



**Faculty of science**

# **Introduction to Analytical Chemistry**

## **Analysis of Errors**

**3<sup>rd</sup> Year students Chemistry- Education**  
**Course: Analytical chemistry**

**Lecture #1**

**Date: February 16, 2020**

# What is Analytical Chemistry?

The science & art of recognizing composition of matter and determining its amount (how much is there?)

## “Science of Chemical Measurements”

Qualitative: Provides information about the identity of an atomic, molecular or biomolecular species

Quantitative: provides numerical information about the relative amounts of species

# Why do we need Analytical Chemistry?

## Applications

*Medicine*

*Industry*

*Environmental*

*Food and Agriculture*

*Forensics*

*Archaeology*

*Space science*

## Role of Analytical Chemists

1. Improve the existing techniques for faster, cheaper, more sensitive measurements.
2. Develop new types of measurements and use advanced technologies (microfluidics and microfabrication) for construction of implantable microchip sensors and lab on a chip.

# Progressing in the Analytical Methods

## **(A) Classical:**

- a) Separation via precipitation, extraction or distillation
- b) Qualitative: recognized by color, boiling point, solubility, taste
- c) Quantitative: gravimetric or volumetric measurements

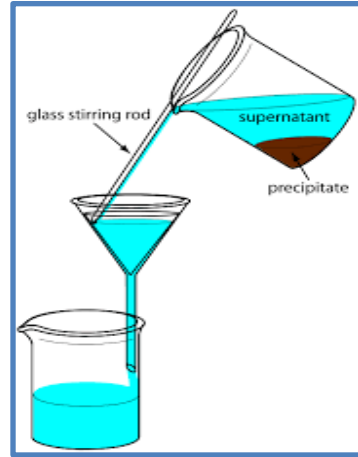
## **(B) Instrumental:**

- a) Separation via chromatography and electrophoresis
- b) Qualitative and Quantitative: use the interaction with radiation (spectroscopy)  
their mass (mass spectrometry)  
their **Electrical properties**  
their interaction with environment (temperature, humidity)

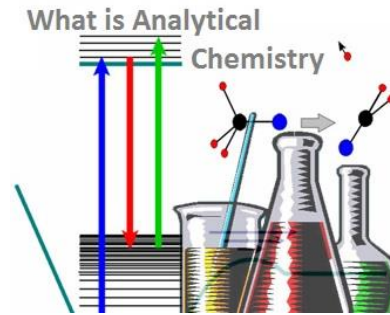
# Progressing in Quantitative chemical analysis



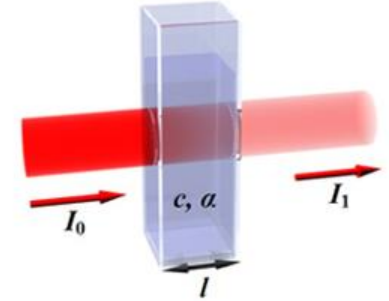
**Volumetric titration**



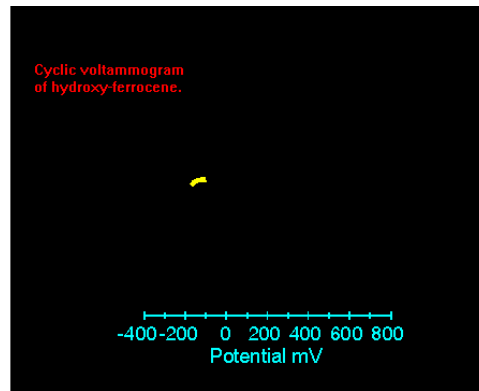
**Gravimetric analysis**



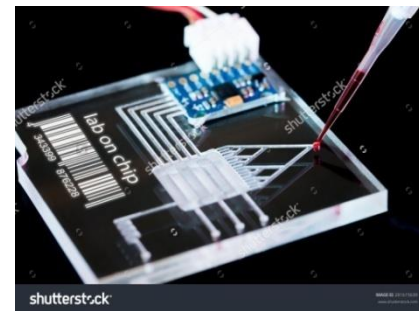
**Spectrophotometry**



**Liquid Chromatography**



**Electroanalytical methods**



**Lab on a chip**



**Pregnancy test**

**Sensors**

# What is instrumental analysis?

Investigation of species using an instrument by measuring physical properties such as color, current/potential, and optical rotation.

## Instrumental Analysis: why?



To follow up the glucose level for diabetes patients



To keep children safe  
Baby toys analysis for Pb



To keep food resources are safe

# Modern Instrumental Techniques

## Separation techniques

Gas chromatography (GC)  
High performance liquid chromatography (HPLC)  
Ion exchange chromatography  
Super critical fluid chromatography  
Capillary electrophoresis (CE)  
Planar chromatography

## Mass Spectrometry techniques

Electron ionization MS  
Chemical ionization MS  
High resolution MS  
Gas chromatography MS  
Fast atom bombardment MS  
Liquid chromatography MS  
Laser MS  
Ambient ionization MS

## Electroanalytical techniques

Amperometry  
**Potentiometry**  
Voltammetry  
Conductometry

# Spectroscopic techniques

Infrared spectrometry (IR)

Raman spectrometry

Nuclear magnetic resonance (NMR)

X-ray spectrometry

Atomic absorption spectrometry (AAS)

Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma MS

Atomic fluorescence spectrometry (AFS)

Ultraviolet/visible spectrometry (UV-Vis)

Circular dichroism (CD)

Molecular fluorescence spectrometry

Chemiluminescence spectrometry

X-Ray Fluorescence spectrometry

## Microscopic and surface techniques

Scanning electron microscope (SEM)

Atomic force microscopy (AFM)

Auger electron spectroscopy

X-ray photon electron spectroscopy (XPS)



# Analytical Problem

You are a researcher at the research and development unit of A company for fabrication of cheap biosensors for simultaneous detection of **blood electrolytes ( $H^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ )** in patient's body fluids for proof of concept commercialization.

**Your job: Plan and design the chemical analysis approach to perform these task.**



[Glucose] = 4.0- 6.0 mmol/L (72 -108 mg/dL)

[ $Ca^{2+}$ ] = (2.2 -2.7 mmol/L)

[ $Na^+$ ] = 135–145 mmol/L

[ $K^+$ ] = 3.6 - 5.2 mmol/L

# Steps for solving an Analytical Problem

1. Defining the problem by looking at the history of the material to be analyzed.
2. Choosing the analytical technique(s) and running the experiments
3. Analyzing the data and reporting of results

# 1. Defining the Problem

- What is the accuracy needed?
- Is there a time or money limit?
- How much sample is available?
- What is the concentration range of the analyte?
- What about interferences and their components?
- What about the sample matrix properties?
- How many samples need to be analyzed?

# History of sample and background of the problem

## Sample history:

- How was the sample collected, transported, and stored?
- How was it sampled?
- If synthesized, which synthetic route?
- What raw materials were used to make the sample?
- What analysis has already been performed?

## Background information:

Can be obtained from literature searches on related systems

## 2. Choosing the Analytical Technique

- Consider the physical characteristics of sample (nature, color, stability)

- Choose an instrument (and ultimately a method) that can obtain the desired information

Example: (Amperometric & potentiometric based sensors for detection of glucose in blood)

- Do we need to develop a new technique?

(such as sensor or biosensor) (amperometric sensors for dopamine: need recognition receptors (antibody or DNA fragments for higher selectivity))

# Technique Selection

## Analysis type

- Quantitative, Qualitative

## Location of sample

- bulk or surface

## Physical state of sample

- gas, liquid, solid, dissolved solid, dissolved gas

## Amount of Sample

- macro, micro, nano, ...

## Fate of sample

- destructive, non destructive

## Estimated purity of sample

- pure, simple mixture, complex mixture

## Sensitivity needed

- High, low , vey high

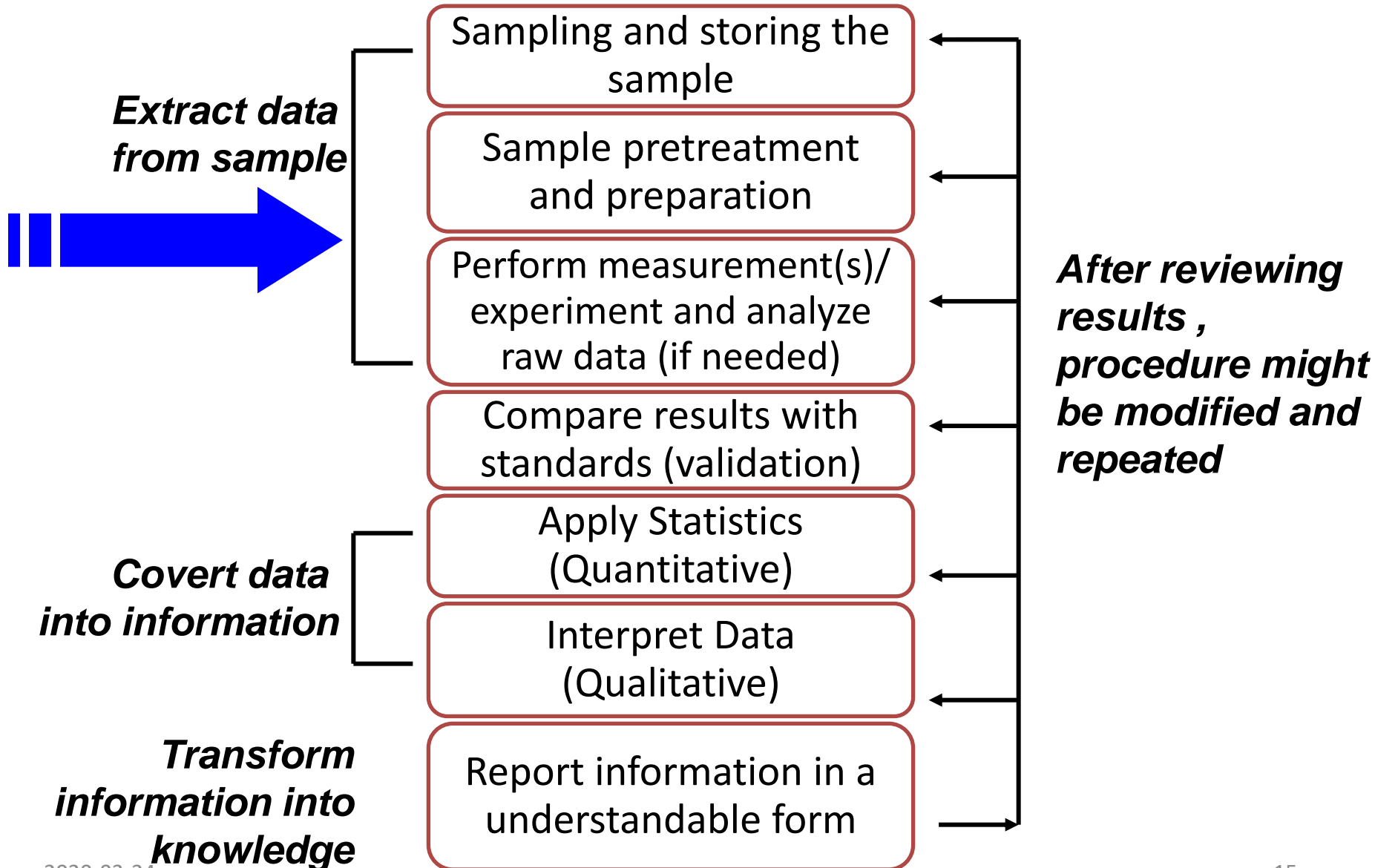
## Elemental information

- total analysis, speciation, mass analysis

## Molecular information

- compounds present, polyatomic ionic species, functional groups, structure

# Components of an Analytical Method



# 3. Analyzing Data and Reporting Results

- Data analysis takes many forms: **statistics**, simulations, etc...
- Analytical results can be criticized by reviewers and challenged by experts.
- Results can be reported in
  - Peer-reviewed papers (publications)
  - Technical reports to be published

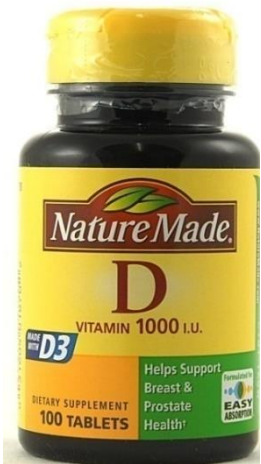


# Analysis of Errors

Precision and accuracy in measurements

How good does your number have to be?

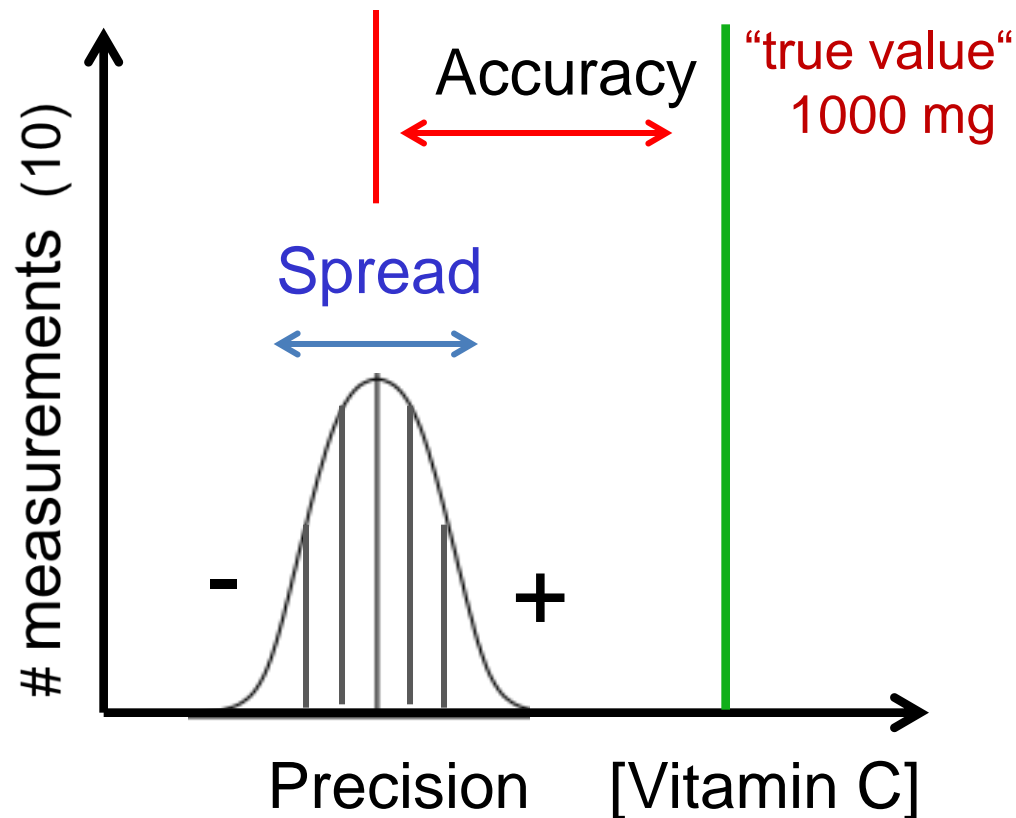
Does the pill contains 1000 mg **ascorbic** or less?  
Report the error of your measurements



**Nothing is perfect!!**

# Two main Types of Errors

1. Random (indeterminate error)– precision (**spread**)
2. Systematic (determinate error) –accuracy (**trueness**)



# Indeterminate (Random) Errors

Random errors are always associated with measurements

## -Examples

- Limitations of reading from analytical balances
- Electrical noise in instruments

# Determinate (Systematic) Errors

- Caused by faults in procedure or instrument
- Fault can be found out and corrected

## -Examples

- Improperly calibrated balances
- Uncalibrated volumetric flasks and pipettes
- Analyst error (misreading or inexperience)
- Contaminated or decomposed reagents
- Interferences

# Precision: How to report errors

We will focus on the precision to express the errors

Averages and <b>standard deviation</b>	Value = $30.2 \pm .3$ ml
Averages and SD: using <b>confidence limit</b>	Value = $6.2 \pm .5$ ml with 95 % confidence

# The Standard Deviation

- The standard deviation indicates the spread of data
- The sample standard deviation (for a data set of limited size) is given by  $s$ :

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}} \quad \text{Mean} = \bar{x}$$

