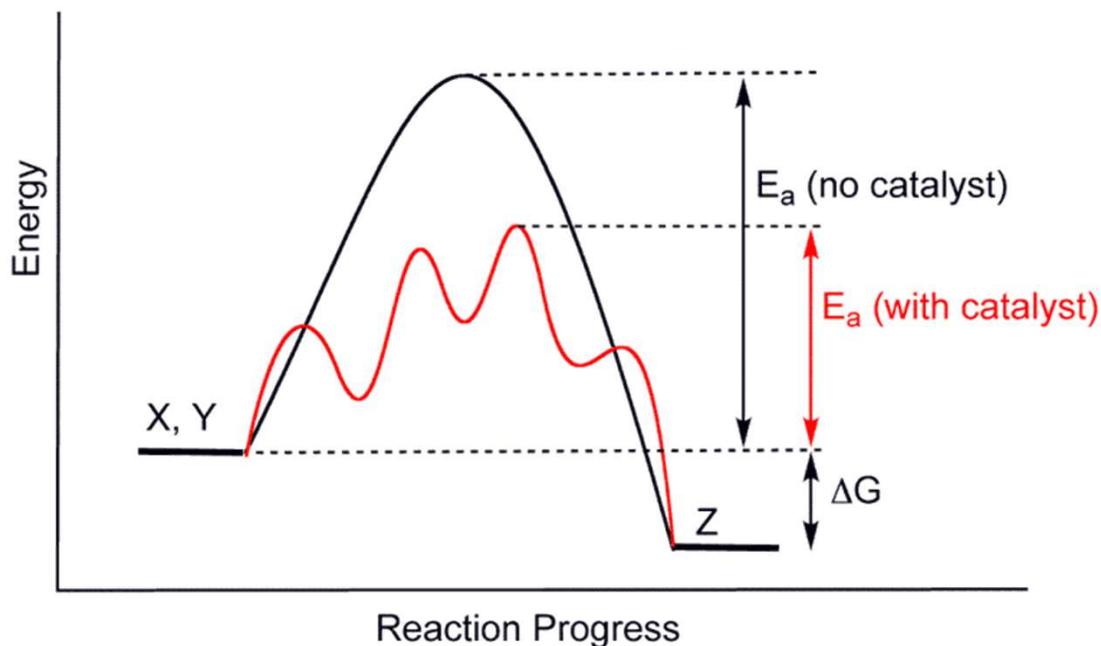
<https://web.stanford.edu/~kaleeg/chem32/kinT/>

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching_wintersemester_2012_2013/raimund_horn_thermodynamics_121026.pdf - Thermodynamic Aspects of Heterogeneous Catalysis

<https://www.youtube.com/watch?v=IWlb31eWBQs> – catalysis and thermodynamics

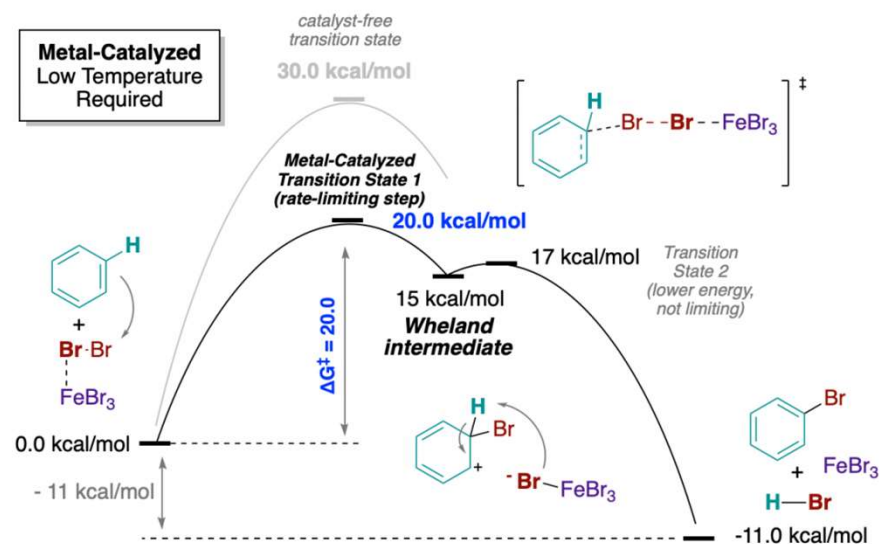


Catalysis



Catalysis is a term describing a process in which the rate and/or the outcome of the reaction is influenced by the presence of a substance (the catalyst) that is not consumed during the reaction and that is subsequently removed if it is not to constitute as an impurity in the final product.

Catalysts increase the rate of a reaction without undergoing any chemical or physical change. Catalysts just decrease the energy barrier for the conversion of reactants to products.

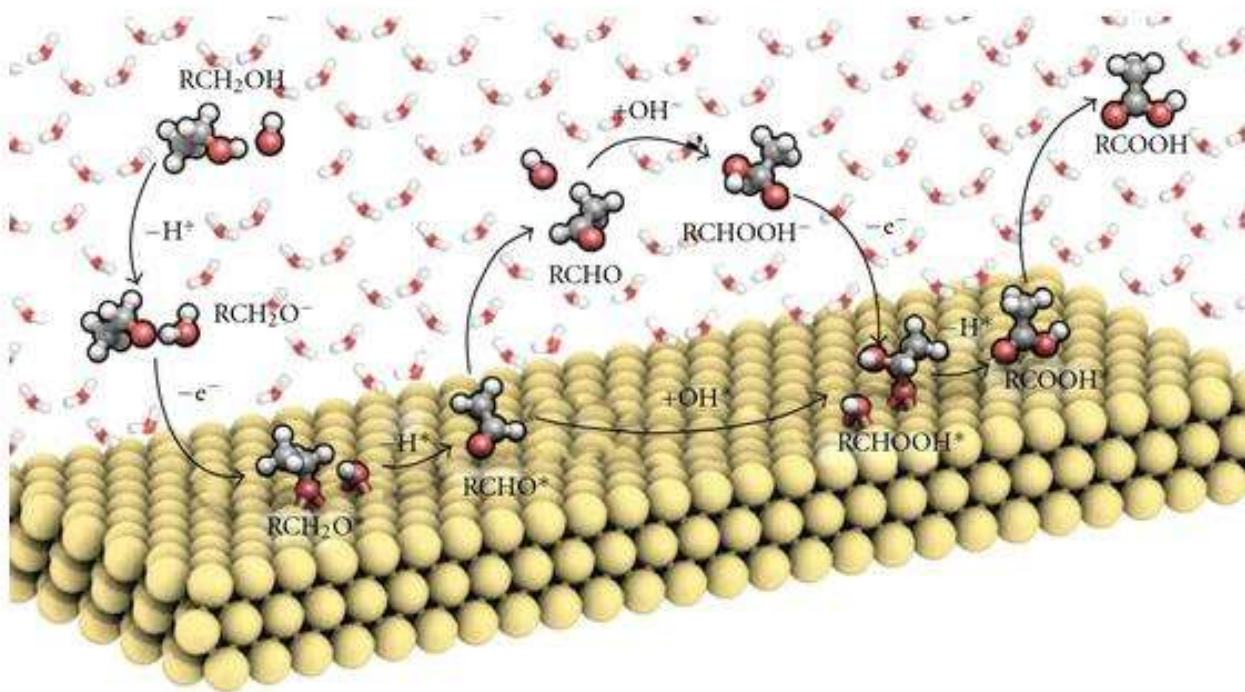


Catalysis

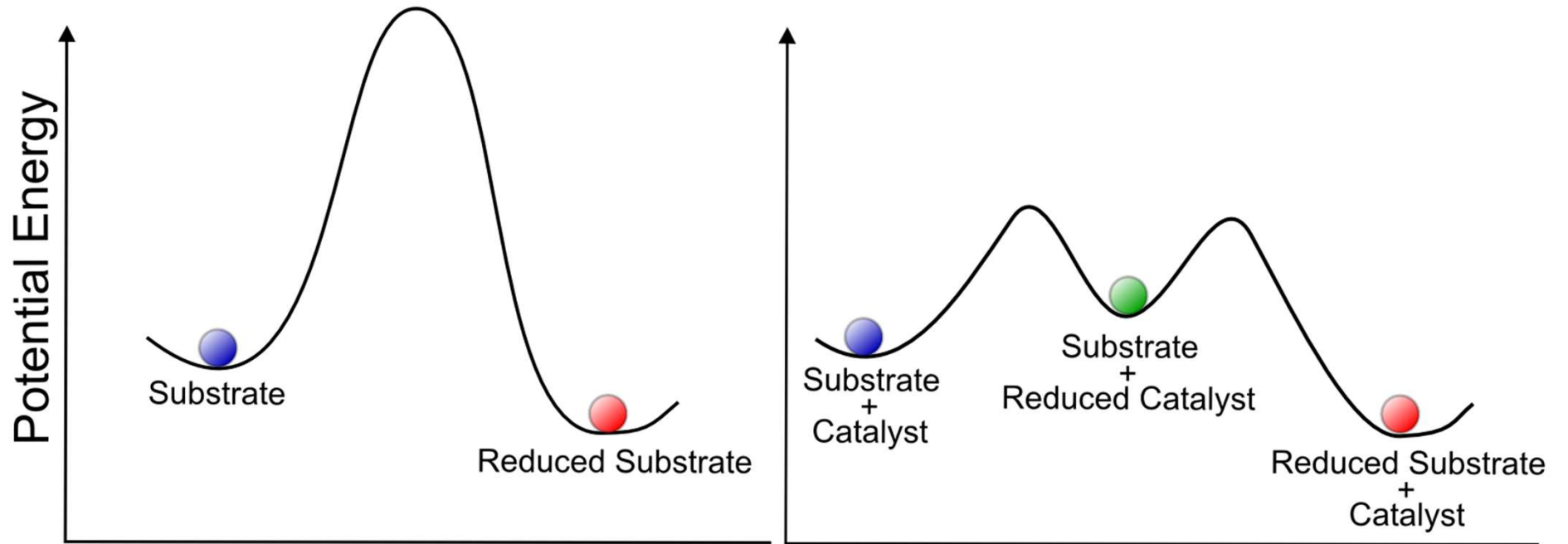
Mechanism of Heterogeneous Catalysis of Chemical Reactions:

The modern theory of adsorption proposed a five-step mechanism for the catalysis of chemical reactions. These steps are:

- Introduction and diffusion of reactant molecules on the catalytic surface.
- Adsorption of molecules of reactants on the catalytic surface.
- Formation of intermediate on a catalytic surface by a chemical reaction between the reactant molecules.
- Desorption of product molecules from the catalytic surface.
- Diffusion of product molecules away from the catalytic surface to form final products.