- Relative standard deviation (RSD) (%)

$$RSD = \frac{s}{\bar{x}} * 100$$

See pg. 54-56 of Harris's book, Quantitative Chemical Analysis, Chapter 3

Measurement = average  $\pm$  uncertainty

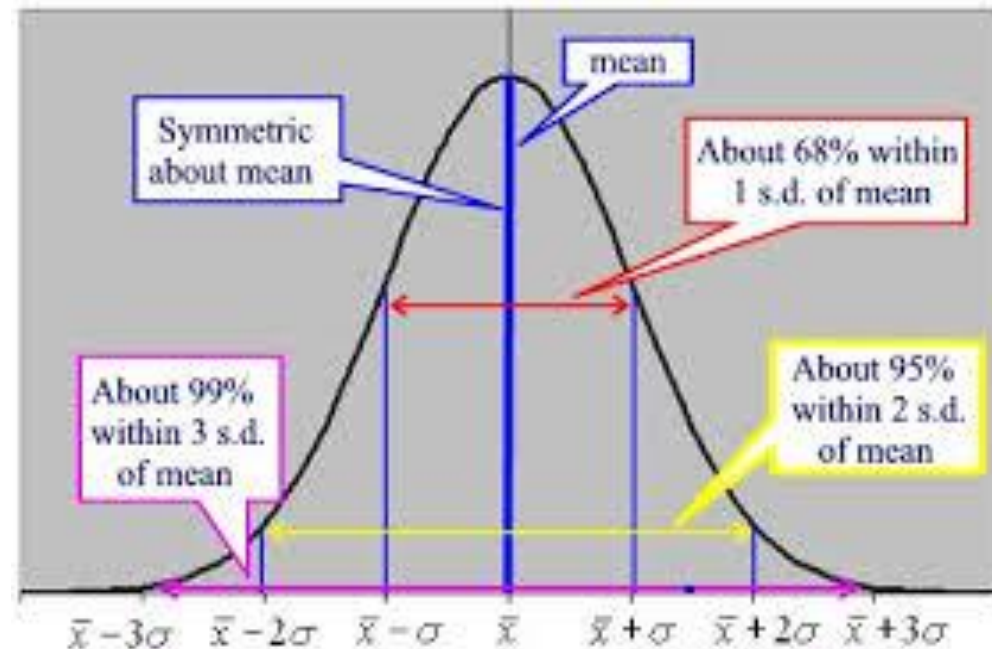
Measurement = average  $\pm$  Standard deviation

## How certain is your uncertainty?

The standard deviation, **s** means that 68.3 % of measurements will fall between average  $\sigma$ - and average  $+\sigma$

But **2s** means that 95 % of measurements will fall between average  $2\sigma$ - and average  $+2\sigma$

### The Gaussian Probability Distribution



Measurement = average  $\pm$  uncertainty (CL=95%)

## Example:

You are measuring the Ca in patients' blood samples and find in 6 samples: 102.3, 100.1, 98.56, 104.3, 99.89, 101.0. what is the average and the uncertainty (both absolute and relative of this dataset)? How do you report the data?

The average of these six measurements is 101.0 ppm (4 Sig. Fig.)

The standard deviation is 1.851 ppm

You would report either  $101.0 \pm 1.9$  ppm (absolute error)

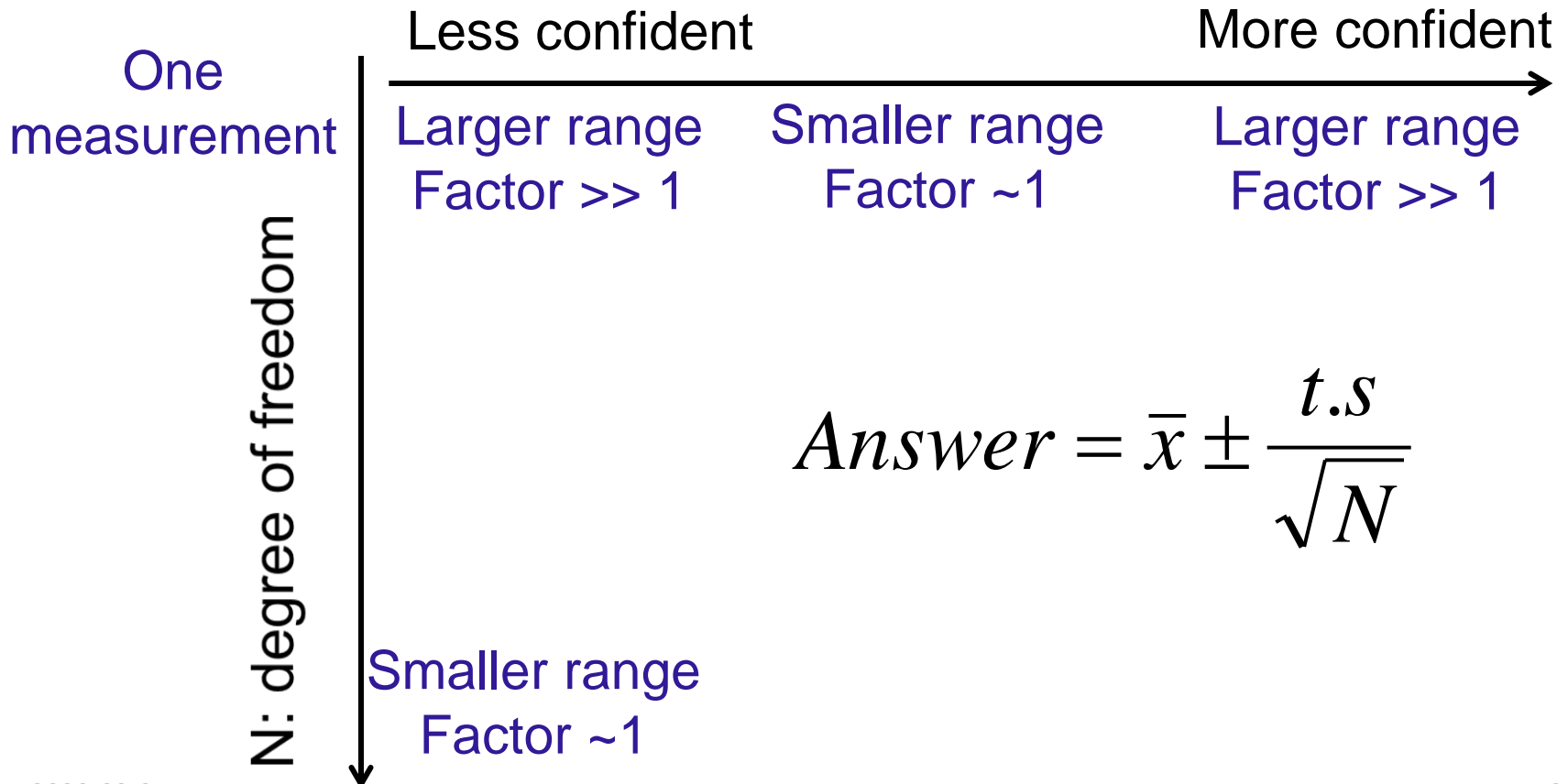
Or you would report  $101.0 \pm 2\%$  or  $(\pm 1.9\%)$  (relative )

# Defining error more precisely: Confidence Intervals

$$\text{Answer} = \bar{x} \pm (\text{factor}).s$$

$$\text{Factor} = \frac{t}{\sqrt{N}}$$

A t- table gives the exact factors



$$\text{Answer} = \bar{x} \pm \frac{t.s}{\sqrt{N}}$$



# T-table

Student t Table						
Degrees of Freedom	Confidence Interval					
	80% $t_{.90}$	90% $t_{.95}$	95% $t_{.975}$	98% $t_{.99}$	99% $t_{.995}$	99.73% $t_{.9985}$
1	3.078	6.314	12.706	31.821	63.657	235.800
2	1.886	2.920	4.303	6.965	9.925	19.207
3	1.638	2.353	3.182	4.541	5.841	9.219
4	1.533	2.132	2.776	3.747	4.604	6.620
5	1.476	2.015	2.571	3.365	4.032	5.507
6	1.440	1.943	2.447	3.143	3.707	4.904
7	1.415	1.895	2.365	2.998	3.499	4.530
8	1.397	1.860	2.306	2.896	3.355	4.277
9	1.383	1.833	2.262	2.821	3.250	4.094
10	1.372	1.812	2.228	2.764	3.169	3.975
11	1.363	1.796	2.201	2.718	3.106	3.850
12	1.356	1.782	2.179	2.681	3.055	3.764
13	1.350	1.771	2.160	2.650	3.012	3.694
14	1.345	1.761	2.145	2.624	2.977	3.636
15	1.341	1.753	2.131	2.602	2.947	3.586
16	1.337	1.746	2.120	2.583	2.921	3.544
17	1.333	1.740	2.110	2.567	2.898	3.507
18	1.330	1.734	2.101	2.552	2.878	3.475
19	1.328	1.729	2.093	2.539	2.861	3.447
20	1.325	1.725	2.086	2.528	2.845	3.422
25	1.316	1.708	2.060	2.485	2.787	3.330
30	1.310	1.697	2.042	2.457	2.750	3.270
40	1.303	1.684	2.021	2.423	2.704	3.199
60	1.296	1.671	2.000	2.390	2.660	3.310

$$Answer = \bar{x} \pm \frac{t.s}{\sqrt{N}}$$

Degrees of Freedom = n-1  
n = # of observations

# Probability Distributions and Measuring confidence Intervals

**Example 1**: Consider the following eight results:

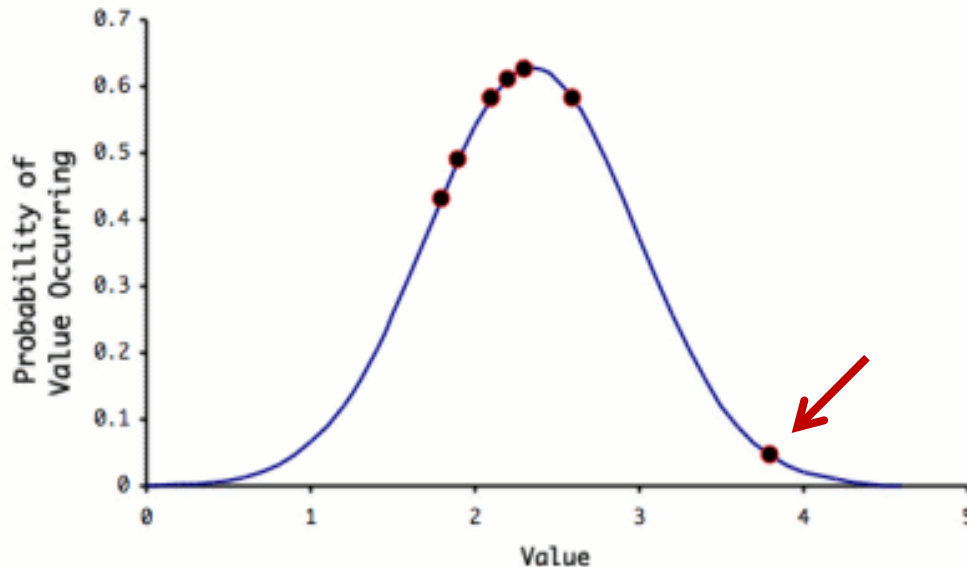
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2.1	2.3	2.6	2.1	1.9	2.2	1.8	3.8
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Mean = 2.35 and std deviation = 0.635

What is the chance that the large value of **3.8** occurred by random chance assuming a Gaussian distribution?



# Confidence Intervals – An example

$N = 8$ , mean = 2.35, and  $s = 0.635$

Choose a 95% confidence level.


Use t-table to obtain  $t$  (95% CL, degree of freedom =7)

$$\begin{aligned} \text{Answer} = \bar{x} \pm \frac{ts}{\sqrt{N}} &= 2.35 \pm (2.36 * 0.635) / \text{Sqrt}[8] \\ &= 2.35 \pm 0.53 \end{aligned}$$

**Result:** 3.8 is outside the range of  $2.35 \pm 0.53$ .

**Conclusion:** We could be 95% confident that the value of 3.8 is from a different system.

**Example 2**: Using a method you developed yourself for measuring iron in tablets, you find 14.1, 15.2, 14.8, 15.5, 15.3, 14.6 and 14.9 mg Zinc per capsule. Find the error bars on the average value of Iron in the tablets at a 95% confidence limit.


Look up in t-table!

$$\text{Answer} = \bar{x} \pm \frac{t.s}{\sqrt{N}} \quad \text{Answer} = 14.9\text{mgZn} \pm \frac{t.s}{\sqrt{N}}$$

S: calculate the standard deviation using a calculator to be =.47  
 t= we find “t” from the t-test table. We use a DF =7-1=6 and a 95% CL: t=2.45

N: we use N=7 as that is the actual measurements

$$\text{Answer} = 14.9\text{mgZn} \pm \frac{2.45, .47}{\sqrt{7}} = 14.9\text{mgZn} \pm 0.4\text{mgZn} \left| \begin{array}{l} 95\% \\ 95\%, 7 \end{array} \right.$$

**Example 3:** You measure the dopamine level in tablets using a voltammetric method that reports the standard error to be  $\pm .30$  mg Zinc. How many replicate measurements would you need to get the 95% confidence limits to under  $\pm .42$  mg dopamine?

$$\text{Answer} = \bar{x} \pm \frac{t.s}{\sqrt{N}} \rightarrow \text{error} = \pm .42 \text{mg at } 95\% = \pm \frac{t.\sigma}{\sqrt{N}}$$

You get “t “ from the t-table but you use degree of freedom (DF) as infinite since you know  $\sigma$

$$N = \left( \frac{t.\sigma}{\pm \text{error}} \right)^2 = \left( \frac{1.96.,30}{.42} \right)^2 = 1.96 \text{ Round to } 2$$

Note the error 0.3 was after a lot of measurements, 0.42 is what we can tolerate

# Check For Systematic Error

## Is there Systematic Error?



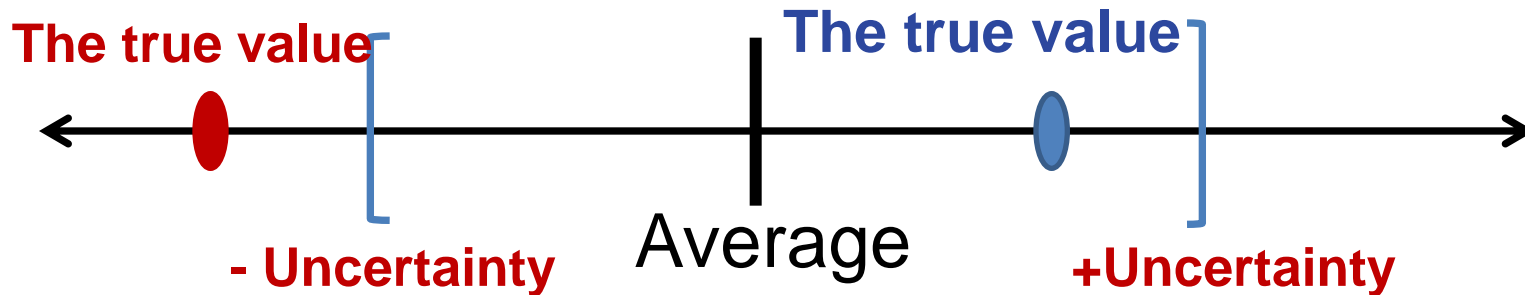
Certified Reference Materials  
for Testing and Research

- Before running an “unknown” run a standard (certified reference material)
- Many companies sell standard reference materials, and these should be incorporated into experimental design

**Systematic error? Run a known standard (ideally several) and troubleshoot**

**Answer= Average  $\pm$  uncertainty**

$$Known = \bar{x} \pm \frac{t.s}{\sqrt{N}}$$



Systematic error check. You are comparing an experimental result against **a known precise and accurate value**. If the precise and accurate value is within your error limits, then there is no systematic error.

- Run sample and standard material measurements
- Calculate **the mean and stdev**
- Calculate **t value and compare it with the table value at CL (say, 95%)**

**Systematic Error Exists in the new method if  $t_{cal} > t_{tab}$  for the given CL**

**Example 4:** You have bought a standard for chloride analysis that has a chloride content of 20.00 %. Six repeated measurements of this result in an average value of 20.06 %  $\pm$  0.025%. Is there evidence of systematic error in your measurements?

$$Known = \bar{x} \pm \frac{t.s}{\sqrt{N}}$$

$$20.00 = 20.06 \pm \frac{t.(0.025)}{\sqrt{6}}$$

If  $t < t_{95, N}$  Then with 95 % confidence they are the same (look up at the t-table)

First calculate the t value (t exp).

Now you simply use the values from the problem to get an actual t value

$$|t| = \left| \frac{20.06 - 20.00}{0.025} \right| \sqrt{6} = 5.9 > 2.571 = t_{95, 5}$$

From the t-table!

The computed t-value is 5.9 which is greater than the  $t_{95,5}$  or 2.571

We thus conclude that the known value and the experimental values are not the same and that there is a source of systematic error.



# Reference

Daniel Harris,(2007), “Quantitative Chemical Analysis” 7th Edition, New York, Chapters 3, 4.



**Faculty of science**

# **Introduction to Electroanalytical Chemistry**

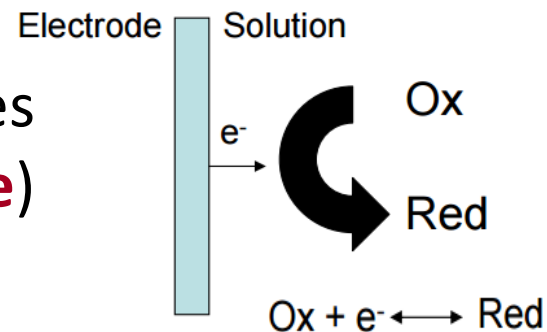
**Lecture# 2**

**Date: February 23, 2020**

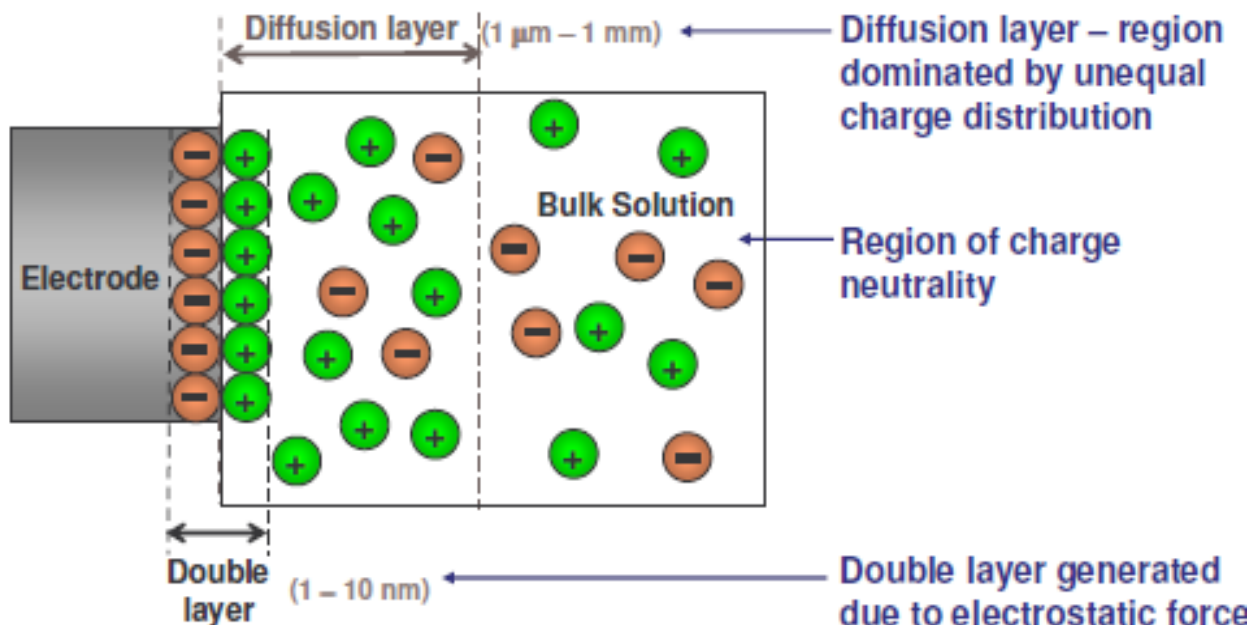
# Electrochemistry

The study of reactions of charged particles (ions or electrons) at the interface of **electrode** and a conductive solution (**electrolyte**).

The electron transfer process (**electrode reaction**) occur within the electrical double layer.



**Electrodes:**  
Pt, Au, Pd, C



# Electrochemistry, uses

## Electrochemistry

Electricity

Chemistry

Use electricity to drive  
chemical reactions  
(Electrolysis)

Use chemical reactions to  
generate electricity  
(Batteries)

Using electrical measurements of  
chemical system for analytical purposes  
(**Electroanalytical applications**)

# Why Electroanalytical Chemistry?

Electroanalytical methods offer some advantages over other analytical methods.

- Electrochemical instrumentation is relatively inexpensive and can be miniaturized (used at on-site applications)
- Useful for the determination of **different oxidation states** of an element in a solution.
- Highly sensitive and provide **low detection limits**.
- Used to characterize the electrode reactions and provide kinetics information and equilibrium constants.

# History of Electroanalytical Methods

- **Michael Faraday**: the law of electrolysis

“...the amount of a substance deposited from an electrolyte by the action of a current is proportional to the chemical equivalent weight of the substance.”



Michael Faraday  
(1791-1867)

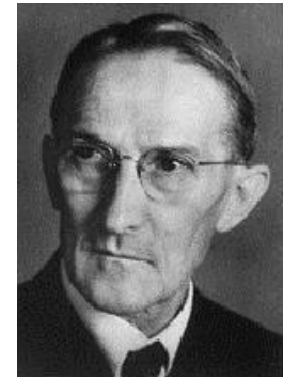


Walther Nernst  
(1864-1941)

- **Walther Nernst**: The Nernst equation (Nobel Prize 1920)

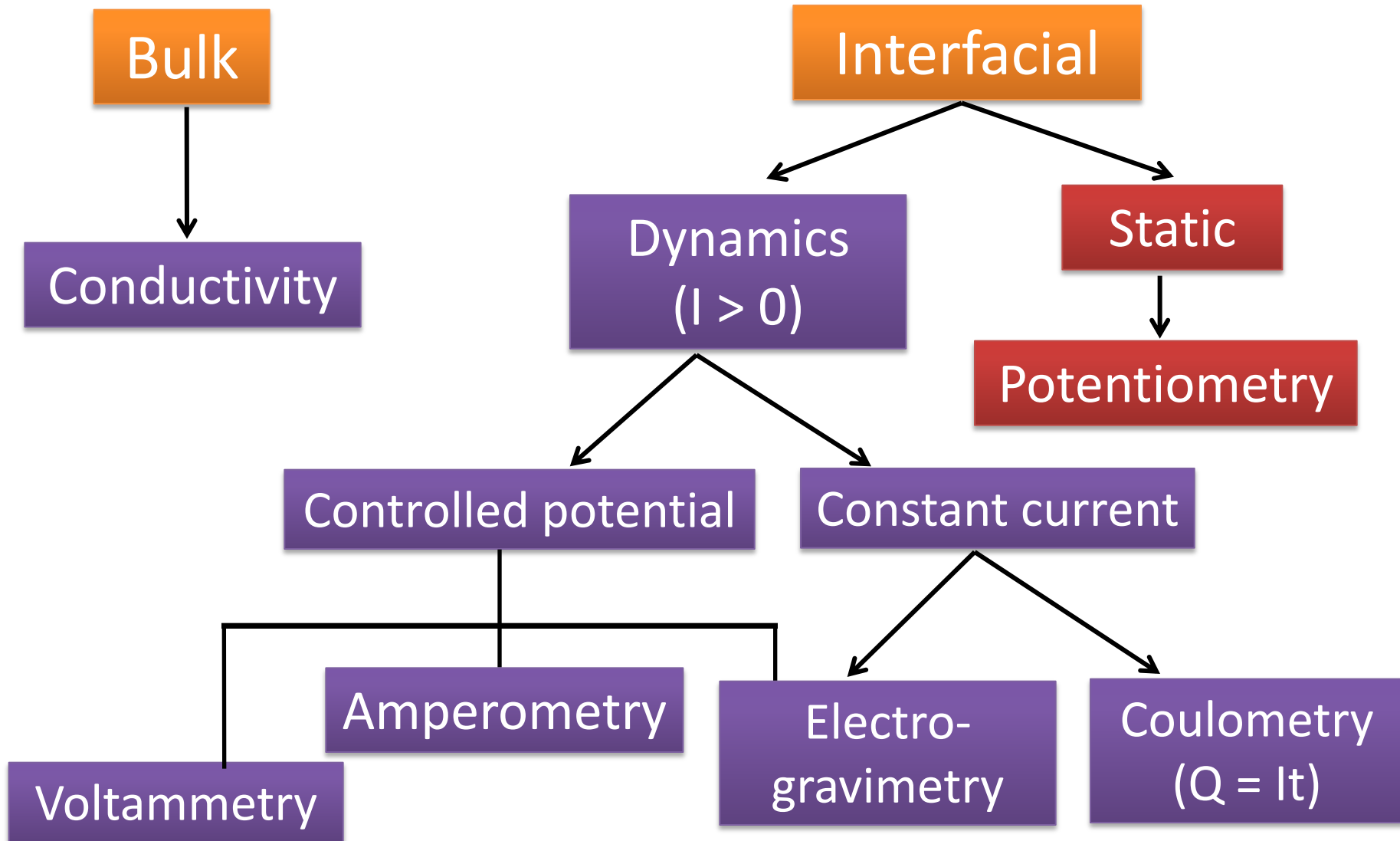
- **Jaroslav Heyrovsky**: The invention of polarography (Nobel Prize 1959)

The current generated by oxidation or reduction in a cell is continuously increased as the A.P. is applied.



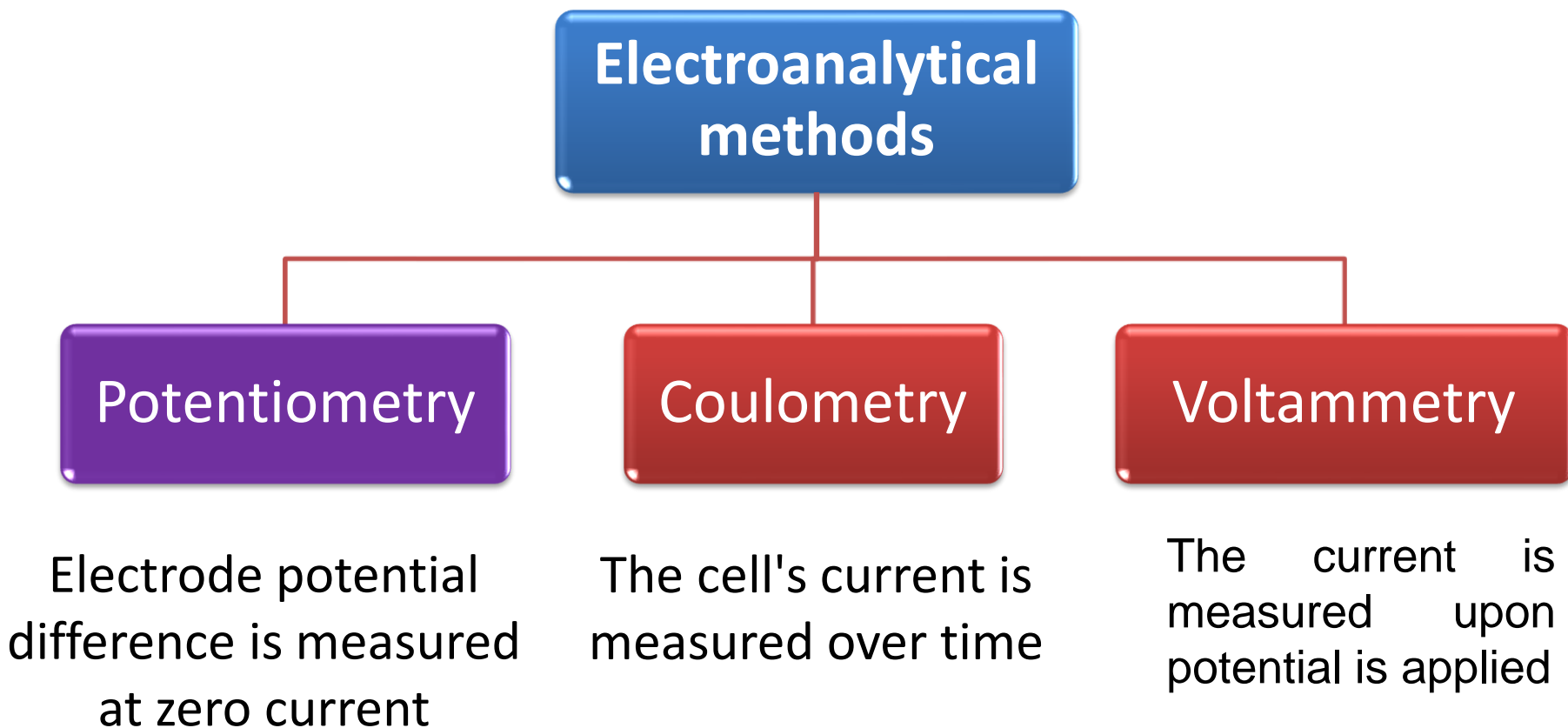
Jaroslav Heyrovsky  
(1890-1967)

# Electrochemical techniques



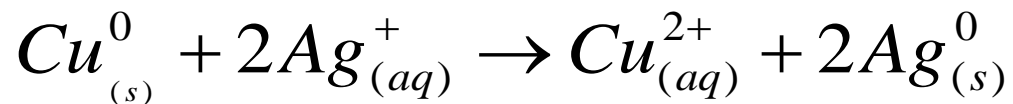
# Electroanalytical methods

Techniques that measured the potential (V), and/or current (A) in electrochemical cell containing the analyte.





# A summary of redox terminology: Reaction of copper wire with silver ion.



Term	Process
<b>Oxidation</b> <ul style="list-style-type: none"><li>• One reactant loses electrons</li><li>• Reducing agent is oxidized</li><li>• Oxidation number increases</li></ul>	<p>Cu loses electrons Cu is the reducing agent and becomes oxidized The oxidation number of Cu increases from 0 to +2</p>
<b>Reduction</b> <ul style="list-style-type: none"><li>• One reactant gains electrons</li><li>• Oxidizing agent is reduced</li><li>• Oxidation number decreases</li></ul>	<p>Silver ion gains electrons Silver ion is the Oxidizing agent and becomes reduced The oxidation number of Ag+ decreases from +1 to 0</p>



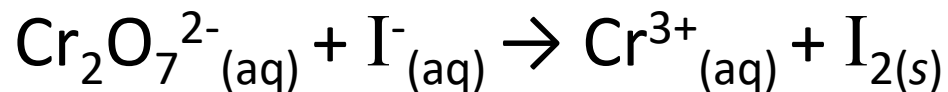


## Reminder

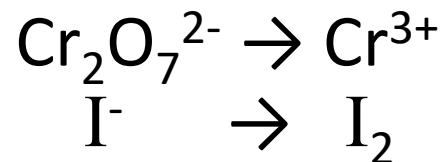
# Half-Reaction Method for Balancing Redox Reactions

- Divide the reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species.
- Balance the atoms and charges in each half-reaction.
  - First balance atoms other than O and H, then O, then H.
  - Balance the electrons at both sides of half reaction.
- If necessary, multiply one or both half-reactions by an integer so that
  - number of  $e^-$  gained in reduction = number of  $e^-$  lost in oxidation
- Add the balanced half-reactions, and include states of matter.

## Example: Balancing Redox Reactions in Acidic Solution



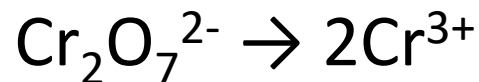
*Step 1: Divide the reaction into half-reactions.*



*Step 2: Balance the atoms and charges in each half-reaction.*

For the  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  half-reaction:

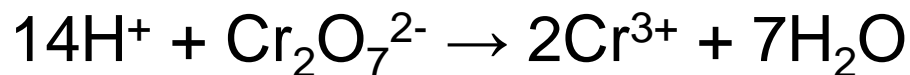
Balance atoms other than O and H:



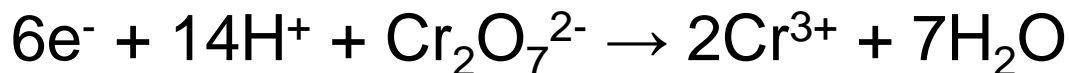
Balance O atoms by adding  $\text{H}_2\text{O}$  molecules:



Balance H atoms by adding H<sup>+</sup> ions:



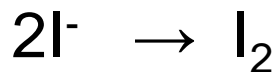
Balance charges by adding electrons:



This is the *reduction* half-reaction. Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is reduced, and is the oxidizing agent. The O.N. of Cr decreases from +6 to +3.