Catalysis



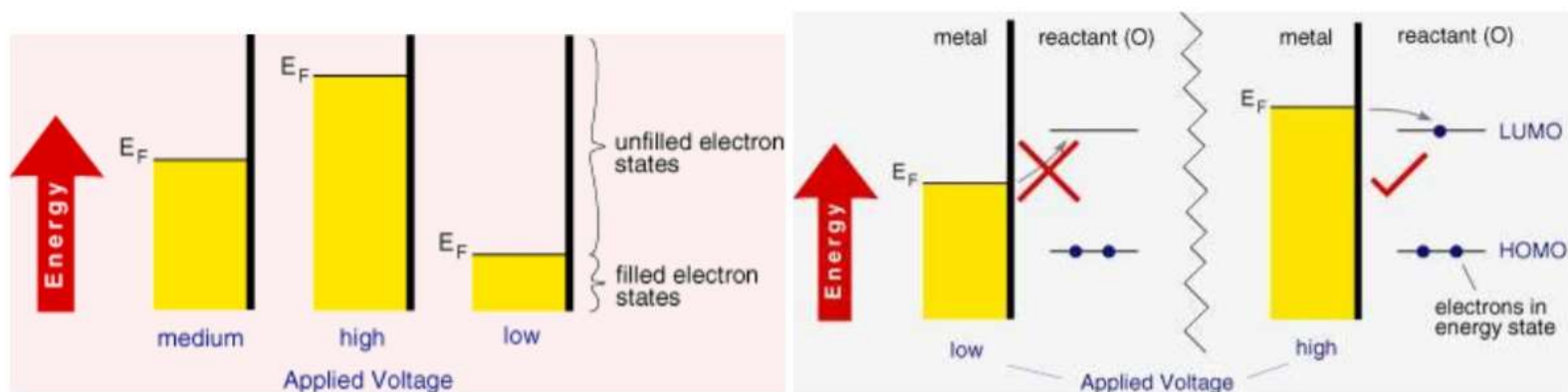


Figure 1.2: Representation of the Fermi-Level in a metal at three different applied voltages (left). Schematic representation of the reduction of a species (O) in solution (right).

This level is not fixed and can be moved by supplying electrical energy. Electrochemists are therefore able to alter the energy of the Fermi-level by applying a voltage to an electrode.

Figure 1.2 shows the Fermi-level within a metal along with the orbital energies (HOMO and LUMO)



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Double layer (surface science)

From Wikipedia, the free encyclopedia

A **double layer (DL**, also called an **electrical double layer, EDL**) is a structure that appears on the surface of an object when it is exposed to a fluid. The object might be a solid particle, a gas bubble, a liquid **droplet**, or a **porous body**. The DL refers to two parallel layers of charge surrounding the object. The first layer, the **surface charge** (either positive or negative), consists of ions adsorbed onto the object due to chemical interactions. The second layer is composed of ions attracted to the surface charge via the **Coulomb force**, electrically **screening** the first layer. This second layer is loosely associated with the object. It is made of free ions that move in the fluid under the influence of **electric attraction** and **thermal motion** rather than being firmly anchored. It is thus called the "diffuse layer".

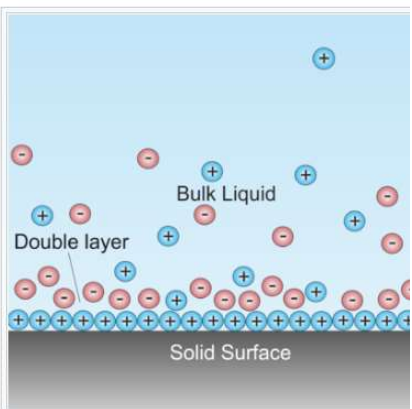
Interfacial DLs are most apparent in systems with a large surface area to volume ratio, such as a **colloid** or porous bodies with particles or pores (respectively) on the scale of micrometres to nanometres. However, DLs are important to other phenomena, such as the **electrochemical** behaviour of **electrodes**.

DLs play a fundamental role in many everyday substances. For instance, homogenized milk exists only because fat droplets are covered with a DL that prevents their **coagulation** into butter. DLs exist in practically all **heterogeneous** fluid-based systems, such as blood, paint, ink and ceramic and cement slurry.

The DL is closely related to **electrokinetic phenomena** and **electroacoustic phenomena**.

Contents [hide]

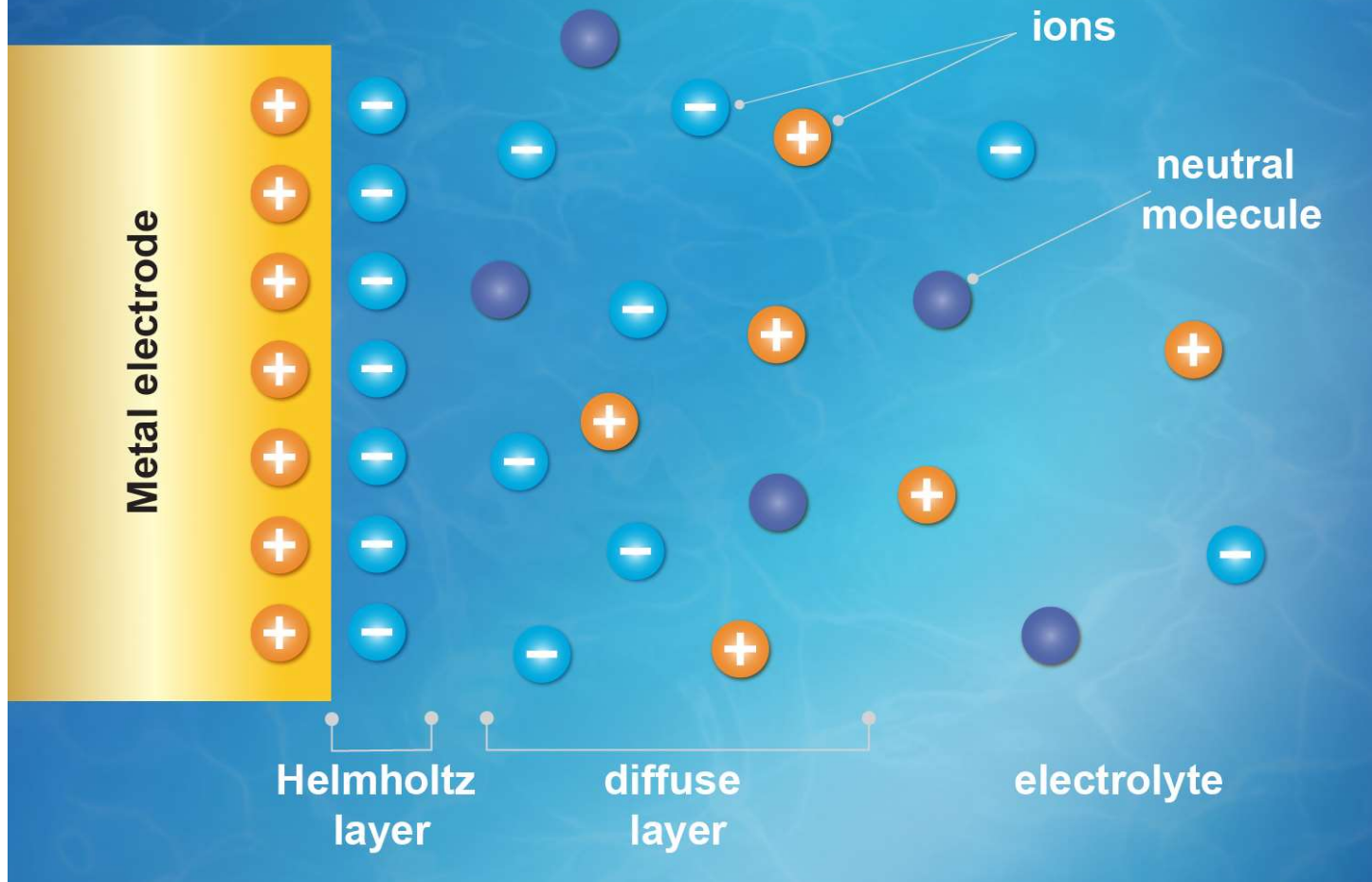
- 1 Development of the (interfacial) double layer
 - 1.1 Helmholtz



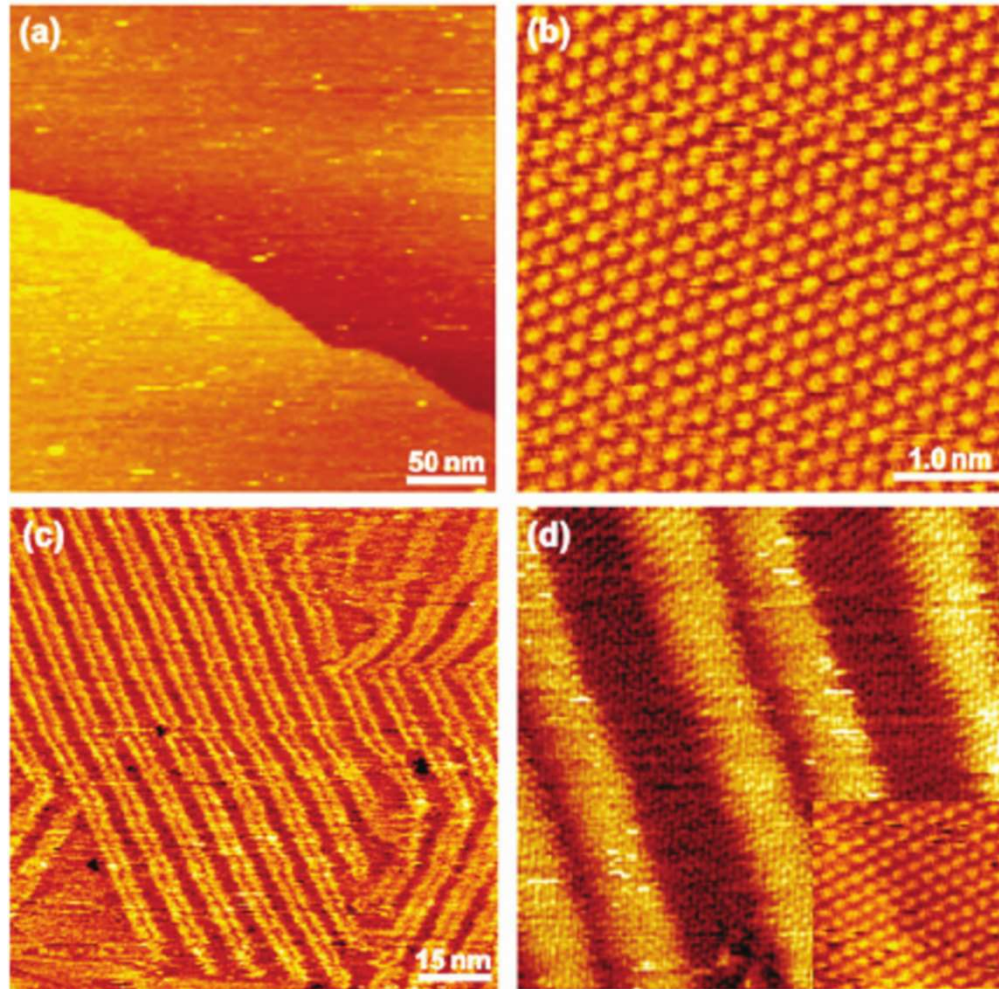
Schematic of the electrical double layer (EDL) in aqueous solution at the interface with a negative charged surface of a mineral solid. Blue + spheres: cations; red - spheres: anions. The number of cations is larger in the EDL close to the negatively-charged surface in order to neutralize these negative charges and to maintain electroneutrality. The drawing does not explicitly show the negative charges of the

https://en.wikipedia.org/wiki/Double_layer_(surface_science)