For the I<sup>-</sup>/I<sub>2</sub> half-reaction:

Balance atoms other than O and H:



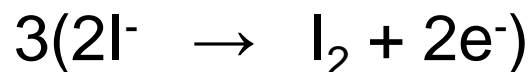
Balance the electrons



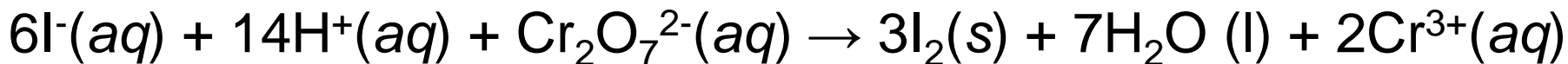
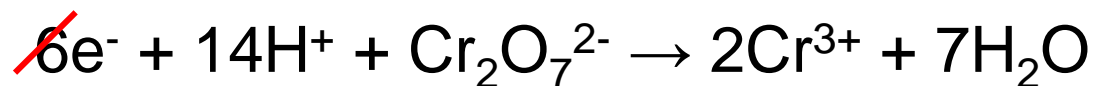
This is the *oxidation* half-reaction. I<sup>-</sup> is oxidized, and is the reducing agent. The O.N. of I increases from -1 to 0.

*Step 3: Multiply each half-reaction, by an integer so that the number of e<sup>-</sup> lost in the oxidation equals the number of e<sup>-</sup> gained in the reduction.*

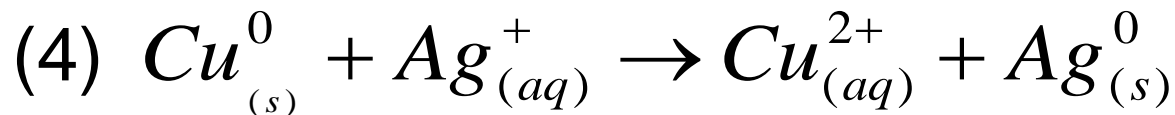
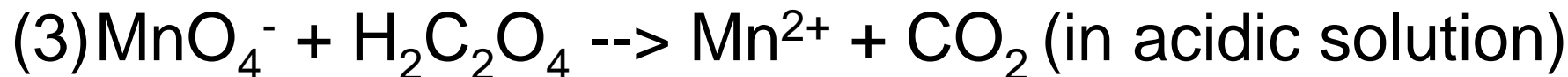
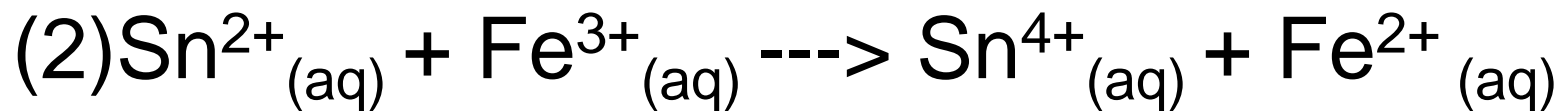
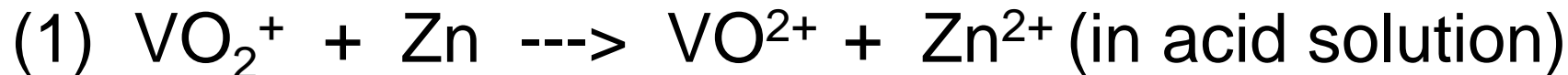
The reduction half-reaction shows that 6e<sup>-</sup> are gained; the oxidation half-reaction shows only 2e<sup>-</sup> being lost and must be multiplied by 3:



*Step 4: Add the half-reactions, canceling substances that appear on both sides, and include states of matter. Electrons must always cancel.*



**Problems:** Balance the following Redox reactions





## Reminder

# Electrochemical Cells

A galvanic (voltaic) cell uses a spontaneous redox reaction ( $\Delta G < 0$ ) to generate electrical energy.

-The system does work on the surroundings.

A electrolytic cell uses electrical energy to drive a nonspontaneous reaction ( $\Delta G > 0$ ).

-The surroundings do work on the system.

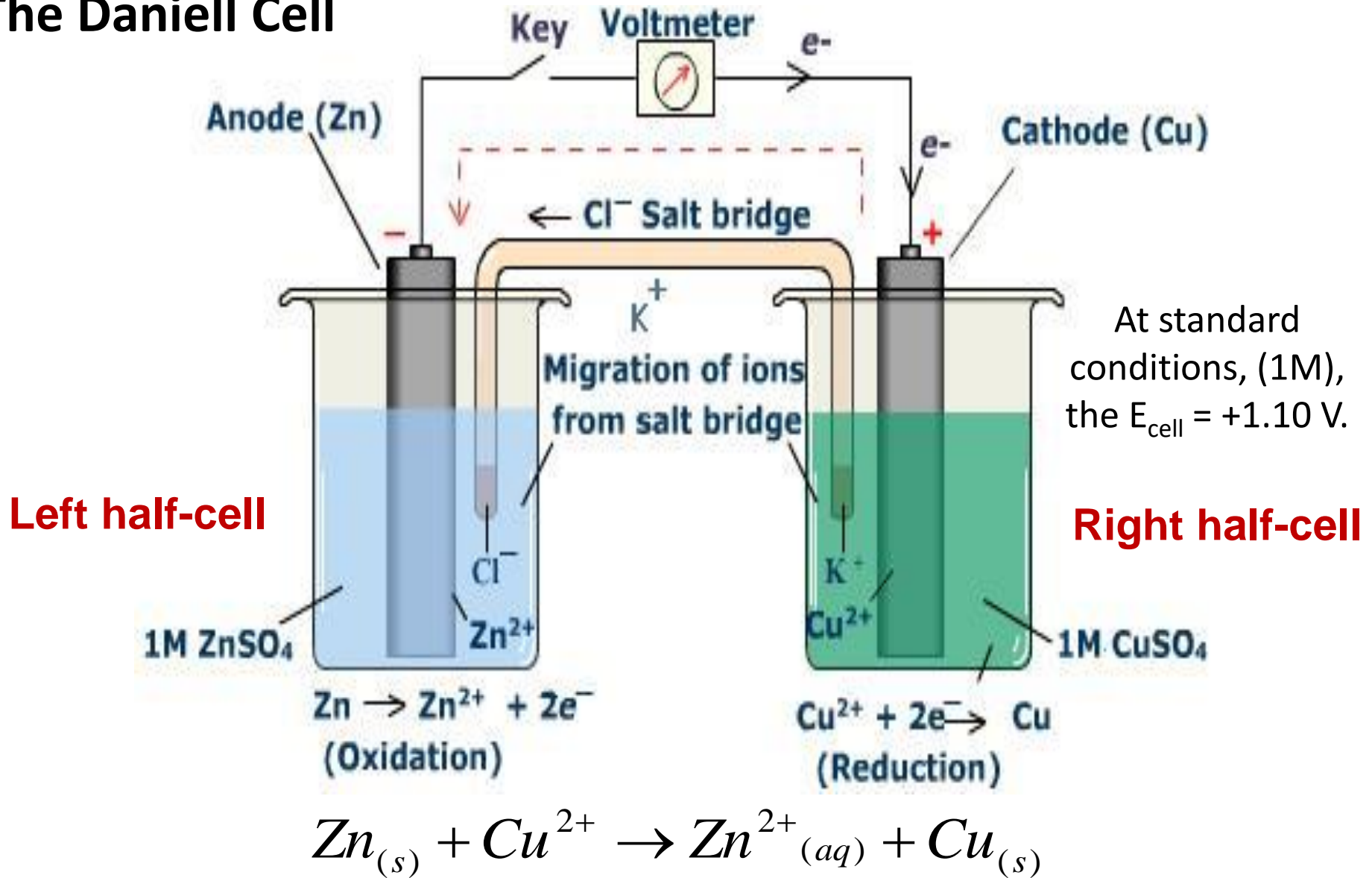
Both cell types are fabricated using two electrodes placed in an electrolyte solution.

The anode is the electrode at which oxidation occurs.

The cathode is the electrode at which reduction occurs.

# A Galvanic (Voltaic) Cell

## The Daniell Cell



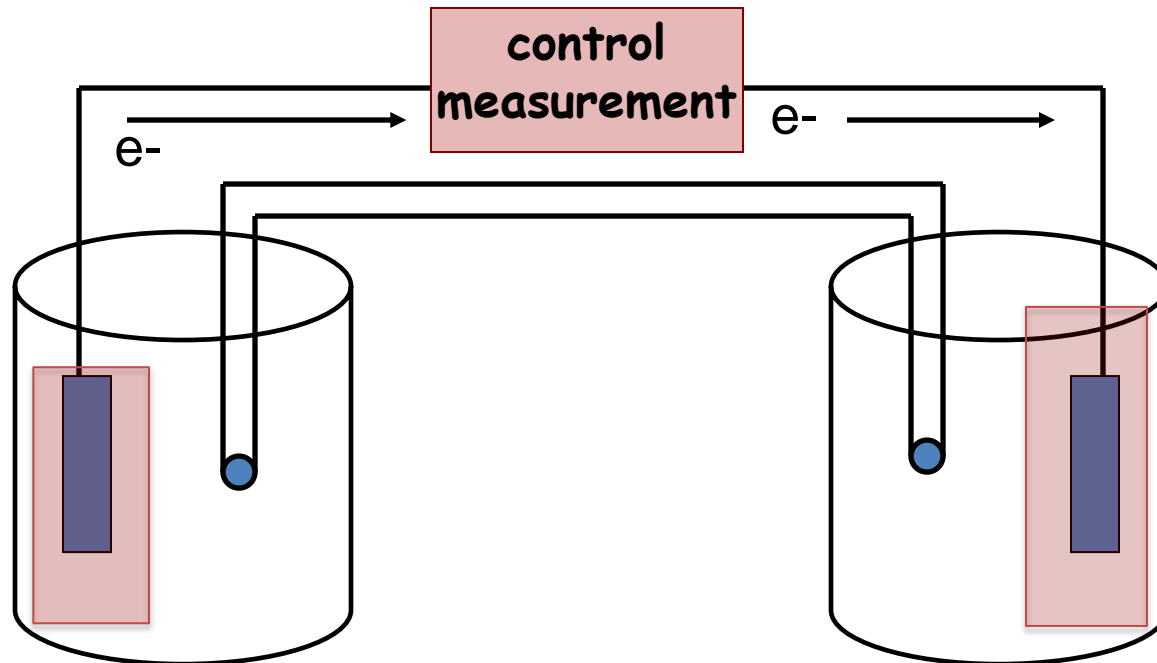


# Electrochemical Cells and Analytical Methods

**Potentiometry:** Measures equilibrium potential  $E$

**Amperometry:** Control  $E$ , measures current  $I = f(t)$  as function of time

**Coulometry:** Control  $E$ , measure total  $Q$  over a period of time



working electrode  
indicator electrode  
detector electrode

reference electrode  
counter electrode

# Nernst Equation

Use the expression for the Gibbs dependence on activity in terms of the cell potential.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

The relation between cell potential  $E$  and free energy gives

$$-nFE = -nFE^\circ + RT \ln Q \quad \Delta G = -nFE$$

Rearrange and obtain the Nernst Equation.

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

This equation relates the dependence of the cell potential on the reaction quotient.

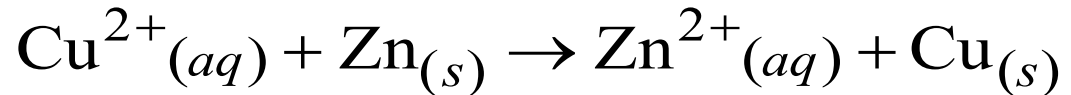
# Nernst Equation, continued

At  $T = 25\text{ }^\circ\text{C}$  and plug in the values for the constants,  $R$  and  $F$ .

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

“ $n$ ” – the number of moles of electrons transferred in the reaction.

For Daniell Cell



$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Cu}} a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}} a_{\text{Zn}}}$$

Annotations:  $a_{\text{Cu}} = 1$ ,  $a_{\text{Zn}} = 1$ , and  $a_{\text{Zn}^{2+}} = \gamma \frac{[\text{Zn}^{2+}]}{[\text{ }]^\circ}$

$$E = E^\circ - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.10 - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

# Electrode & Cell Potential

Electrode reaction either reduction or oxidation occurred is expressed as a reduction)  $M^{n+} + ne^{-} \rightarrow M^{\circ}$

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[M]}{[M^{n+}]}$$

## Standard Cell Potential

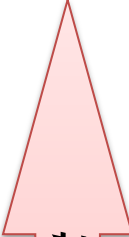
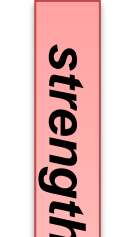
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

## Cell Potential

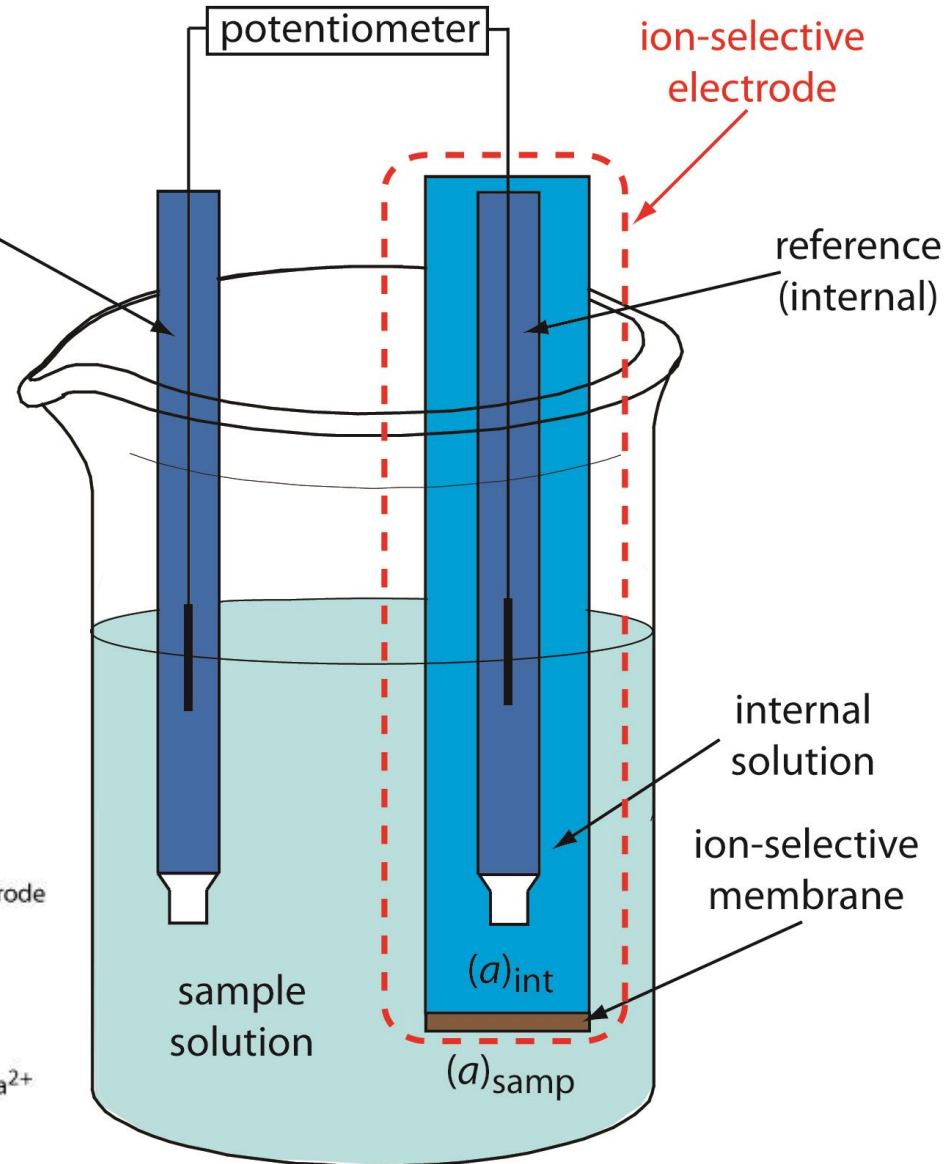
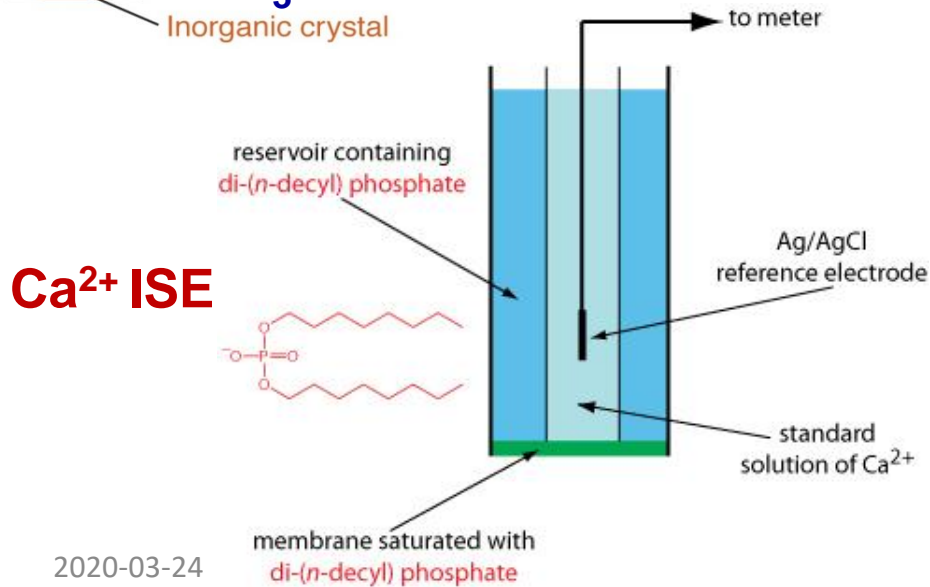
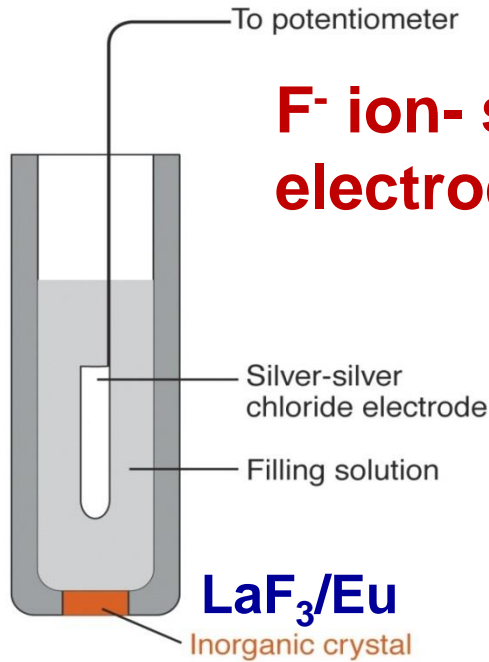
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

# Standard Reduction Potential ( $E^\circ$ )

- SHE used to predict the voltage when different cells are connected

	Half-Reaction	$E^\circ$ (V)	
 <b>strength of oxidizing agent</b>	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87	<b>strength of reducing agent</b> 
	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36	
	$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23	
	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96	
	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80	
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77	
	$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40	
	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34	
	<b><math>2H^+(aq) + 2e^- \rightleftharpoons H_2(g)</math></b>	<b>0.00</b>	
	$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	-0.23	
	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44	
	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83	
	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71	
	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05	

# Potentiometric measurements



# Potentiometric methods

- Based on a **static (zero-current) conditions**
- Measured a potential between two electrodes (**indicator electrode** and **reference electrode**)
- The **indicator (sensing) electrode** responds to changes in the activity of the analyte.
- The analyte concentration is related to the potential difference between the indicator and the reference electrodes (applying the Nernst equation)
- As the **potential of reference electrode is held constant**, we can measure **the concentration of species**.
- Various electrodes **have been designed to respond selectively to specific analytes**

- Reference electrode is connected to the negative terminal of the readout device (**potentiometer**)
- The time taken by the electrode to establish equilibrium with the solution affects the sensitivity of the measurement.
- The most common indicator electrode is the **glass-membrane electrode** used in a pH meter.

$$E_{\text{cell}} = E_{\text{indicator}} - E_{\text{reference}}$$

## Potentiometer

A device for measuring the potential of an electrochemical cell without drawing a current or altering the cell's composition.



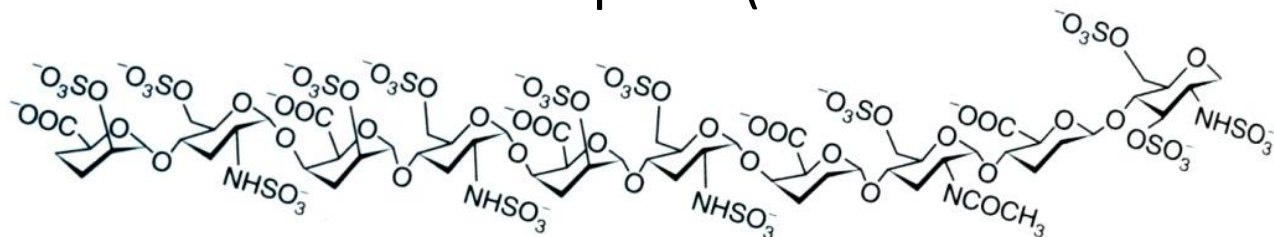
# Application of Potentiometry

- Clinical diagnostics (blood testing, electrolytes in blood electrolytes in hospitals ( $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ )
- Measuring soil samples ( $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ )
- Determination the fluoride-ion concentration of drinking water
- Coupling ion chromatography with potentiometric detection
- Micro ion selective electrodes (ISEs) as probe tips for Scanning electrochemical microscopy
- To determine the end points in titration and reaction rate constants in the study of reaction kinetics
- Environmental monitoring



# Example 1: A Heparin Sensor

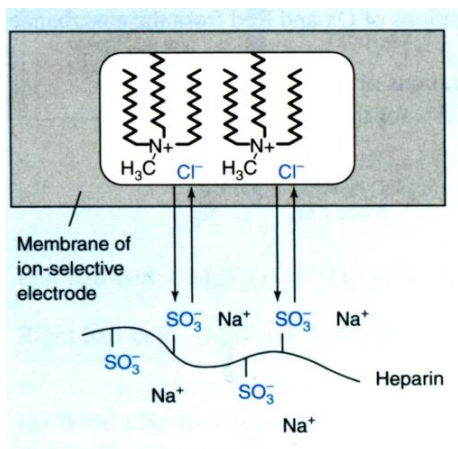
- Potential response is proportional to heparin concentration in blood
- Sensor is selective for heparin (ion-selective membrane)



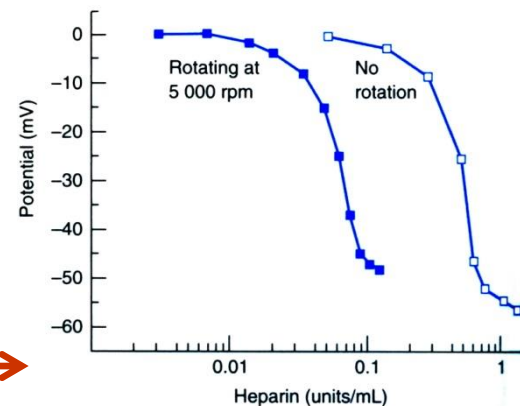
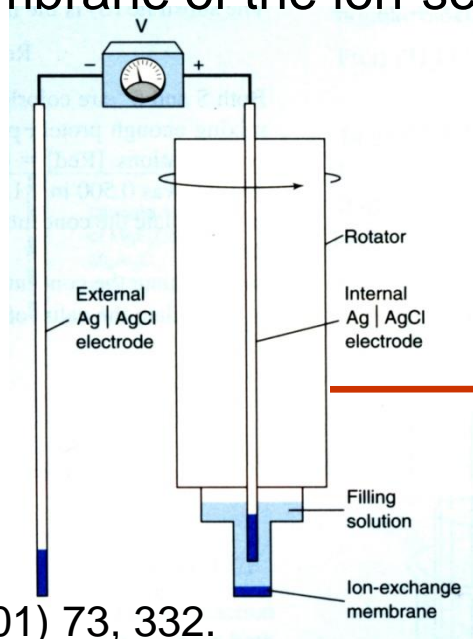
**Heparin**

**Anticoagulant**

Ion exchange between heparin (negatively charged) and Cl associated with tetraalkylammonium ions in the membrane of the ion-selective electrode



Binding generates  
→  
potential difference.



Potential is proportional to [heparin]

Q. Ye and M. E. Meyerhoff, Anal. Chem. (2001) 73, 332.

## Example 2: Using a Pt indicator electrode to respond to $[Fe^{2+}]$ and $[Fe^{3+}]$ concentration

$$E_{cell} = E_{Ind.} - E_{Ref.}$$

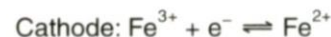
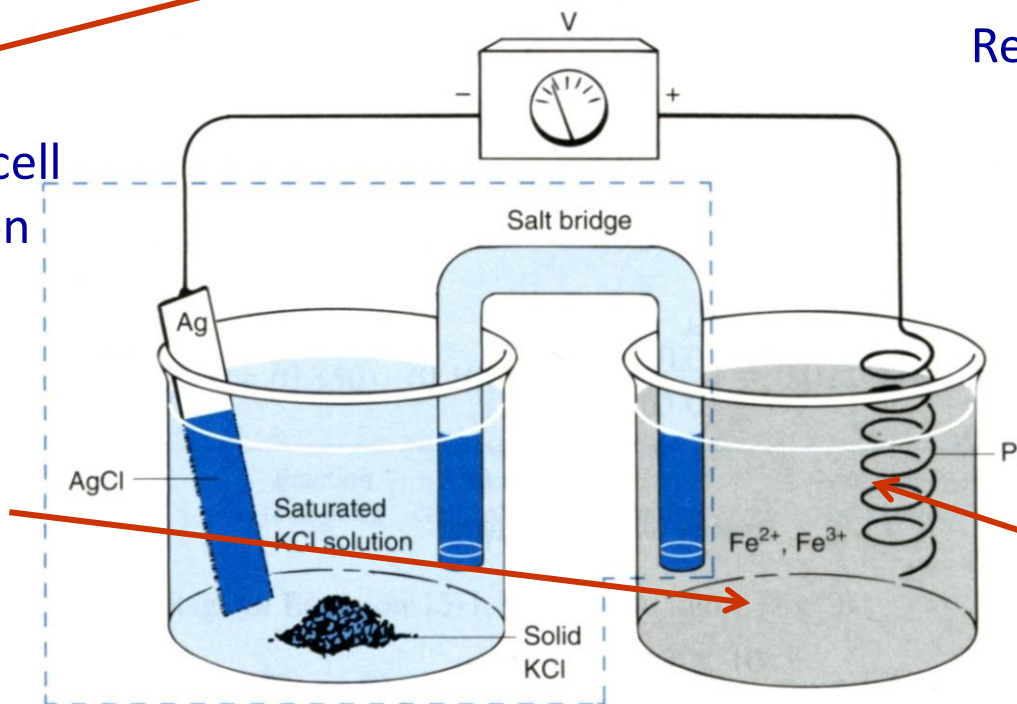
$$E_{cell} = \left\{ 0.771 - \frac{0.05916}{1} \log \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \right) \right\} - \left\{ 0.222 - 0.05916 \log [Cl^{-}] \right\}$$

Potential of the cell only depends on  $[Fe^{2+}]$  &  $[Fe^{3+}]$

Unknown solution of  $[Fe^{2+}]$  &  $[Fe^{3+}]$

Reference electrode,  $[Cl^{-}]$  is constant

Pt wire is indicator electrode whose potential responds to  $[Fe^{2+}]/[Fe^{3+}]$



# Components of a Potentiometric Cell

1. Reference electrode
2. Salt bridge
3. Analyte (unknown solution becomes a half-Cell)
4. Indicator electrode

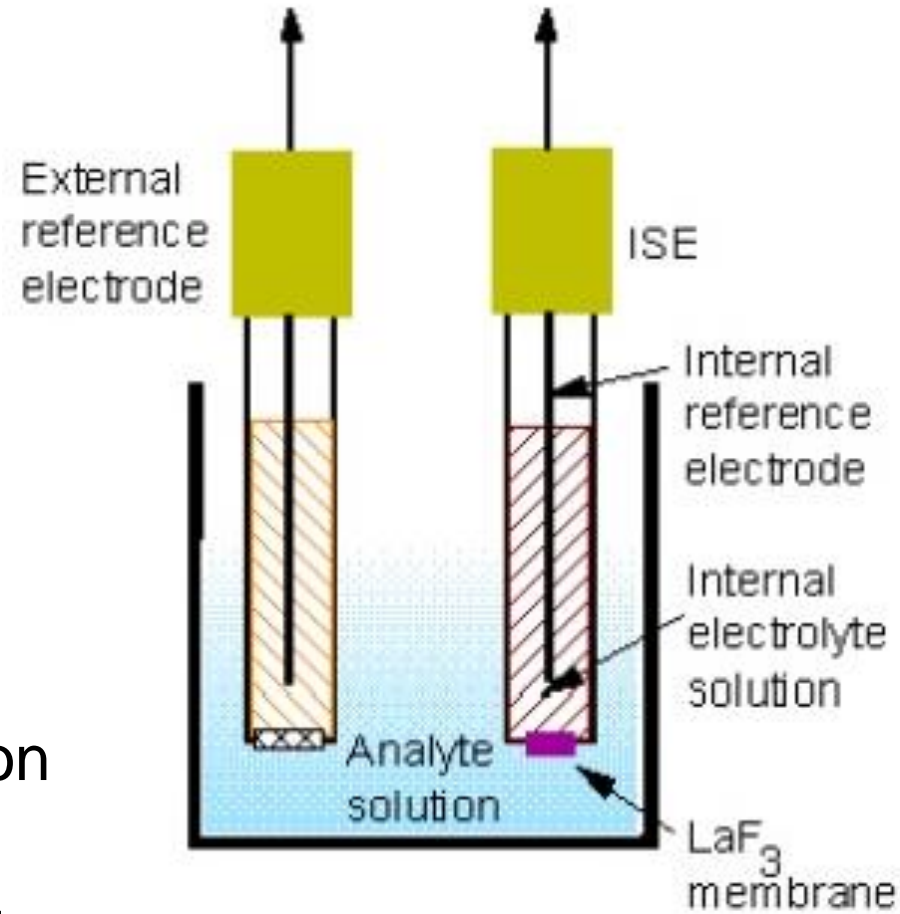
$$E_{cell} = E_{Ind.} - E_{Ref.}$$

## Indicator Electrode:

Responds to analyte concentration

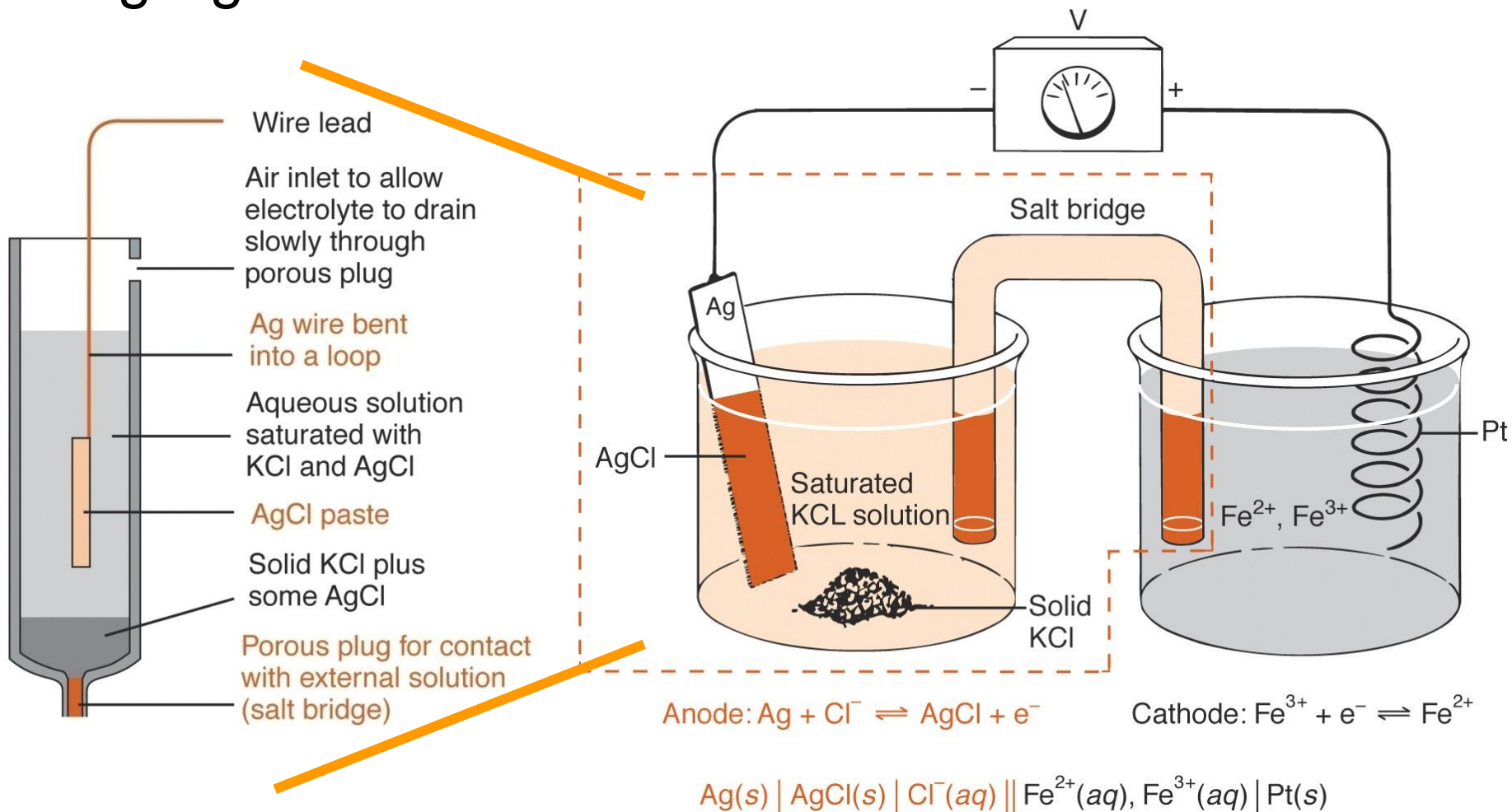
## Reference Electrode:

Second half cell at a constant potential



# Reference Electrodes

## Ag/AgCl



# Reference electrode

An **electrode** of a well known and stable **equilibrium electrode potential**.