Electrochemical Double Layer



TEM – atomic resolution

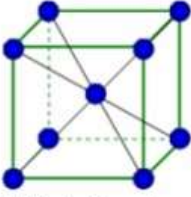
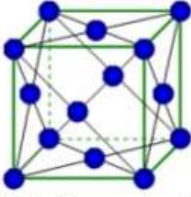
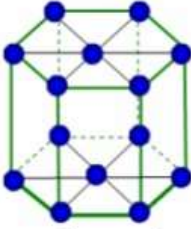


Crystalline structure

Unit cells

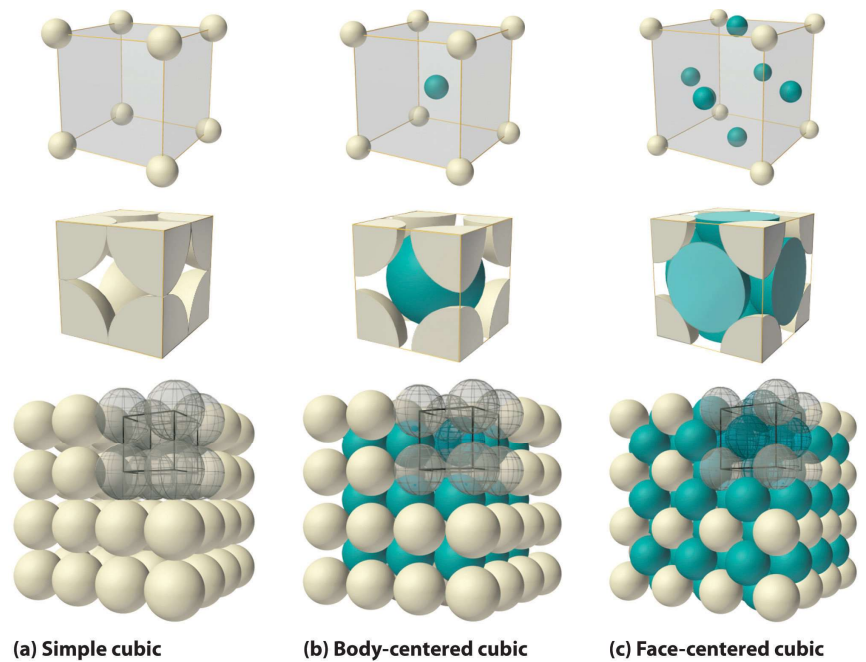
Crystalline structure

Crystal lattice examples

| | | |
|---|---|---|
|  |  |  |
| Cubic body centered (bcc) | Cubic face centered (fcc) | Hexagonal |
| Fe, V, Nb, Cr | Al, Ni, Ag, Cu, Au | Ti, Zn, Mg, Cd |

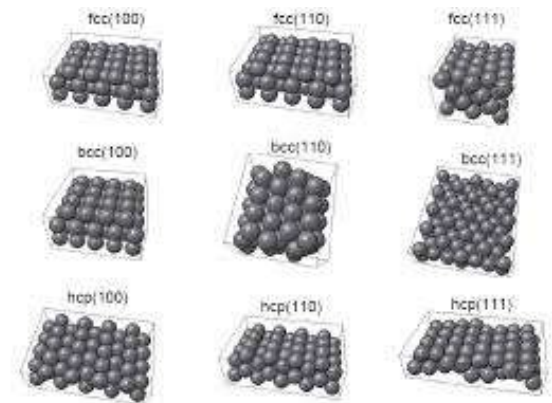
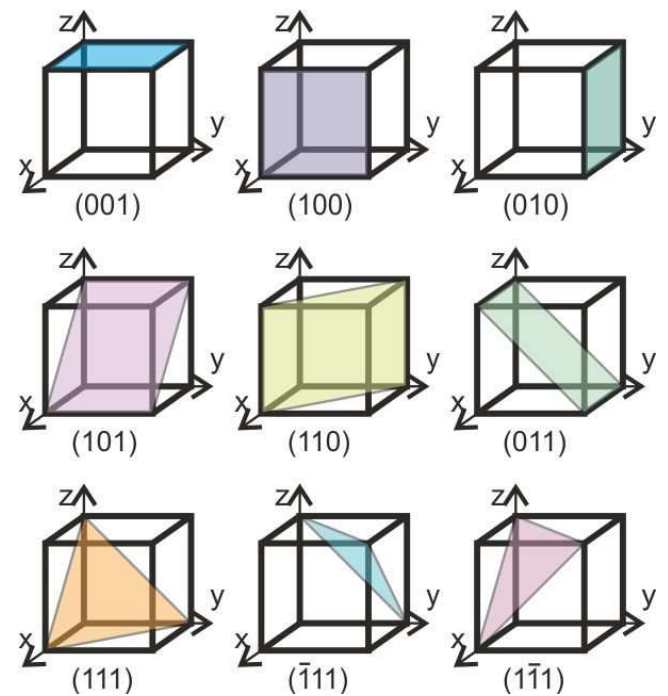
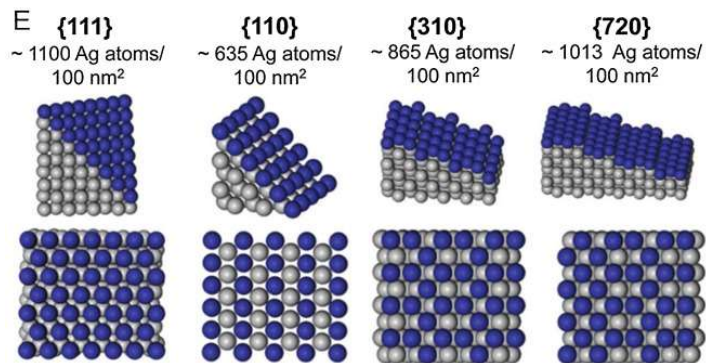
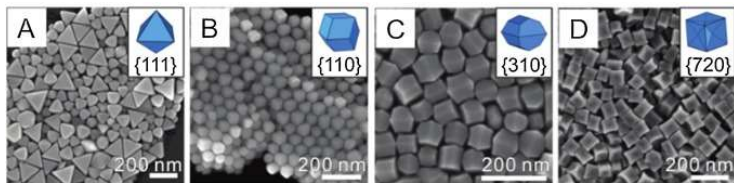
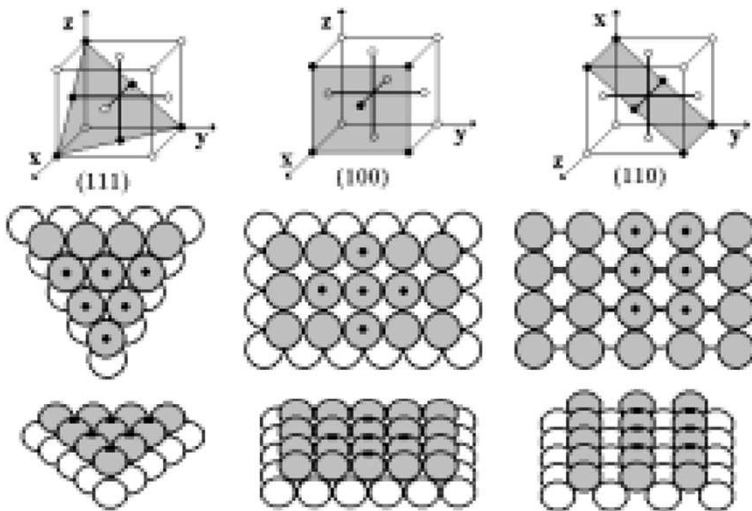
BCC **FCC** **HCP**

Allotropic characteristics?

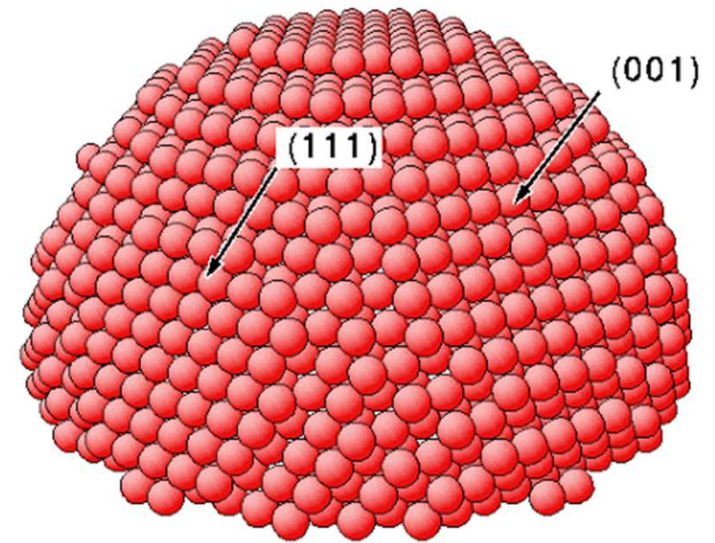
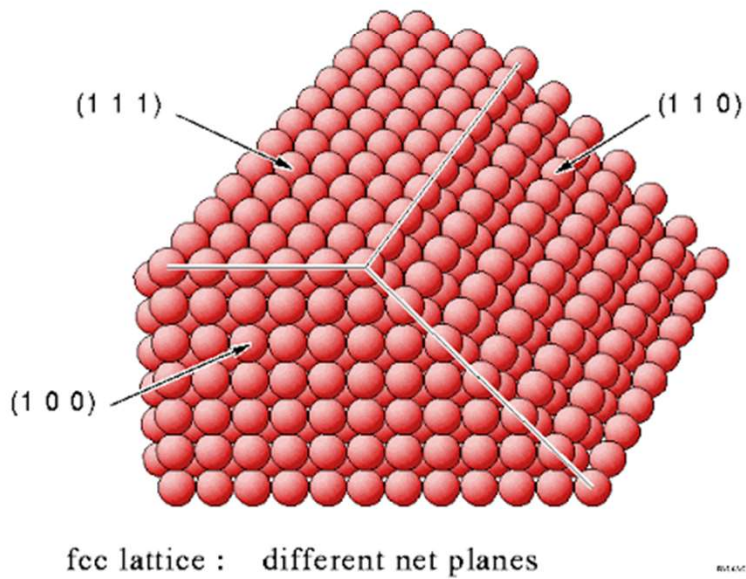
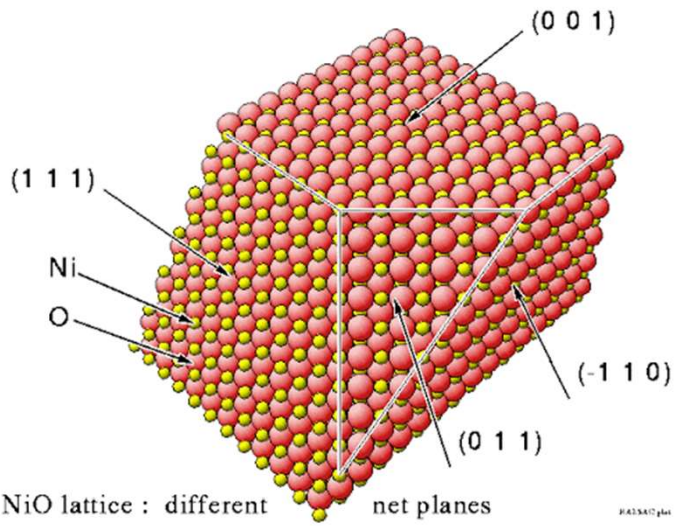


(a) Simple cubic (b) Body-centered cubic (c) Face-centered cubic

Catalytic planes



Catalytic planes

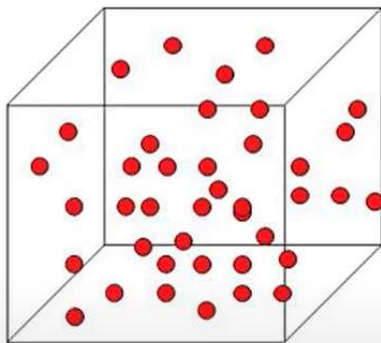


fcc crystal : spherical tip

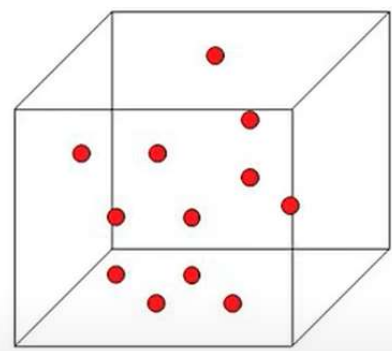
Press Esc to exit full screen

Micro, pico, femto Molar ?!