It is used as a reference point against which the **potential** of other electrodes can be measured in an electrochemical cell.

## Ideal Reference electrode

The potential for an ideal reference electrode should be:

- Constant ( $\pm 0.1$  mV) and have long term stability
- Absolutely independent of the composition of the sample solution
- Set by a **reversible redox couple** and **obeys the Nernst equation**
- Weakly temperature dependent.

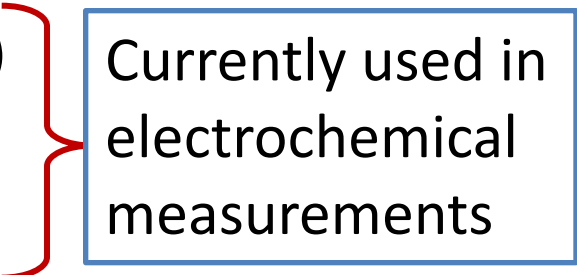


# Reference Electrodes: Types

1. Standard hydrogen electrode (SHE)

2. Saturated Calomel Electrode (SCE)

3. Silver-Silver Chloride Electrode



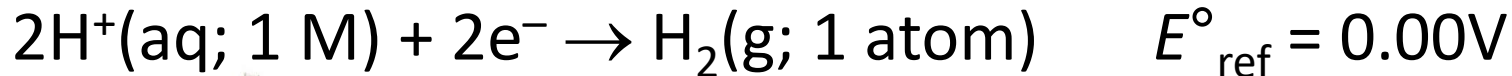
Currently used in  
electrochemical  
measurements

# 1. Standard Hydrogen Electrode (SHE)

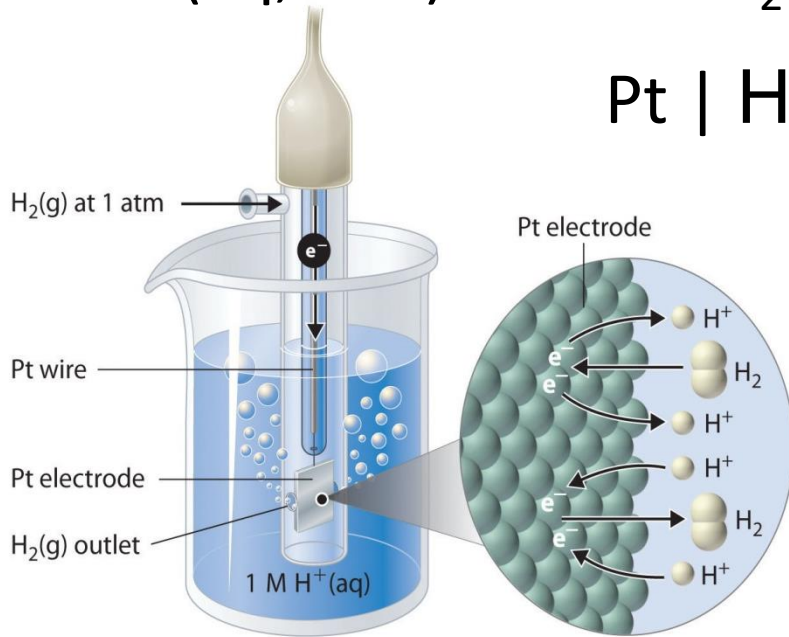
Its equilibrium potential is controlled by (activity) of the hydrogen ions and the dissolved hydrogen gas (pressure).

Uses a platinum electrode at which its surface reduces  $2\text{H}^+$  to  $\text{H}_2$  gas.

Difficult to handle, SCE is used instead.



Pt |  $\text{H}_2$  (1 atm), 1 M  $\text{H}^+$  || half-cell



half-reaction at Pt surface:  
 $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$

This electrode consists of a Pt electrode with  $\text{H}_2$  gas at 1 atm bubbling through it. The Pt electrode is immersed in 1 M strong acid (HCl).

All other standard potential are reported relative to SHE



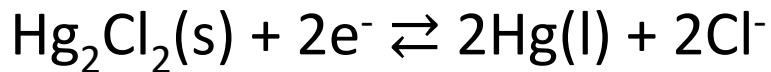
# 2. Saturated Calomel Electrode (SCE)

Hg | Hg<sub>2</sub>Cl<sub>2</sub>(saturated), KCl (X M) || half -cell reaction

X = [KCl] , X=0.1 M, 1 M or saturated (≈4,6 M)

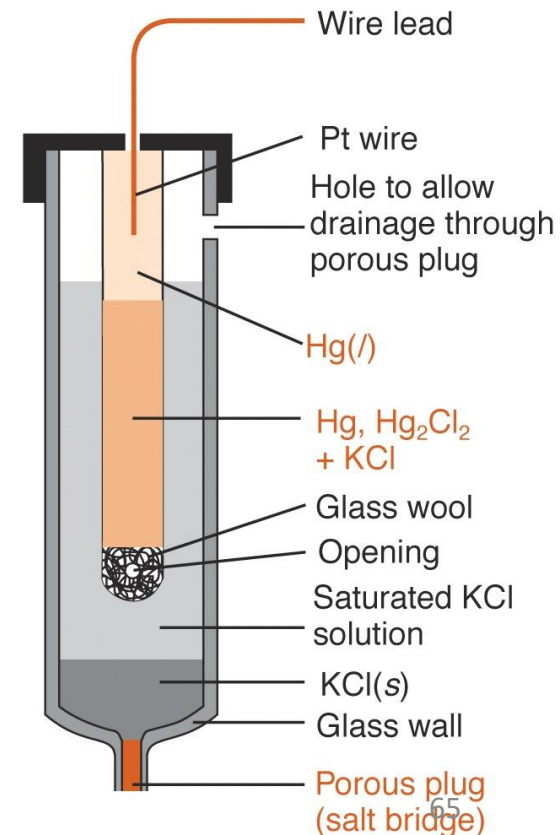
- Easy to prepare
- Temp dependent
- Toxic

The half-reaction for (SCE)



$$E = E^0 - \frac{0.0592}{2} \log(\text{Cl}^-)^2 = 0.241\text{V vs.SHE}$$

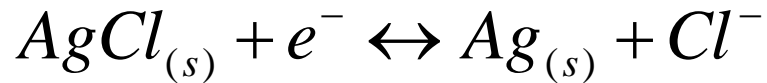
- Composed of metallic Hg in contact with saturated solution of Hg<sub>2</sub>Cl<sub>2</sub> (calomel)
- Pt wire is in contact with the metallic mercury
- Calomel is in contact with saturated KCl solution
- KCl is used to maintain constant ionic strength
- Common, much easier to work, with no gas



# 3. Silver-Silver Chloride Electrode

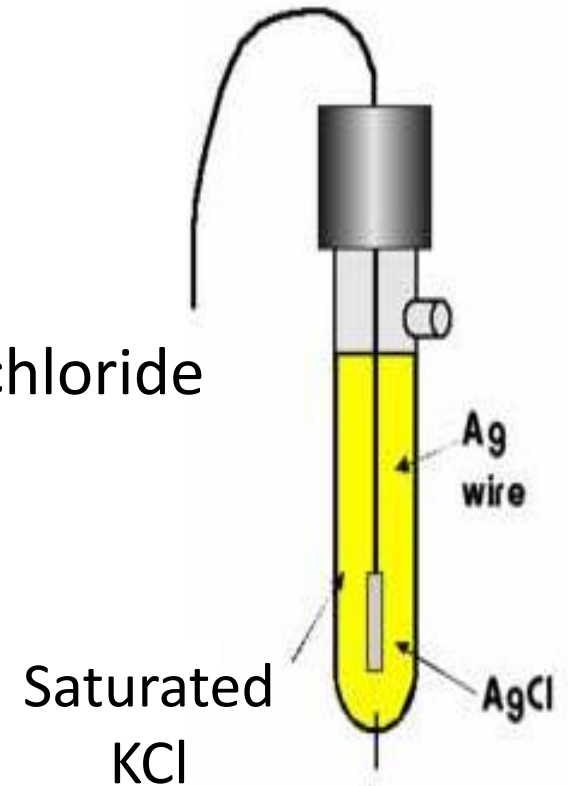
Ag|AgCl(saturated), KCl(saturated) || Reduction half-cell

The half-reaction for the silver-silver chloride electrode:



E =+ 0.197 V vs. SHE at 25°C

- Consists of silver metal coated with silver chloride paste
- Immersed in saturated KCl
- Convenient



# Potentiometric Theory

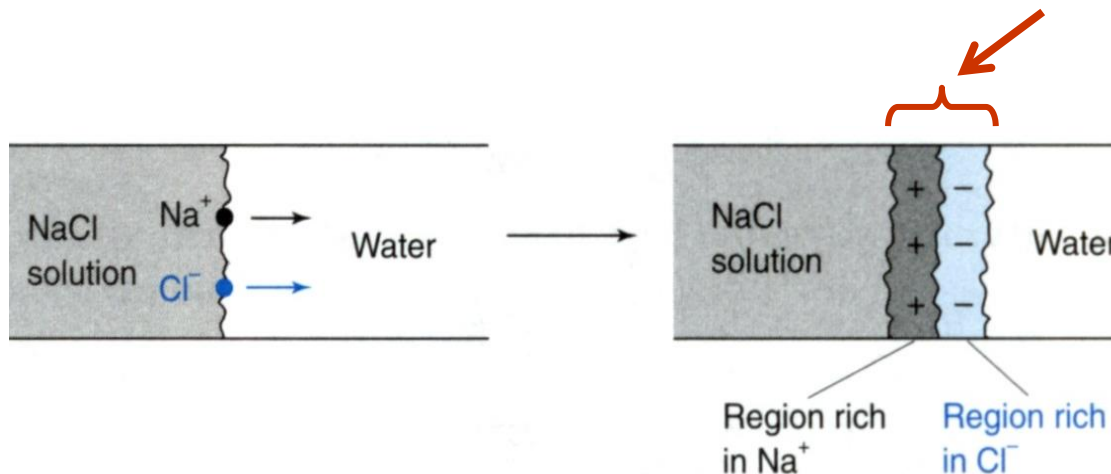
- The cell consists of indicator and reference electrodes
- As the potential of the ref. electrode is constant, the potential developed at the indicator electrode responds to the analyte.
- The origin of the potential at the indicator electrode is the **separation of charge across an interface between solutions of differing ionic strengths** (an inner solution at **fixed analyte activity** and an outer solution with **variable analyte activity**).

The charge separation varies with electrode type, known as **junction potential**

# Junction Potentials

- **Liquid junction:** interface between two solutions containing different electrolytes or different concentrations of the same electrolyte
- A potential develops at any interface where there is a separation of charge (described by Nernst equation).
- Caused by **unequal** mobilities of the +ve and -ve ions

Different ion mobility results in separation in charge



An electric potential is generated by a separation of charge

- Created at the junction of the salt bridge and the solution
- Minimized in KCl salt bridge due to similar mobilities of  $K^+$  and  $Cl^-$
- A source of error
- Small potential (few mV)
- Junction potential limits the accuracy of direct potentiometric measurements

**Table 15-2** Liquid junction potentials at 25°C

<b>Junction</b>	<b>Potential (mV)</b>
0.1 M NaCl   0.1 M KCl	-6.4
0.1 M NaCl   3.5 M KCl	-0.2
1 M NaCl   3.5 M KCl	-1.9
0.1 M HCl   0.1 M KCl	+27
0.1 M HCl   3.5 M KCl	+3.1

# Indicator electrodes

- Respond **to change in analyte activity**
  - Generates a potential ( $E_{ind}$ ) that depends on analyte concentration
  - Show high degree of selectivity
  - Classified according to mechanism by which the electrode potential is produced.
- 
- **Metal indicator electrode:** Develop an electric potential in response to a redox reaction at the metal surface.
  - **Membrane indicator electrode:** develop a potential determined by the difference in concentration of a particular ion on two sides of a special membrane

# Indicator Electrodes: Types

## **I. Metal Indicator electrodes**

- a. Electrodes of the First Kind (first order)
- b. Electrodes of the Second Kind (second order)
- c. Inert Metallic Electrodes (for Redox Systems)

## **II. Membrane Indicator electrodes**

- a. Glass pH IE
- b. Glass IE for other cations
- c. Liquid Membrane IE
- d. Crystalline-Membrane IE

## **III. Gas Sensing Probes**

# First Order Electrodes

- A metal in contact with a solution containing its cation  $M^+$ .

- $M / M^{n+}$



- At the metal/solution interface, a potential develops (proportional to the activity of the metal ion).