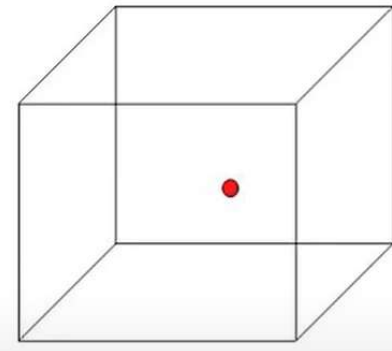
$$1M = 6 \times 10^{23} \text{ molecules/liter} \sim 1 \times 10^{15} / (100 \text{ } \mu\text{m})^3 \text{ box}$$



1 uM ~ 1 billion



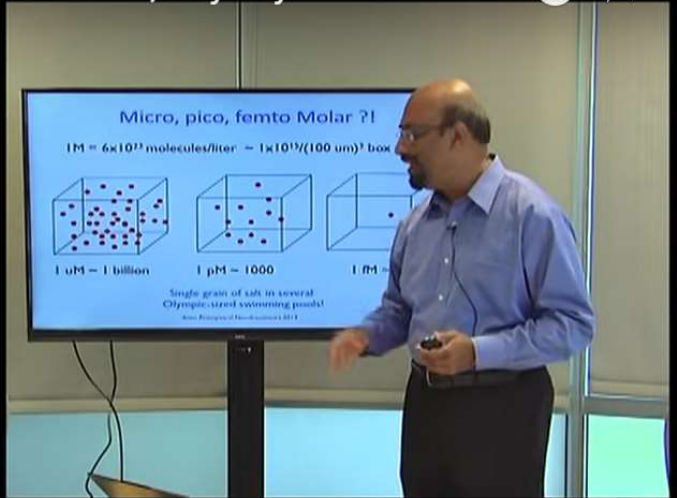
1 pM ~ 1000



1 fM ~ 1

Single grain of salt in several Olympic-sized swimming pools!

Alam, Principles of Nanobiosensors, 2013



Muhammad A. Alam

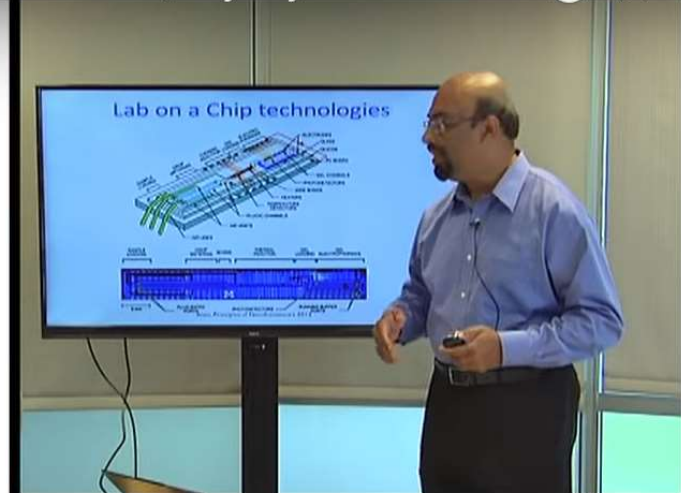
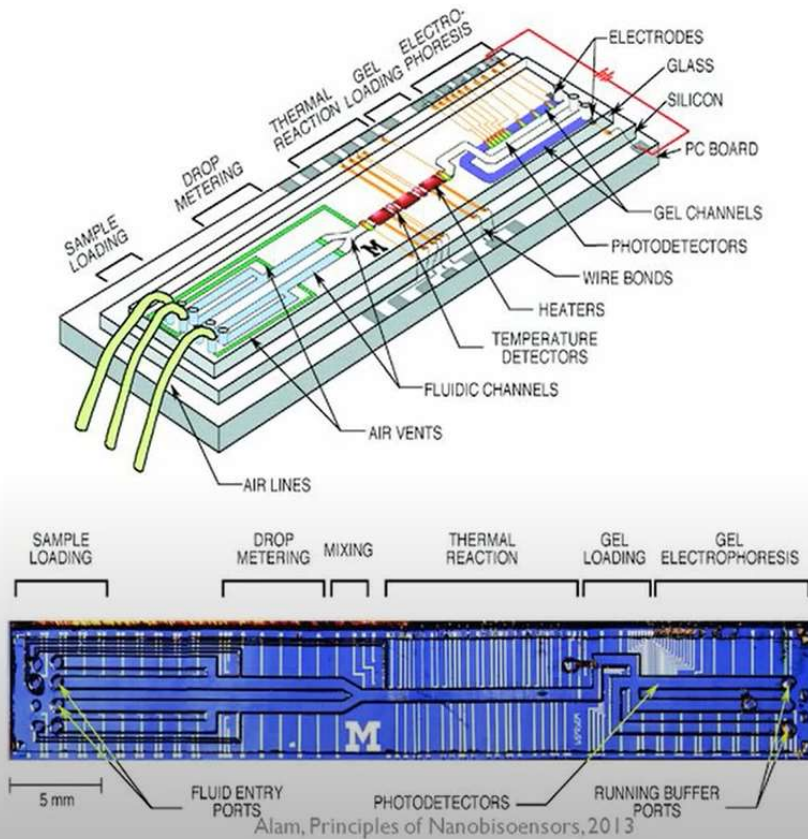
Introduction to Nanobiosensors
Lecture 1.1:
What are Nanobiosensors, Anyway?





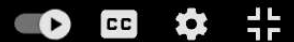
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Lab on a Chip technologies

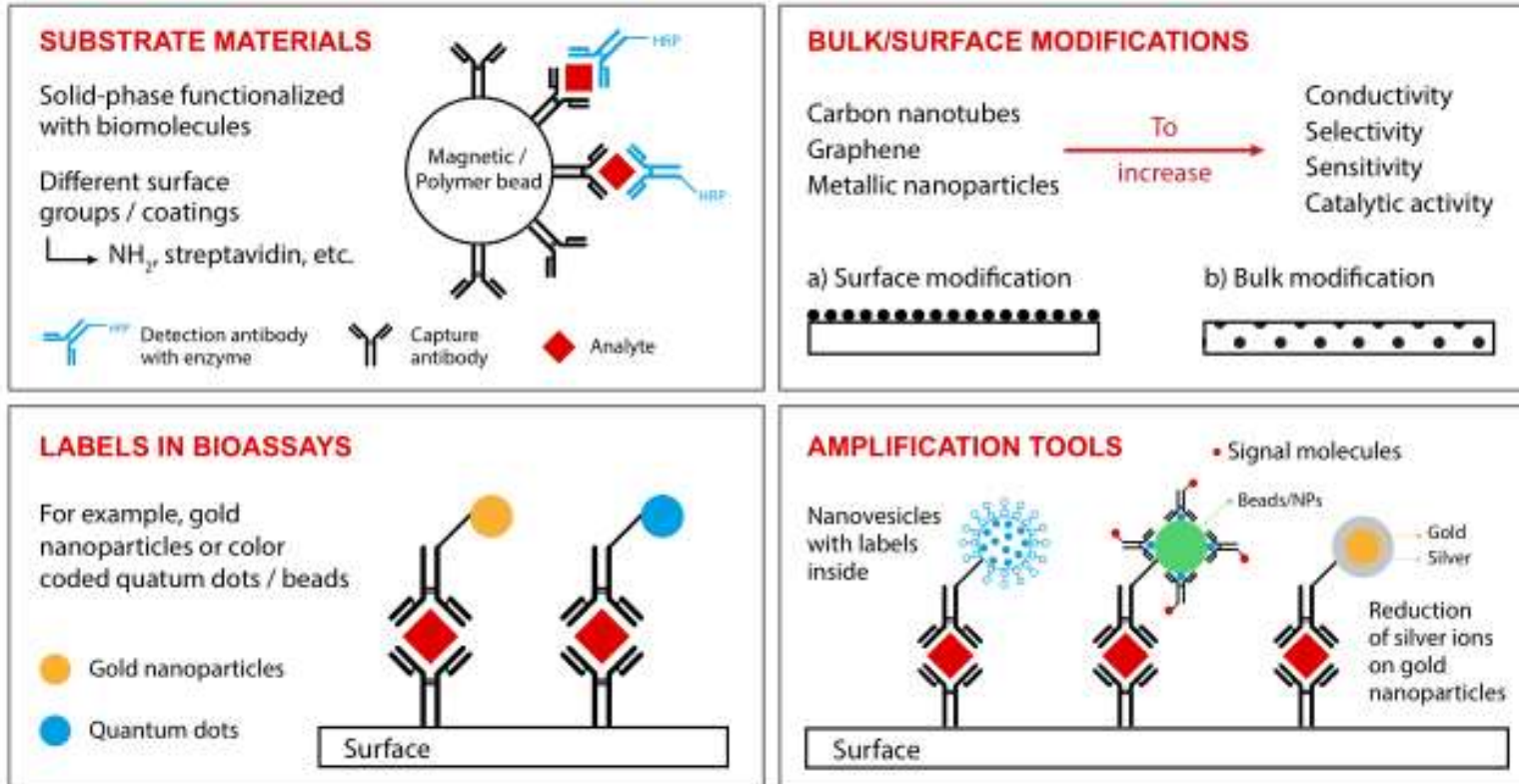


Muhammad A. Alam

Introduction to Nanobiosensors
Lecture 1.1:
What are Nanobiosensors, Anyway?