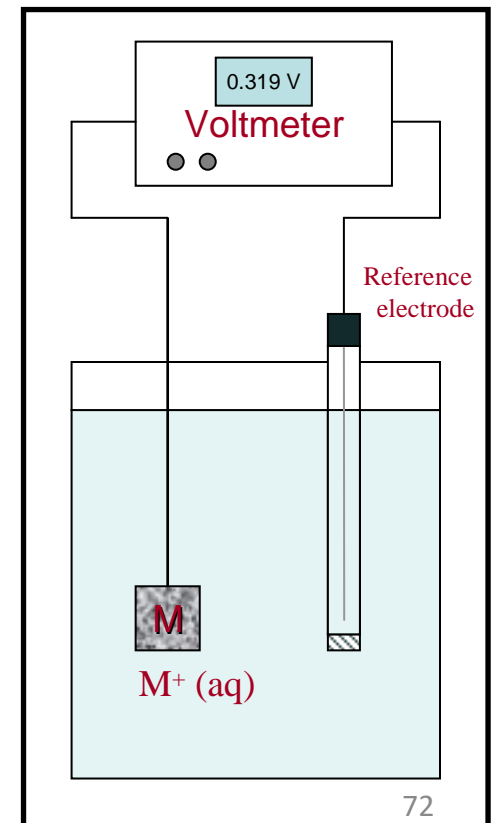
## Example:

Silver electrode (dipped in a solution of  $AgNO_3$ )

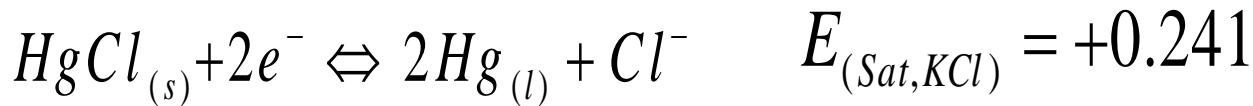
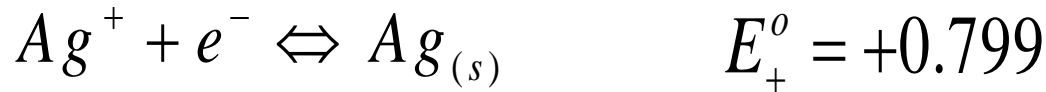


$$E_{ind} = E^o - \frac{0.0592}{n} \log \frac{1}{[Ag^+]}$$

In combination to reference electrode (SCE),  
Cell voltage changes as a function of  $[Ag^+]$







$$E_{cell} = E_{Ind.} - E_{Ref.} = \left\{ \underbrace{0.799 - \frac{0.05916}{1} \log \left( \frac{1}{[Ag^+]} \right)}_{\text{Potential of Ag indicator electrode}} \right\} - \{0.241\}$$

Potential of SCE

## Disadvantages

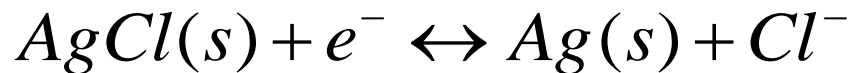
- Not very selective ( $Ag^+$  interferes with  $Cu^{+2}$ )
- May be pH dependent (Zn and Cd dissolve in acidic solutions)
- Easily oxidized (deaeration required)
- Non-reproducible response such as in Fe, Ni, Co, Cr, W because the formation of oxides

# Electrodes of the Second Kind

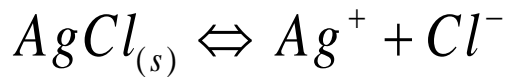
- A metal wire coated with one of its sparingly soluble salt.
- A common example is Ag/ AgCl electrode.
- Respond to anions by forming precipitates or stable complex

## Example

- Ag electrode for Cl<sup>-</sup> determination

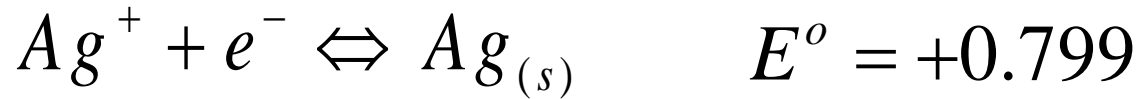


$$E_{ind} = +0.222 - \frac{0.05916}{n} \log a_{Cl^{-}}$$
$$= +0.222 + 0.05916 pCl$$



$$K_{sp} = 1.82 \times 10^{-10}$$

$$K_{sp} = [Ag^+][Cl^-] \Rightarrow [Ag^+] = \frac{K_{sp}}{[Cl^-]}$$



$$E = E^o_{Ag^+/Ag} - \frac{0.05916}{1} \log \left( \frac{1}{[Ag^+]} \right)$$

$$E = 0.799 - \frac{0.05916}{1} \log \frac{[Cl^-]}{K_{sp}}$$

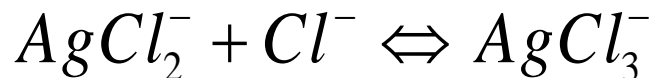
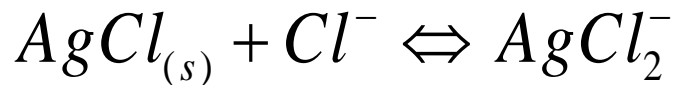
$$E = 0.799 + \frac{0.05916}{1} \log K_{sp} - \frac{0.05916}{1} \log [Cl^-]$$

$$E = 0.799 + \frac{0.05916}{1} \log 1.82 \times 10^{-10} - \frac{0.05916}{1} \log [Cl^-]$$

$$E = 0.223 - \frac{0.05916}{1} \log [Cl^-]$$

## Limitations

- Can be used only over a range of anion concentration to keep the solution saturated with the substance coating the metal
- For Ag/AgCl electrode, too low Cl<sup>-</sup> concentration causes the AgCl coating to dissolve completely.
- Too high Cl<sup>-</sup> concentration has the effect of forming soluble complex ions



Interference from other ions such as Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup>, CN<sup>-</sup> and S<sup>2-</sup>

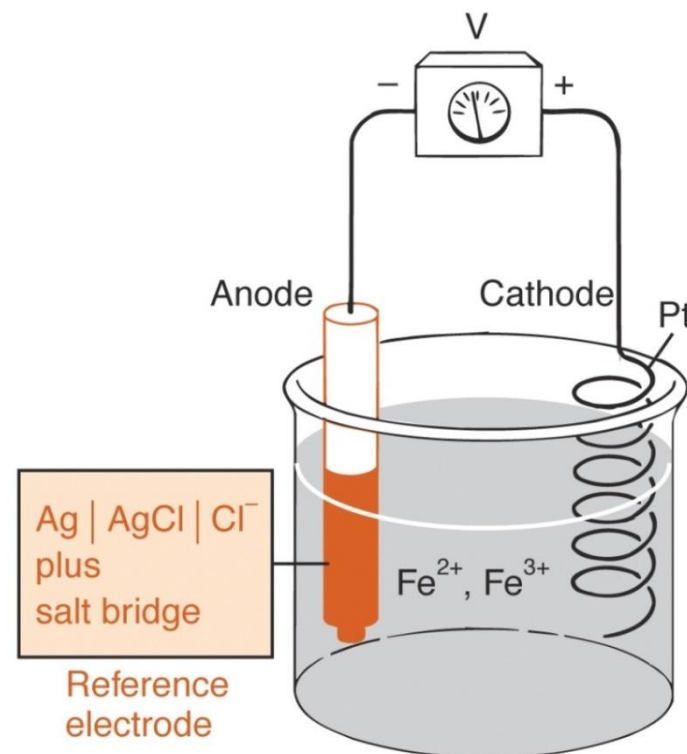
# Inert Metallic (Redox) Electrodes

- Serves as a source of electrons for redox half reaction
- The potential developed at the inert electrode depends on the nature and concentration of redox reagents in the solution
- Inert: does not participate in many chemical reactions
- Irreversible, such as Pt, Au, Pd, C

**Example:** a Pt electrode immersed in solution of  $Fe^{2+}/Fe^{3+}$  develops a potential:

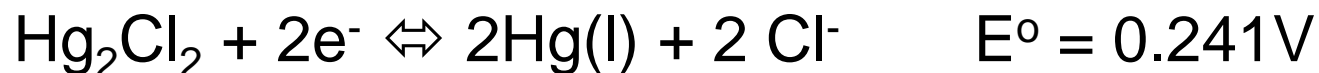
$$E = E^o_{Fe^{3+}/Fe^{2+}} - \frac{0.05916}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

2020-03-24



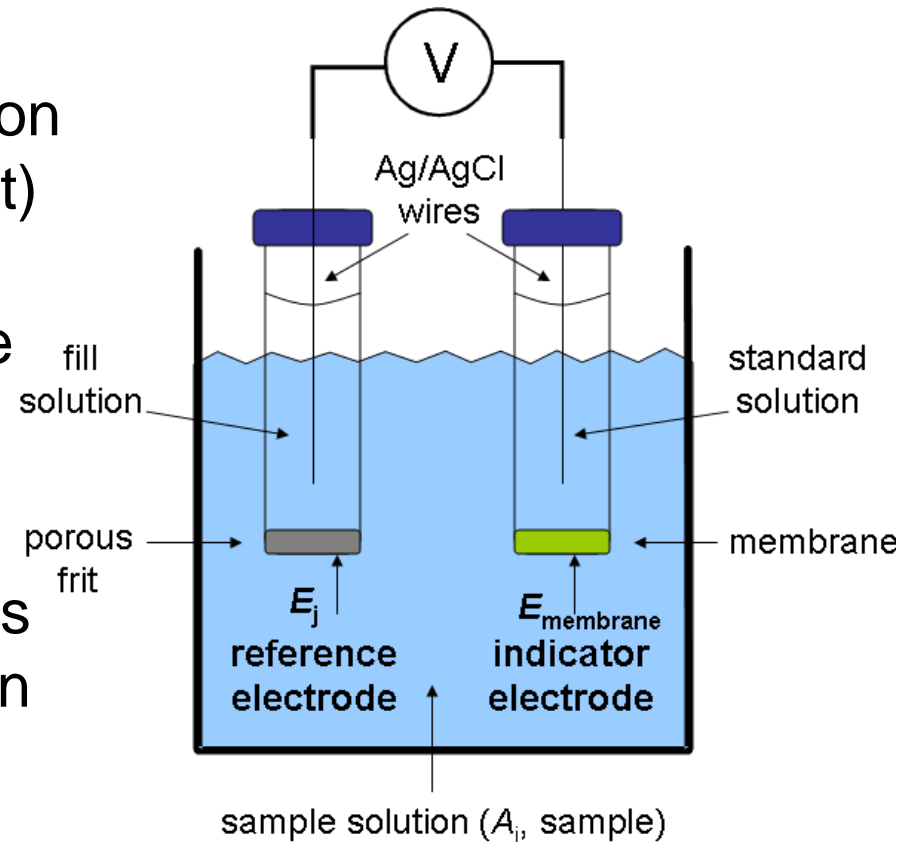
## Problems

1. What is the electrode potential for the electrode  $\text{Ag}|\text{AgI}(\text{s})|\text{I}^-(0.01\text{ M})$ ? for  $\text{AgI}$ ,  $K_{\text{sp}}=1 \times 10^{-16}$
2. A potential of 0.50 V was measured vs. SCE. What is the concentration of  $\text{Ag}^+$ ?



# Membrane electrodes (Ion-selective Electrodes)

- Do not involve redox reactions
- The potential developed results from **an unequal charge buildup** at opposing surfaces of a special membrane.
- Responds selectively to **one** ion (selectively binds the ion of interest)
- Contains a thin membrane capable of only binding the desired ion
- The charge at each surface is governed by the position of an equilibrium involving analyte ions



# Ion –selective electrode, continue

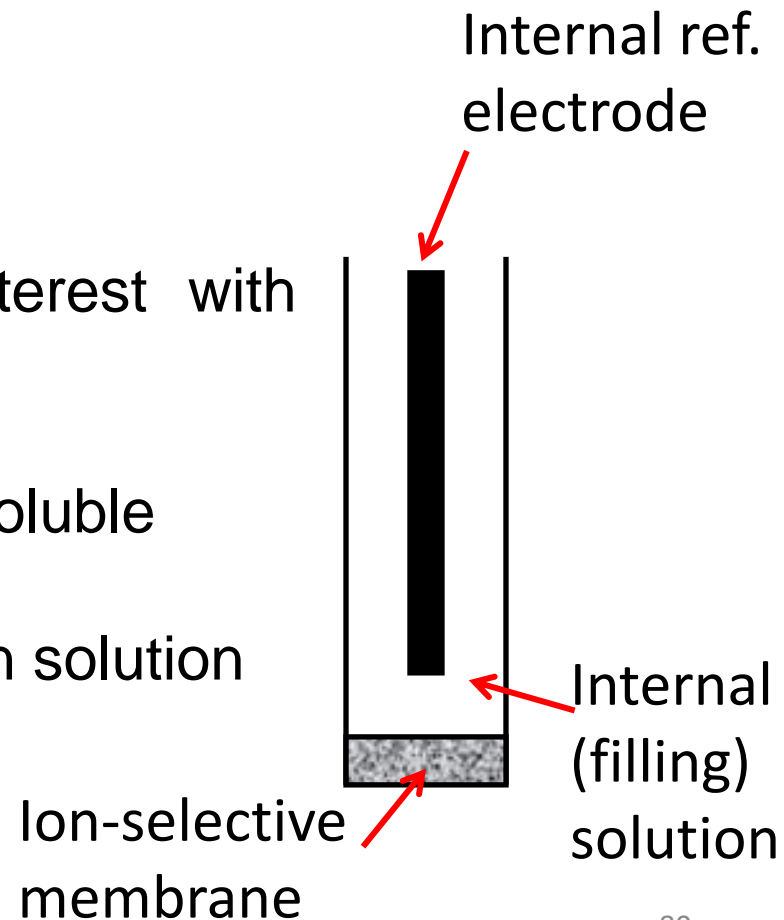
- Made from a **selective ion-conducting membrane** (ion-exchange material that allows ions to pass through)

- Reference electrode is inbuilt

- Internal solution (contains ion of interest with constant activity)

- Membrane is nonporous and water insoluble

- Responds specifically to one species in solution





- If  $C^+$  is the ion of interest
- $[C^+]$  inside the electrode  $\neq$   $[C^+]$  outside the electrode
- Results in a potential difference across the membrane

$$\text{At } 25 \text{ }^\circ\text{C, } E = \text{constant} + \frac{0.0592}{z_i} \log \left( \frac{[C^+]_{\text{outer}}}{[C^+]_{\text{inner}}} \right)$$

**$[C^+]$  inner is constant**

- $z_i$  is the charge on the selective ion (negative for anions)
- $z_i = +1$  for  $K^+$ ,  $z_i = +2$  for  $Ca^{2+}$ ,  $z_i = -2$  for  $CO_3^{2-}$

# Ion –selective electrodes (ISE)

- Respond directly to the analyte
- Used for direct potentiometric measurements

## ISE cell consists of

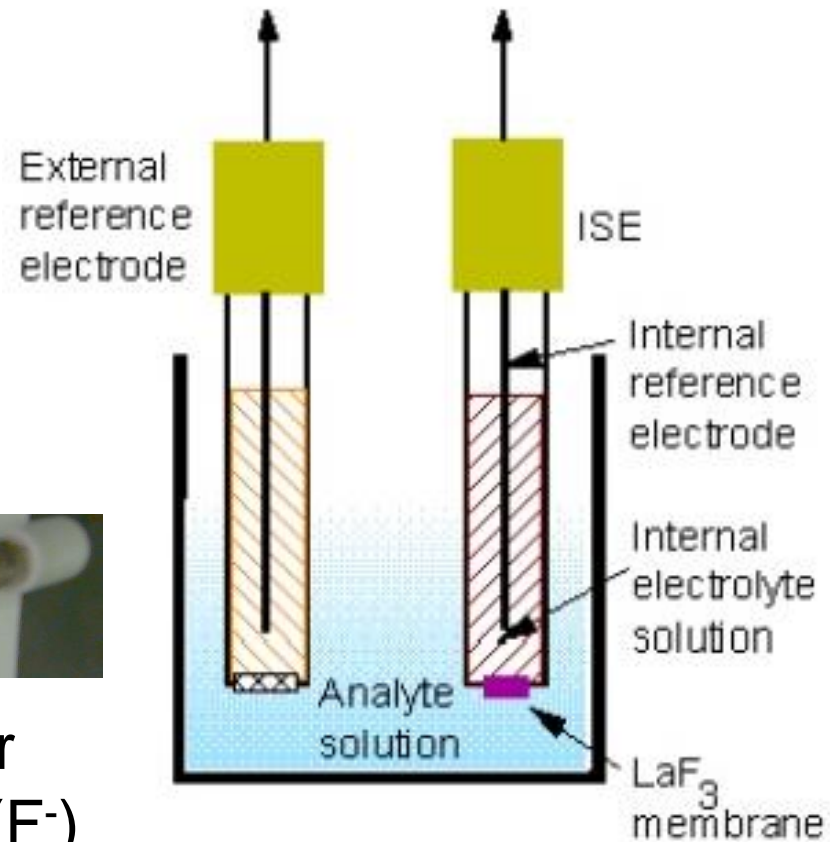
- ion-selective membrane
- an internal reference electrode
- an external reference electrode
- a voltmeter.