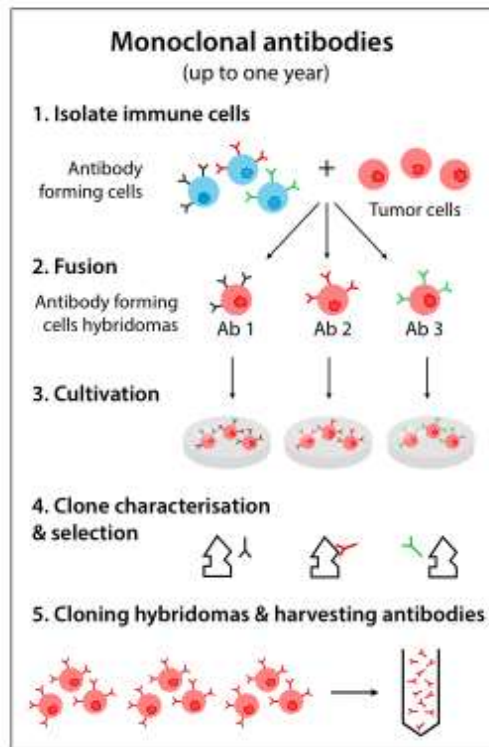
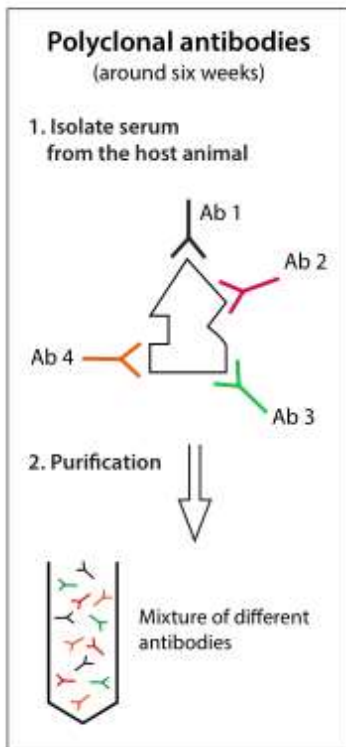
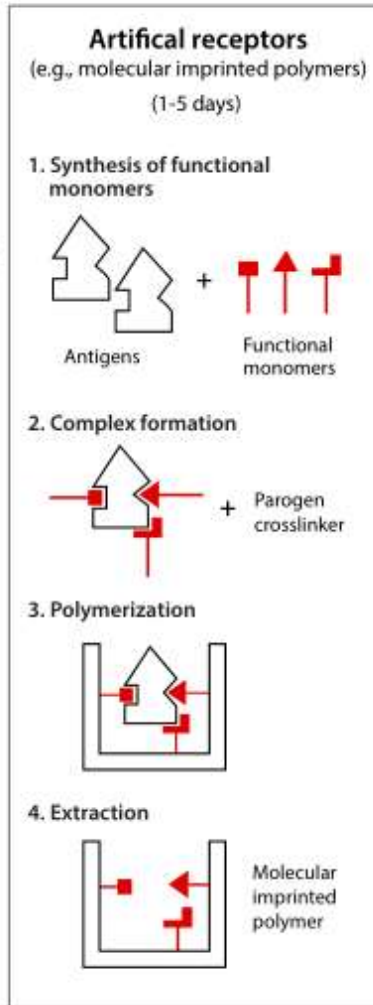
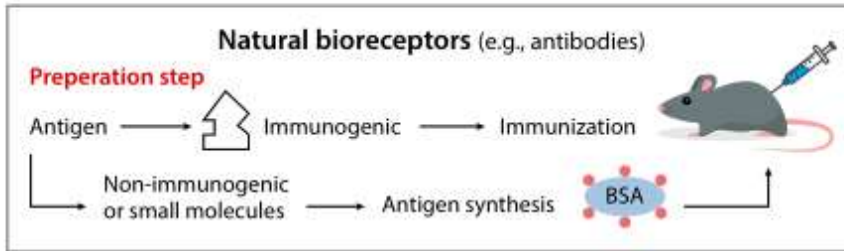


- MICRO- AND NANOMATERIALS -



Overview of micro- and nanomaterials with respect to their use for signal amplification as substrate materials, labels in bioassays, and bulk/surface modifiers and tools for enhancing the signal generating events and signaling components.

- BIORECEPTORS -



Schematics of the production of natural and artificial recognition elements illustrated on the example of antibodies and molecular imprinted polymers.

- MAGNETIC -

Speed/direction/rotation/angle/
presence (e.g., magnetic beads)

cause

a variation of the magnetic field.

SETUP

Giant magnetoresistance (GMR)

CIP: current in plane



CPP: current perpendicular to plane

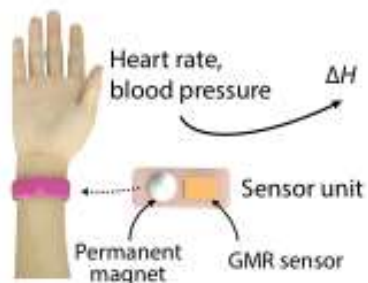


V... Voltage

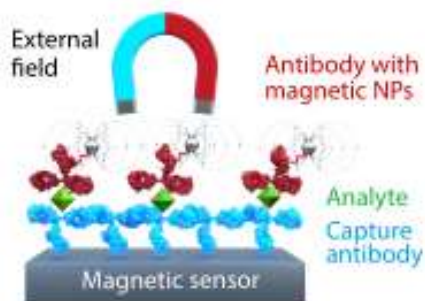
Multiple very thin (about 3-5 nm thick) layers of alternating ferromagnetic (e.g., iron) and non-magnetic (e.g., chromium) materials.

APPLICATIONS

a) Physical sensing

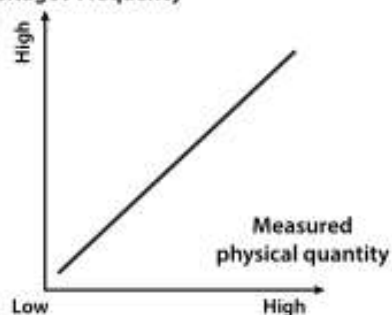


b) Biosensing

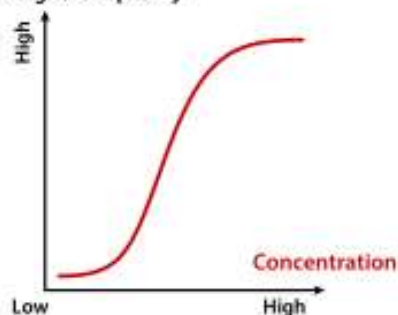


RESULTS

Voltage / Frequency



Voltage / Frequency



Magnetic signal transduction. A variation in the magnetic field caused by speed, direction, rotation, angle, or the presence of magnetic particles (like beads) results in an electrical signal, providing information concerning the magnitude or concentration of the analyte. One of the most promising examples using magnetic signal transduction is the giant magnetoresistance (GMR) sensor. GMR sensors can be built using multiple thin films of ferro- and non-magnetic materials, and in two different designs where the current can flow either in plane or perpendicular. GMR sensors can be applied to: a) physical (heart rate, blood pressure), or b) biological (detection of biomarkers) sensing.

- THERMOMETRIC -

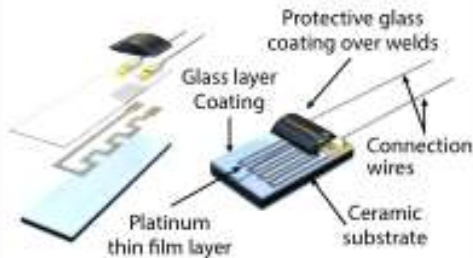
Temperature change

induces

an electrical signal.

SETUP

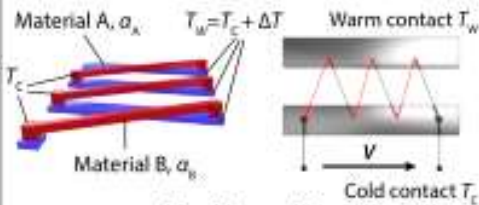
Thin film thermistors



$$R(T) = R(T_0) \cdot (1 + \alpha \cdot \Delta T)$$

α ... Temperature coefficient
 $R(T)$... Resistance at measurement temperature
 $R(T_0)$... Resistance at reference temperature

Thermopiles

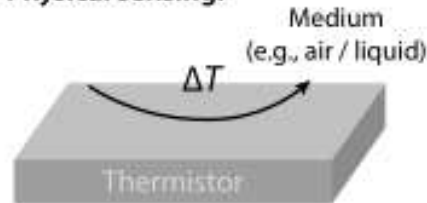


$$V = N \cdot \alpha_s \cdot \Delta T$$

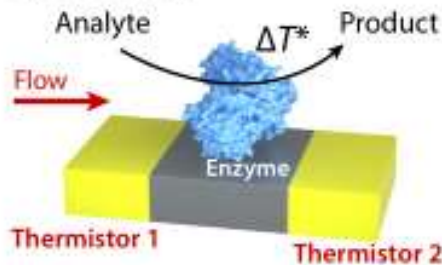
N ... Number of thermocouples
 α_s ... Seebeck coefficient, $\alpha_s = \alpha_b - \alpha_a$

APPLICATIONS

a) Physical sensing:

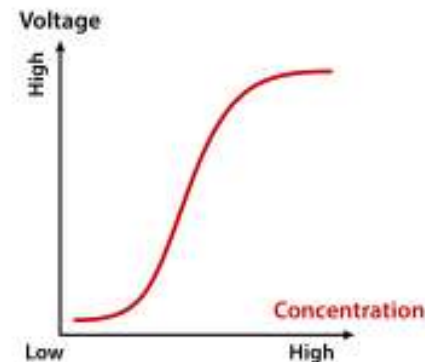
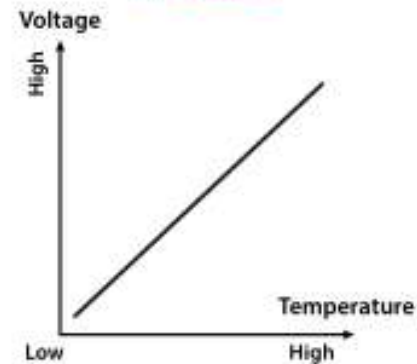


b) Biosensing:



*Depending on the analyte, the temperature difference can be positive (**exothermic**) or negative (**endothermic**).

RESULTS



Thermometric signal transduction in disposable sensors. A temperature change caused by (a) the medium (such as gas or liquid) or (b) a target (bio)chemical substance (for example, a chemical reaction catalyzed by an enzyme for a certain substrate) produces an analytical (electrical) signal. Two notable examples are thin film thermistors (temperature-dependent resistors), and thermopiles. Thermopiles consist of a number of thermocouples, which generate a temperature-dependent voltage due to the thermoelectric effect (for example, Seebeck effect).

- MICROGRAVIMETRIC -

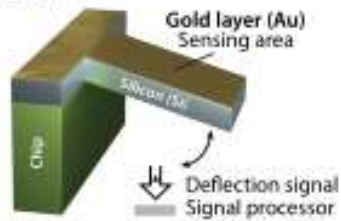
Force, mass, acoustic wave

induce

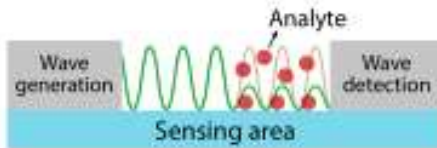
a signal difference.

SETUP

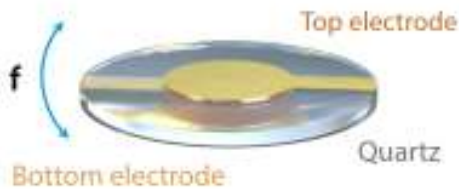
Cantilever



Surface acoustic wave sensor



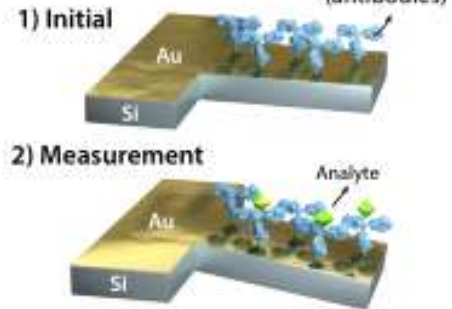
Quartz crystal microbalance (QCM)



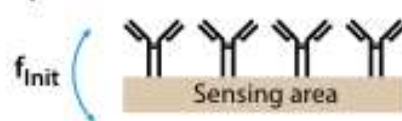
Addition of mass on the resonator changes its resonance frequency.

APPLICATIONS

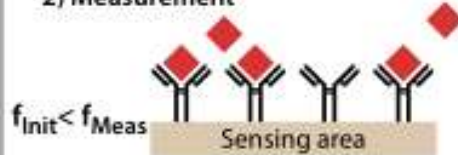
Cantilever



1) Initial **QCM**

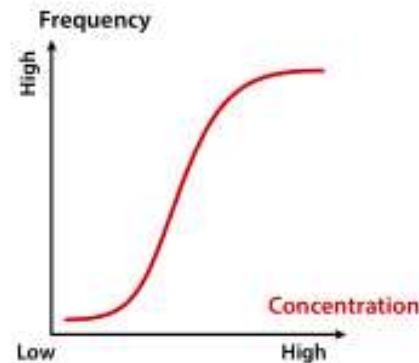
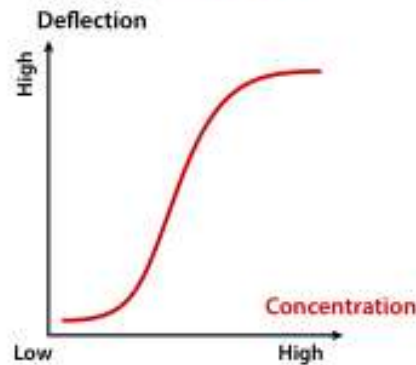


2) Measurement

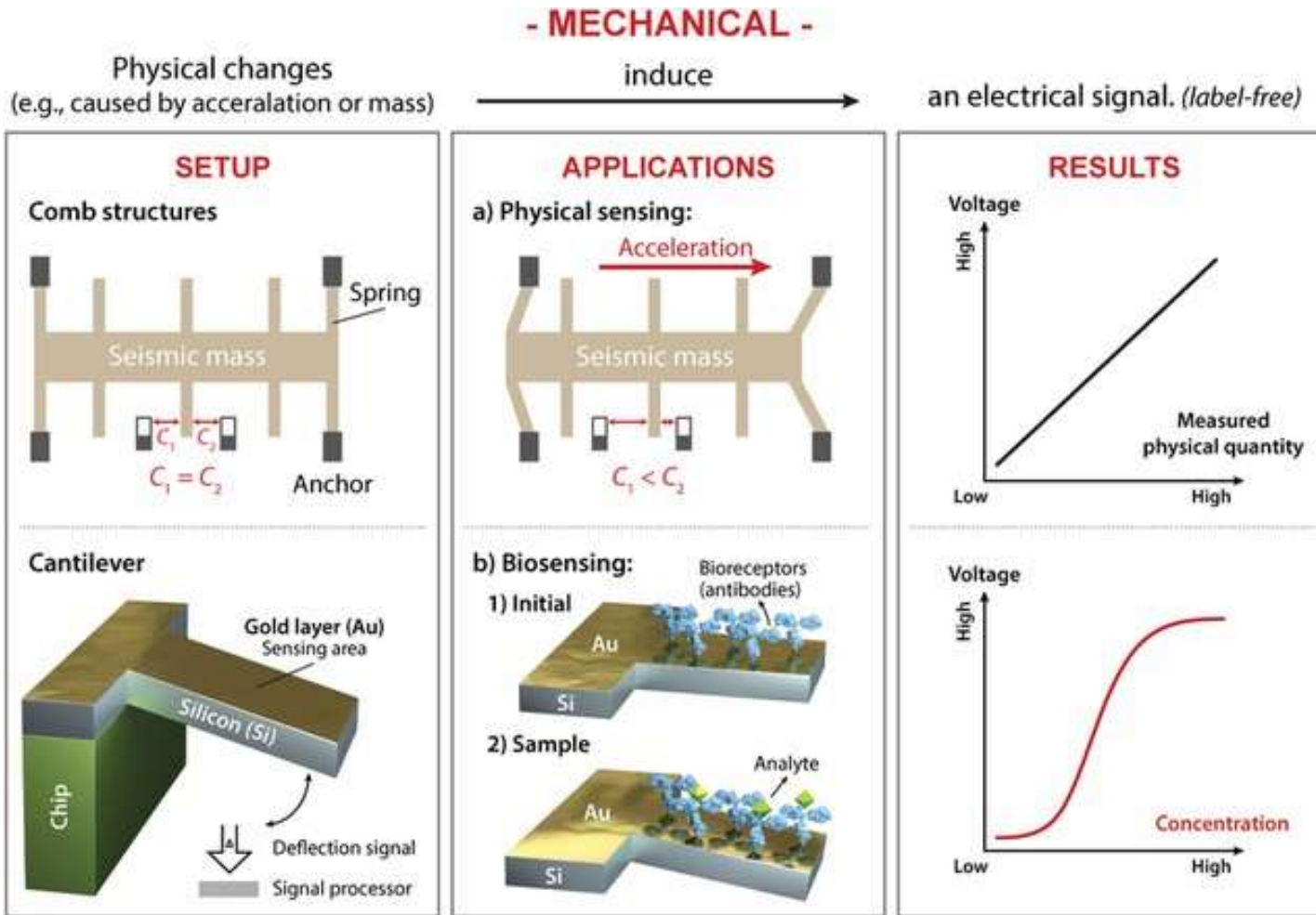


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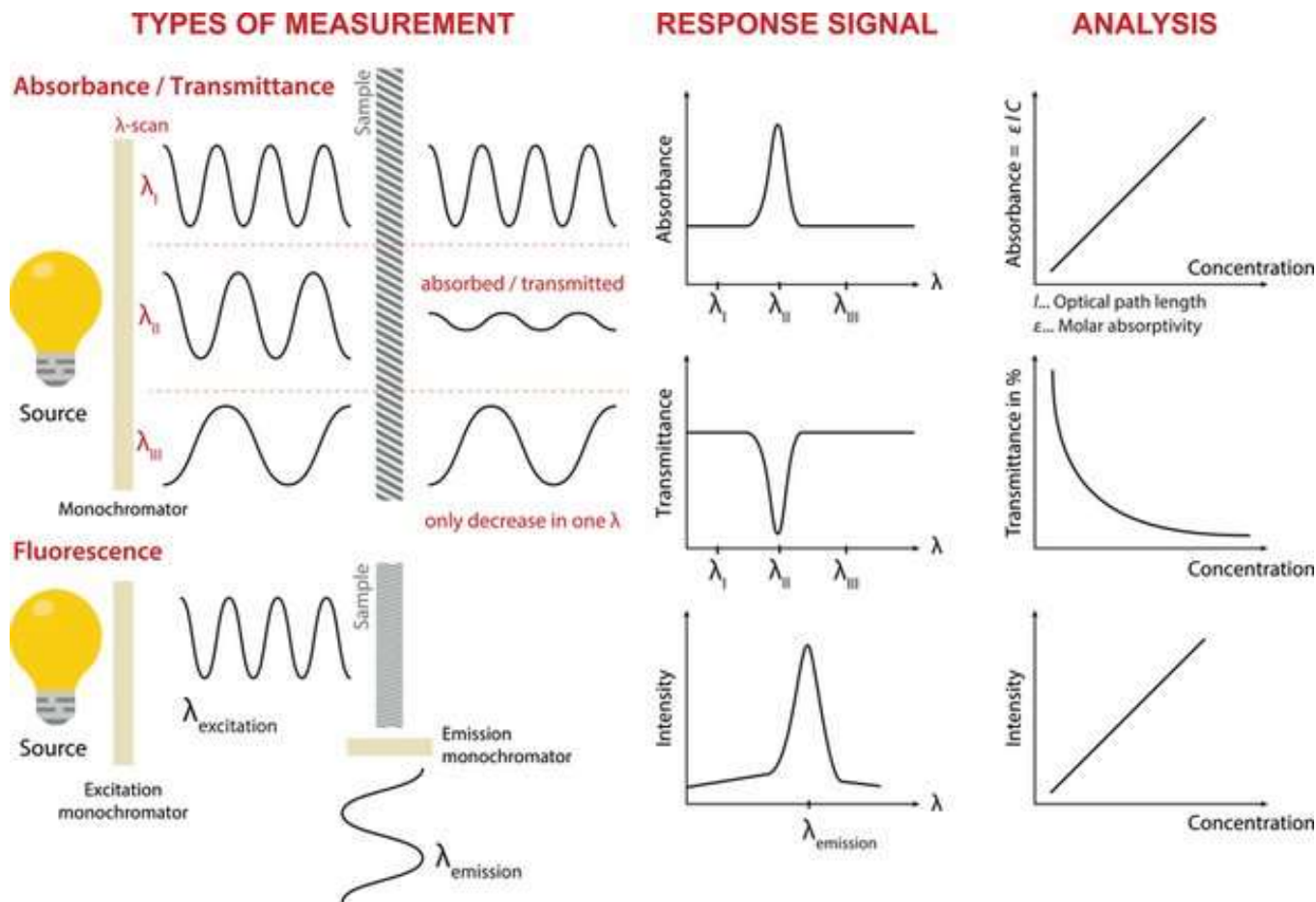
RESULTS



Microgravimetric signal transduction is a subclass of mechanical methods of transduction, however, due to its high sensitivity, microgravimetric methods are particularly suited for applications in label-free (bio)chemical sensing in disposable sensors. For example, increased mass due to captured analytes can bend a cantilever or shift the resonant frequency of a quartz crystal microbalance (QCM), producing an analytical signal. Surface acoustic wave type microgravimetric sensors can also detect analytes captured on a surface of a disposable sensor.



Mechanical signal transduction. Physical changes caused by acceleration or force can be converted to an analytical signal related to the magnitude of the physical quantity measured.

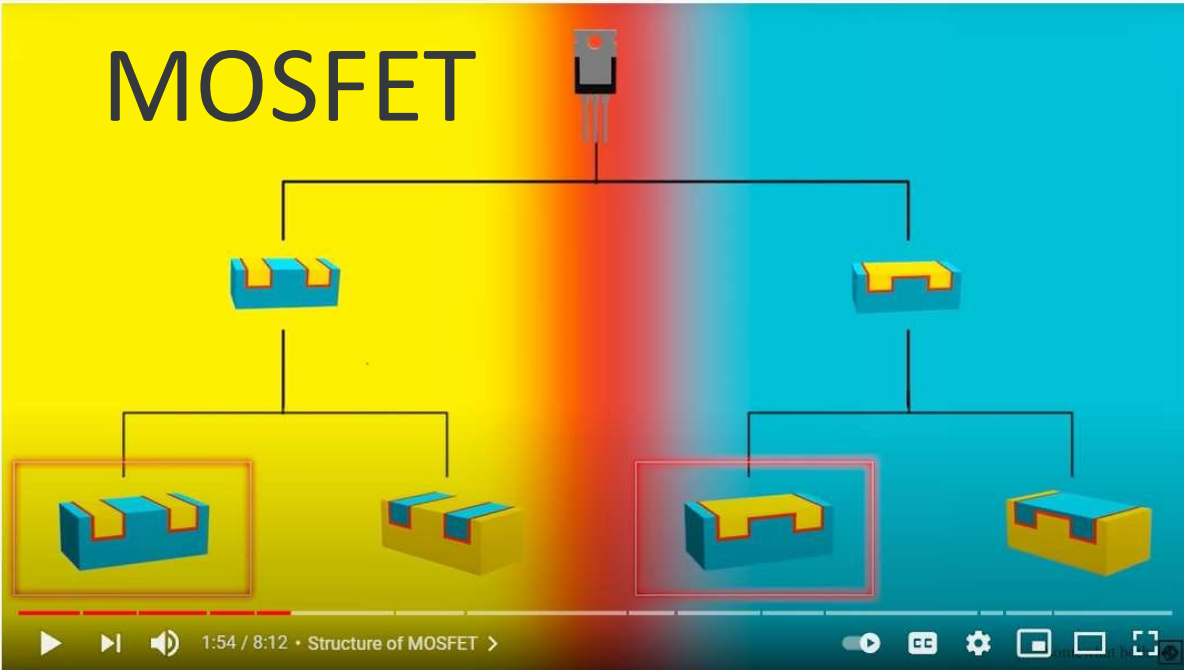


Optical signal transduction. Absorbance/transmission involves passing a beam of light (single or spectrum of wavelengths containing, for example λ_I , λ_{II} , and λ_{III}) through the sample and measuring the amount of light absorbed or transmitted (here, λ_{II}) on the opposite side using an optical detector. Note that in the illustration shown above, λ_I and λ_{III} do not interact with the sample; hence, the intensities of signals do not change. A monochromator can be used to scan (λ -scan) by selecting a specific wavelength from the source. The amount of light absorbed or transmitted varies (λ_{II}) with the concentration of the analyte in the sample. Fluorescence involves excitation of a fluorescent compound with a beam of light. The excited molecule itself then emits light with an energy smaller than the energy of the source ($\lambda_{emission} < \lambda_{excitation}$). The intensity of the emitted light depends on the concentration of the fluorescent compound in the sample.

https://www.researchgate.net/publication/333132057_Disposable_Sensors_in_Diagnostics_Food_and_Environmental_Monitoring/figures?lo=1



Historical timeline of the discovery of various sensors and their development with respect to materials (green), sensor technologies (blue), and biotechnology (black).248



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| | Working: Cut-Off Region 2:40 |
| | Working: Channel Formation 3:10 |
| | For future people 4:20 |
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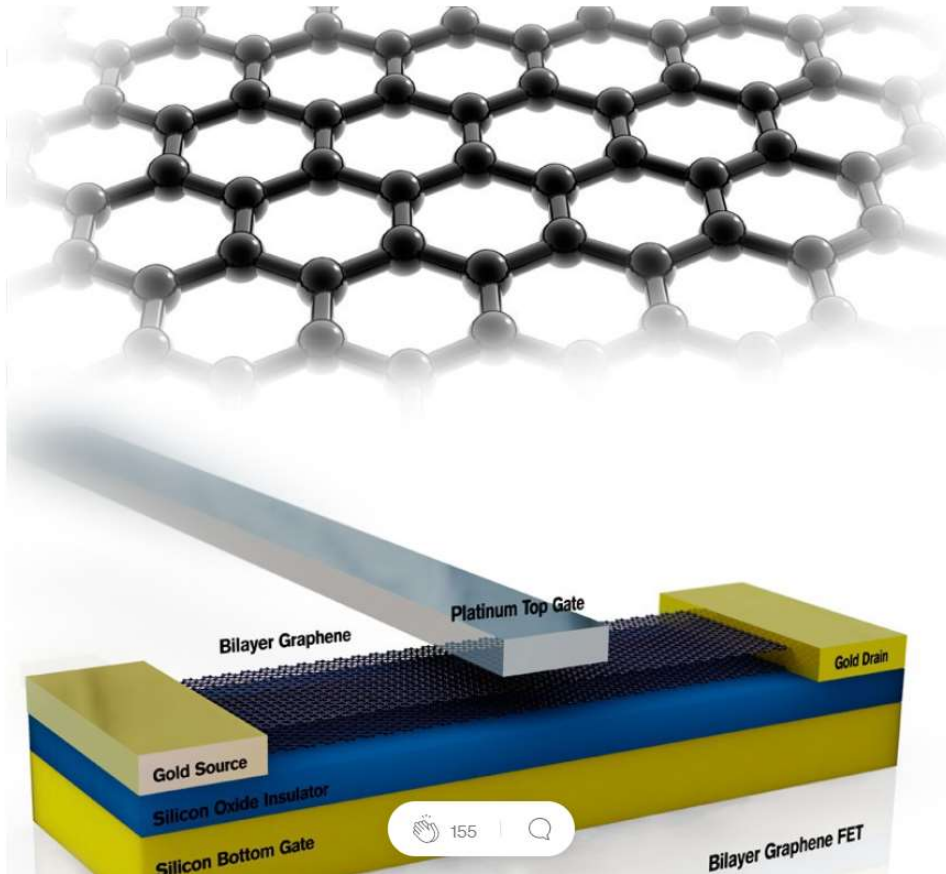
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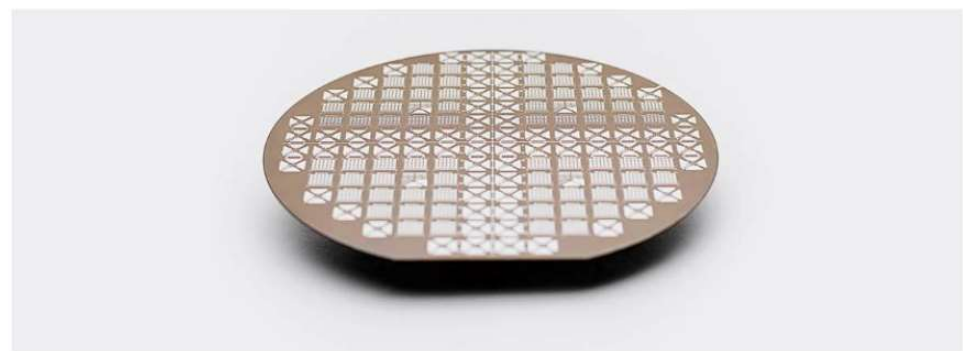


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- Surface Modification and Functionalization of Chem/BioFETs
- Readout Circuit and Systems
- Conclusions
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FET sensor

IK

double layer) changes the oxide electric field that eventually contributes to changing the potential at the outer surface of the sensing conductive channel. Afterward, the generated potential alters the space charge distribution inside the conductive channel and leads to source-drain current variations inside FET conduction channel.

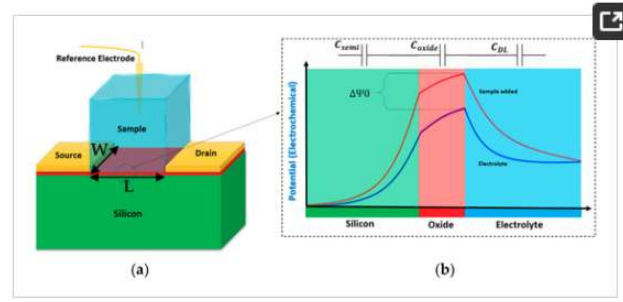
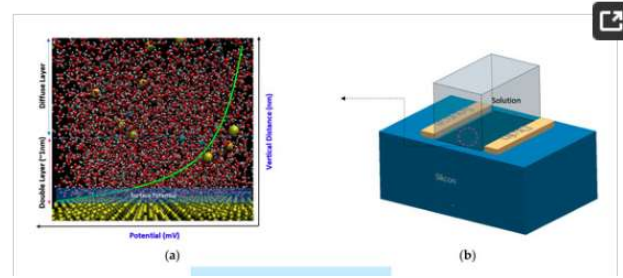


Figure 1. (a) The standard structure of a Bio-field-effect transistor (FET); (b) the corresponding potential diagram showing the effect of electrolyte on the potential of interfaces. The potential at the oxide layer and solution interface arises then will be decreased gradually to the solution potential. Adding the sample would manipulate this potential curve influencing the charge transport inside the silicon channel. There are three main capacitances involved in the system consisting of the oxide, channel depletion capacitance, and the solution double layer (C_{DL}).



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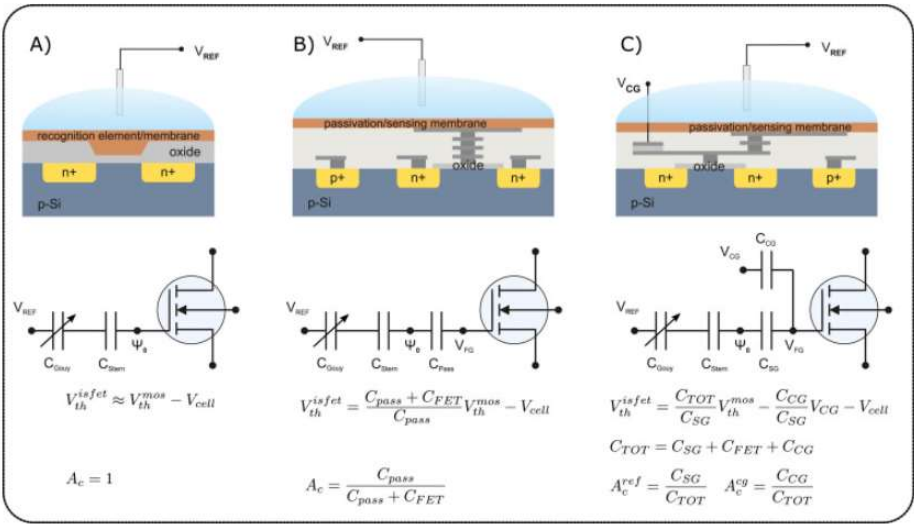
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layer for pH sensing. This structure is shown in Fig. 3-B.

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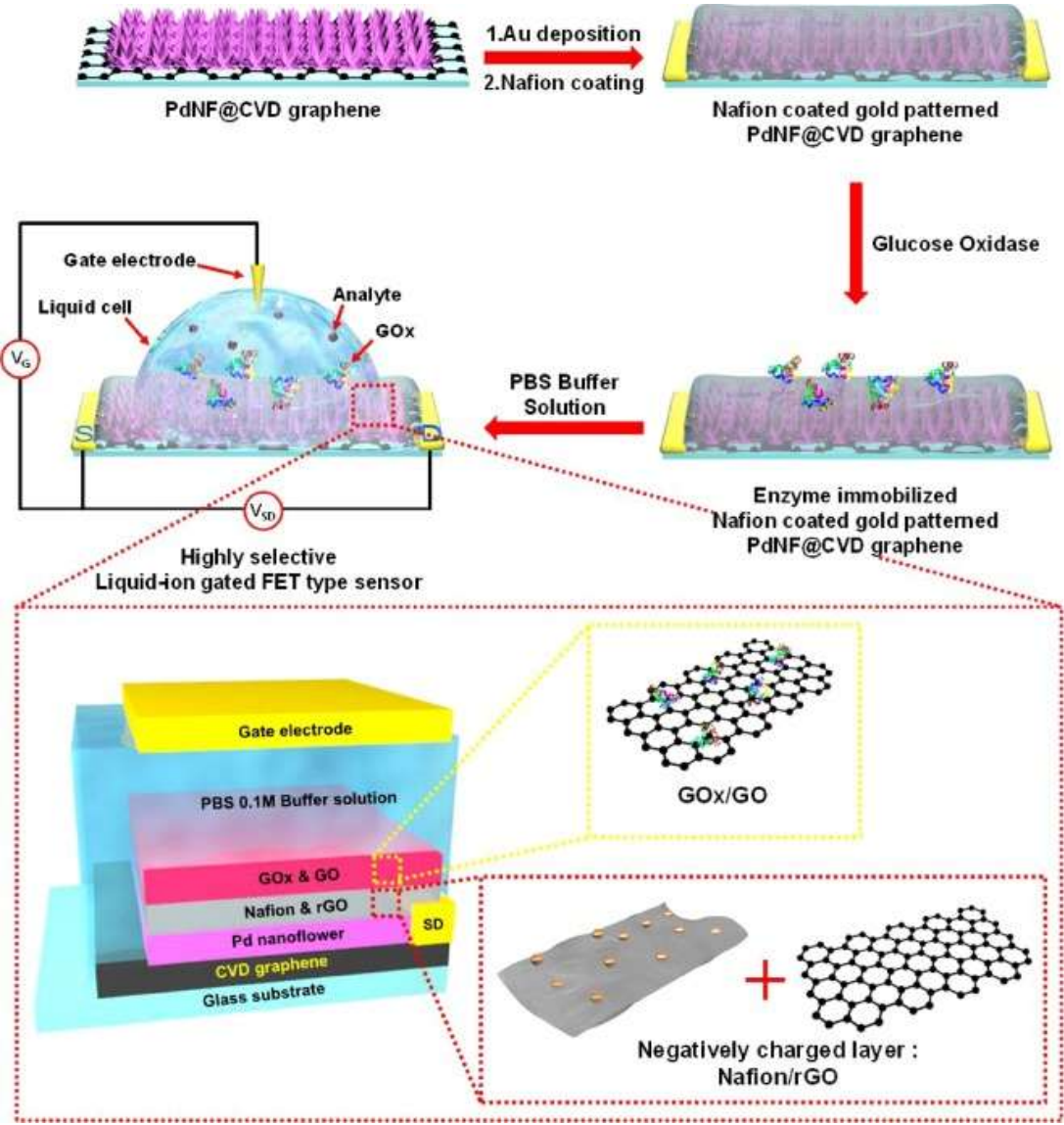
Fig. 3. Different FET sensor structures. A) Conventional

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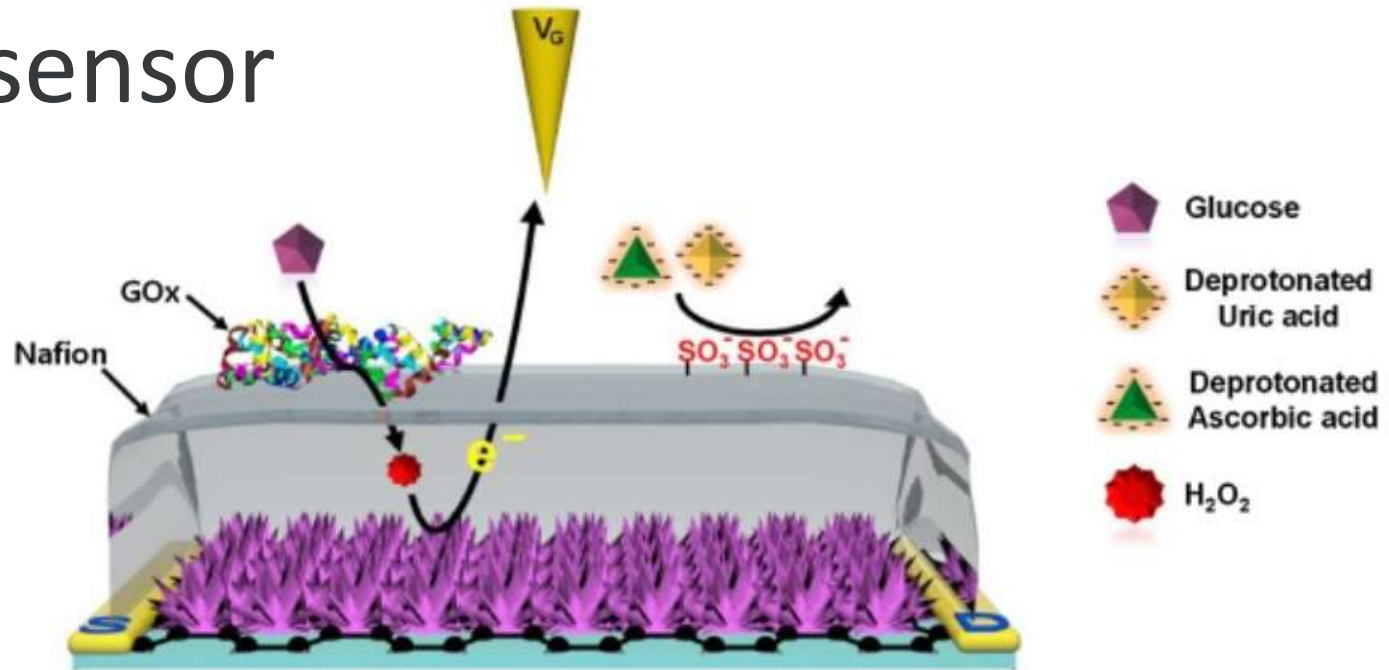
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Fig. 6. Illustrative diagram of uric acid (UA) and ascorbic acid (AA) blocking and glucose sensing mechanism about GOx/Nafion/SPNFG FET-type sensor.

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phene FETs can be improved when vertical scaling-down of the dielectric layer continues. To this regard, we explore in detail the effect of quantum capacitance on the plasma resonance by employing a rigorous plasmonic modeling technique conditions.²⁷ The distributions of intraband and interband conductivities in the terahertz region are plotted schematically in Fig. 2b, from which it can be seen that the intraband Drude term can be orders of magnitude larger than the interband

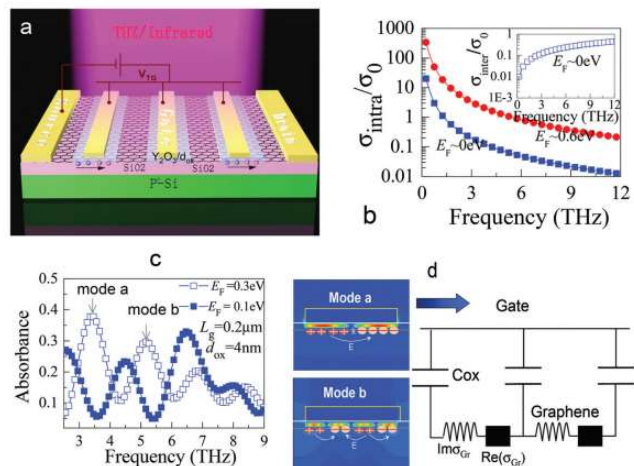


Fig. 2 Spectral characteristics of plasma waves in graphene FETs and their equivalent circuit model. (a) Sketch of a one-dimensional periodic array of graphene plasma wave FETs under excitation by THz/IR radiation. The plasma wave oscillations are depicted in the channel schematically. (b) The dynamical intra and interband conductivity of graphene based on the Kubo theory, the inset indicates the energy loss ratio the between intraband and interband processes at room temperature near the Dirac point, the imaginary part of conductivity is not shown in the figure, as it is dominated by the intraband conductivity, and thus the frequency of plasma waves in graphene FETs is mainly determined by the intraband part. (c) The spectral characteristics of plasma resonance in grating-gated graphene FETs at the Fermi level $E_F \sim 0.1\text{ eV}$ (solid symbols) and $E_F \sim 0.3\text{ eV}$ (open symbols) obtained by solving the Maxwell equations embedded with Kubo conductivity theory (see ESI†). The gate length L_g is $0.2\text{ }\mu\text{m}$, and oxide layer thickness d_{ox} is 4 nm . (d) Mode profiles of resonances a and b in (c), and the equivalent R-L-C model for plasma wave oscillation in the gated channel. It should be noted that the sheet conductance in local approximation is given by $\sigma W/L_g$, L_g is the gate length and W is the gate width, the capacitance is given by CWL_g , the kinetic inductance is given by $Im(L)/\sigma L_g/W$, which leads to a similar expression for the plasma wave frequency as the Boltzmann and RPA approximation theories in the ESI.†

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Chemical industry is a key national industry and produces diverse products closely related to food, clothing, and shelter of human society and also is basic industry that provides necessary raw materials to all industries. Therefore, industrial development of one nation starts from chemistry industry and Korean industrial development also started from chemistry industry after Korean War and has grown to the level of developed country. Current chemistry industry has traditional chemical field such as refinery, petrochemical, organic synthesis, and process design and automation, and at the same time occupies an important position to have advanced fields such as bio chemical engineering, DNA engineering, high molecule materials and processing, processing of semiconductor and electronic materials, electrical chemistry, new materials industry, use of solar energy, and development of environment friendly clean technology.

In this department, we have basic courses such as process thermal dynamics, reaction engineering, and thermal and material transmission in order for students to exhibit their best ability in these fields and we also have application courses such as separation process, computer use for chemical engineering, process control, electrical chemistry, molecule bio engineering, design of chemical plants, guideline of catalytic agents, high molecule engineering, and environment engineering technology. Besides, we are emphasizing taking courses of practical testing, chemical industry management, and seminar. In graduate course, we are focusing on educational purpose of training leaders combined with broad viewpoints and human nature through carrying out research of deepened field and experiments in parallel.

In this department, we have two research institutes: institute of chemical processes and institute of ultra fine elements technology, as well as 10 venture companies in which our department professors are involved and also several additional large scale research tasks supported by the government are now underway. We are contributing to society directly through application of our academic achievements within the university to actual domestic industries.

Department of Chemical and Biological Engineering provides challenge and opportunity for the future to train talented manpower equipped with international competitiveness and exerts our efforts for realization of convenient, healthy, and pleasant future for human beings.

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level: Graduate
year: 2019
term: Fall
staff: Prof. LEE, CHANGHA
department: Chemical and Biological Engineering

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code: 458.303_2011S
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year: 2011
term: Spring
staff: Prof. Lee, Youn-Woo
c_regdate: 2011-12-09 13:12:36
department: Chemical and Biological Engineering