## Examples

- pH electrode
- Calcium ( $\text{Ca}^{2+}$ ) electrode
- Fluoride ( $\text{F}^-$ ) electrode



ISE for fluoride ( $\text{F}^-$ )



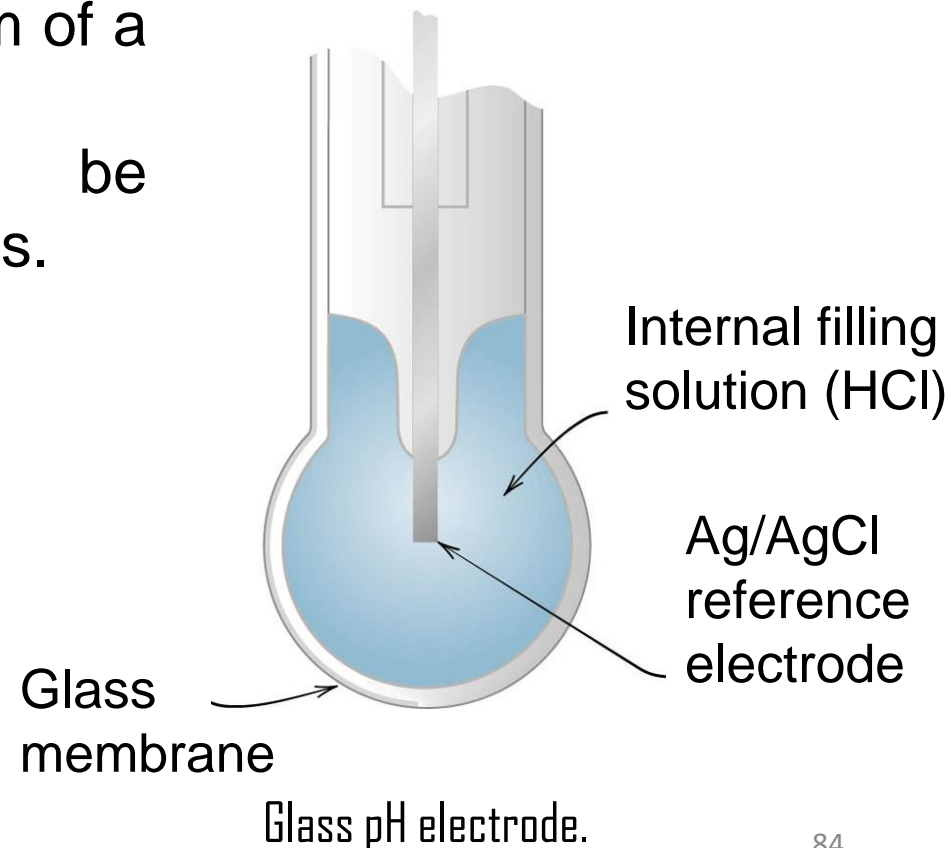
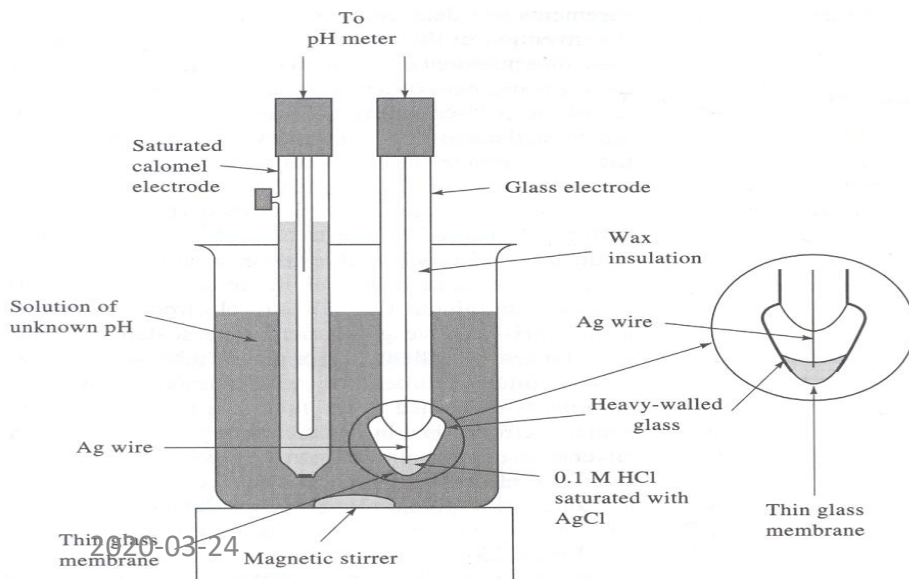
# Ion-Selective electrode (ISE): Classifications

## ISE classified according to the membrane they employ

- Glass
- Polymer
- crystalline
- Glass membrane in conjunction with a gas- permeable membrane to determine the concentration of gases

# Glass membrane electrodes

- The internal element consists of a Ag/AgCl electrode immersed in a pH 7 buffer saturated with silver chloride.
- The **thin ion-selective glass membrane** is fused to the bottom of a nonresponsive glass tube
- The entire membrane can be submerged during measurements.



# Glass membrane electrodes, continued

When placed in a H<sup>+</sup> ions solution, it represented as half-cell

Ag(s) | AgCl [sat'd], Cl<sup>-</sup>(inside), H<sup>+</sup> (inside) | glass membrane | H<sup>+</sup>(outside)

$$E = E_{\text{AgCl/Ag}}^{\circ} - \frac{0.0592}{1} \log[\text{Cl}^{-}] + \frac{0.0592}{1} \log \frac{[\text{H}^{+}]_{\text{outside}}}{[\text{H}^{+}]_{\text{inside}}}$$

$$E = E_{\text{AgCl/Ag}}^{\circ} - 0.0592 \log[\text{Cl}^{-}] + 0.0592 \log \frac{1}{[\text{H}^{+}]_{\text{inside}}} + 0.0592 \log [\text{H}^{+}]_{\text{outside}}$$

As [Cl<sup>-</sup>] and [H<sup>+</sup>] in the internal electrolyte solution are constant the first three terms may be combined into constant Q

$$E = Q + 0.0592 \log [\text{H}^{+}]_{\text{outside}}$$

# pH glass membrane

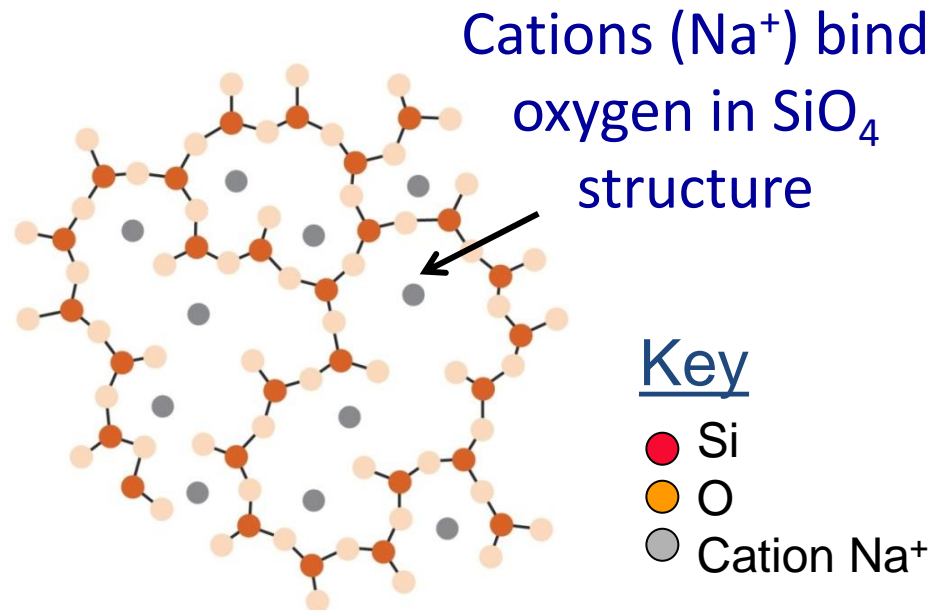
- The relationship between the chemical composition of a membrane and its response is poorly understood.
- Thin glass membrane with different selectivities for  $H^+$  and  $Na^+$  are found
- Both glasses consists mainly of  $SiO_2$  (about 70%).
- In hydrogen-selective glass, the remaining 30 % is a maximum of  $CaO$ ,  $BaO$ ,  $Li_2O$  and  $Na_2O$
- For sodium-selective glass it contains  $Al_2O_3$  and  $Na_2O$
- Glass must be hydrated to allow for diffusion of  $H^+$  and  $Na^+$

# pH glass membrane, continued

- Glass membrane are a irregular network of tetrahedral  $\text{SiO}_4$  units connected through shared oxygen atoms.
- Such a network contains many negatively charged oxygen which bind cations such as  $\text{Li}^+$  and  $\text{Ca}^{2+}$ .

## Glass membrane contains

- Dilute HCl solution saturated in AgCl
- Inbuilt reference electrode (Ag wire coated with AgCl)



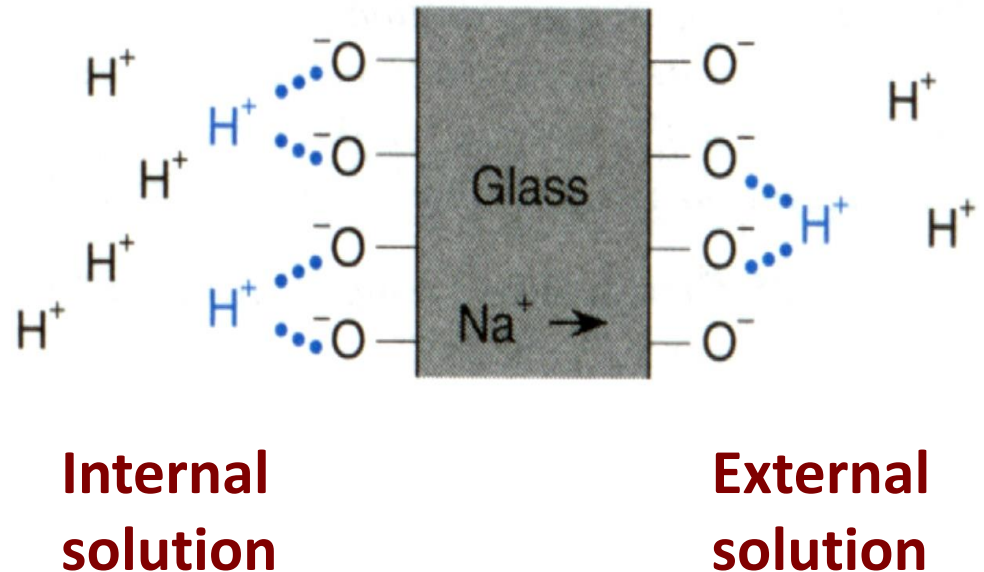
# Theory of the glass membrane potential

- For the electrode to become operative, it must be soaked in water.
- The outer surface of the membrane becomes hydrated.
- So, the sodium ions are exchanged for protons in the solution
- The protons are free to move and exchange with other ions.



Charge is slowly carried by migration of  $\text{Na}^+$  across glass membrane

Potential is determined by external  $[\text{H}^+]$





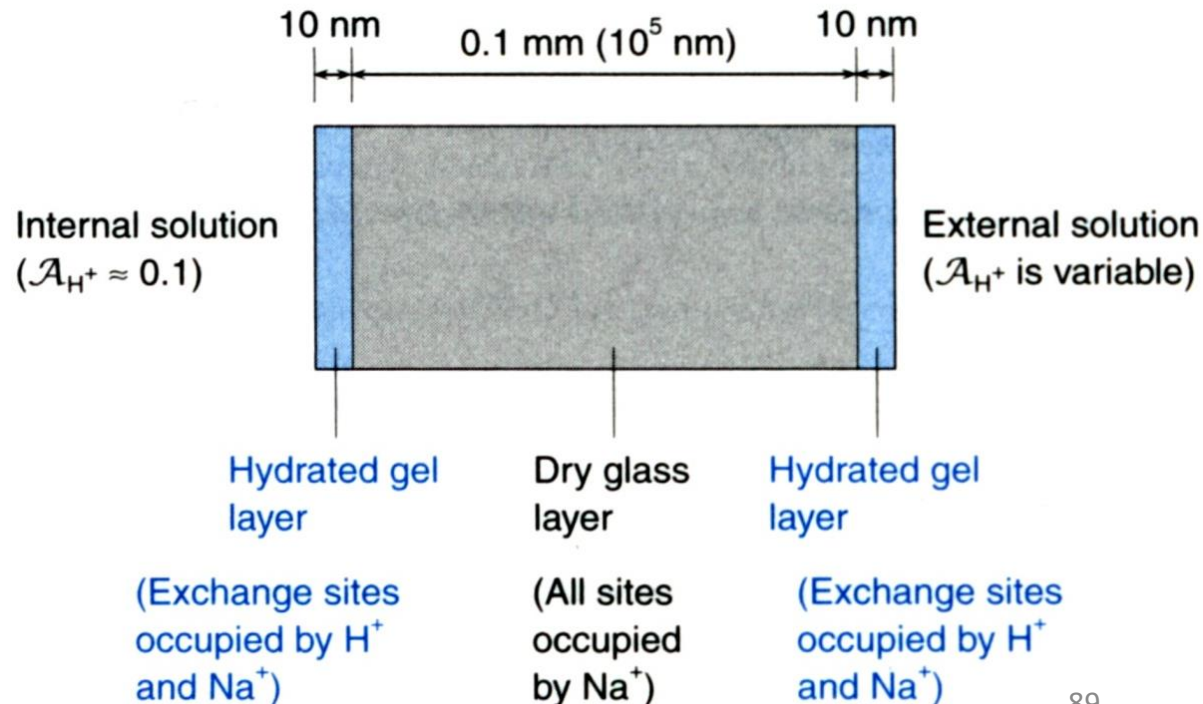
- $H^+$  diffuse into glass membrane and replace  $Na^+$  in hydrated gel region
- Selective for  $H^+$ , because  $H^+$  only binds significantly to the hydrated gel layer

$$E = \text{constant} - \beta(0.0592) \text{ pH}$$

Constant and  $\beta$ : measured when electrode is calibrated with known pH

Two surfaces of glass “swell” as they absorb water

Surfaces are in contact with  $[H^+]$



# pH Measurements

- The surface of the glass is hydrated, which allows exchange of hydronium ions for the cation in the glass (sodium or lithium).
- There are four interface regions, the external solution and hydrated glass, hydrated glass and dry glass on the outside, dry glass and hydrated glass on the inside, and hydrated glass and the internal solution.
- If the glass is uniform, the two hydrated glass/dry glass interfaces should be identical and should have the same junction potential.
- Thus, the glass interface junction potentials cancel each other, the junction potential is then the difference between the internal and external solutions.

# pH Measurements

Why does the pH change the interfacial potential of the glass/aqueous interface?

- The motion of the sodium ions leave behind a negatively charged glass layer that is neutralized to a lesser or greater extent according to the pH.
- The  $\text{Na}^+$  ions must move through the dry part of the membrane and this process is slow.
- For this reason, the membrane is made very thin.
- A low-current voltmeter is used to read the cell voltage so that only a few sodium ions must move through the dry glass in a given time period.

**Problem:** If  $E_{\text{Cell}} = -0.115 \text{ V}$  at a pH of 4.00, what is the pH of a solution for which  $E_{\text{Cell}}$  is  $-0.352 \text{ V}$ ?

## Solution

Recall that  $E_{\text{cell}} = Q - 0.0592 \text{ V pH}$

•First, find L from the measurement of the standard:

$$-0.115 \text{ V} = Q - 0.0592 \times \text{pH}$$

$$-0.115 \text{ V} = Q - 0.0592 \times 4.00 \rightarrow \text{Therefore, } Q = 0.122 \text{ V}$$

•Second, use this value of Q to find pH:

$$-0.352 \text{ V} = 0.122 \text{ V} - 0.0592 \text{ V} \times \text{pH}$$

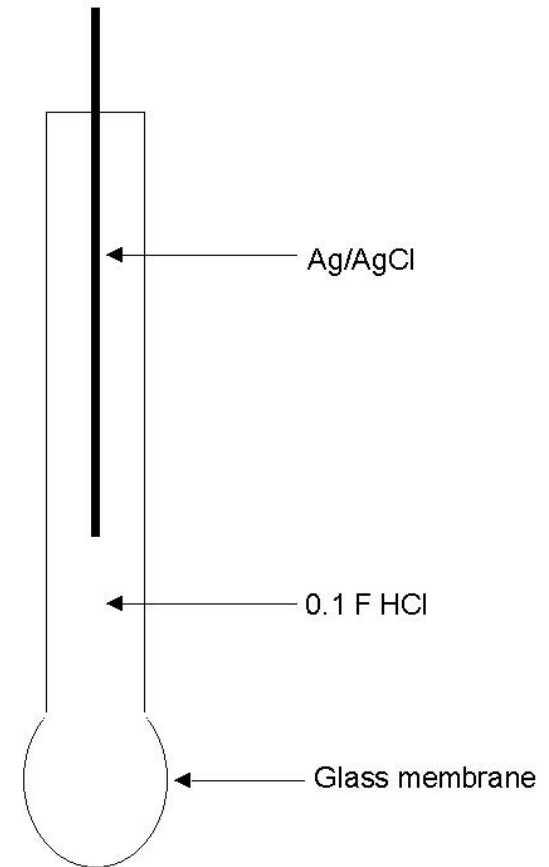
$$\text{pH} = (0.122 \text{ V} - (-0.352 \text{ V})) / 0.0592 \rightarrow \text{pH} = 7.84$$

# The Glass pH Electrode

- The glass pH electrode uses junction potentials to determine the  $[H^+]$  ion in a sample solution.
- The glass pH electrode is used with a Ag/AgCl reference electrode.
- For modern pH electrodes the ref. electrode is incorporated with the pH indicator electrode.

$$E_{cell} = E_{ref1} + E_{ij} + E_{oj} + E_{ref2}$$

- $E_{ij}$  and  $E_{oj}$  : the junction potentials at the inner and outer layers of the glass membrane.
- Junction potential: occurs at the interface of two electrolytes, caused by unequal diffusion rates of cation and anions across the boundary



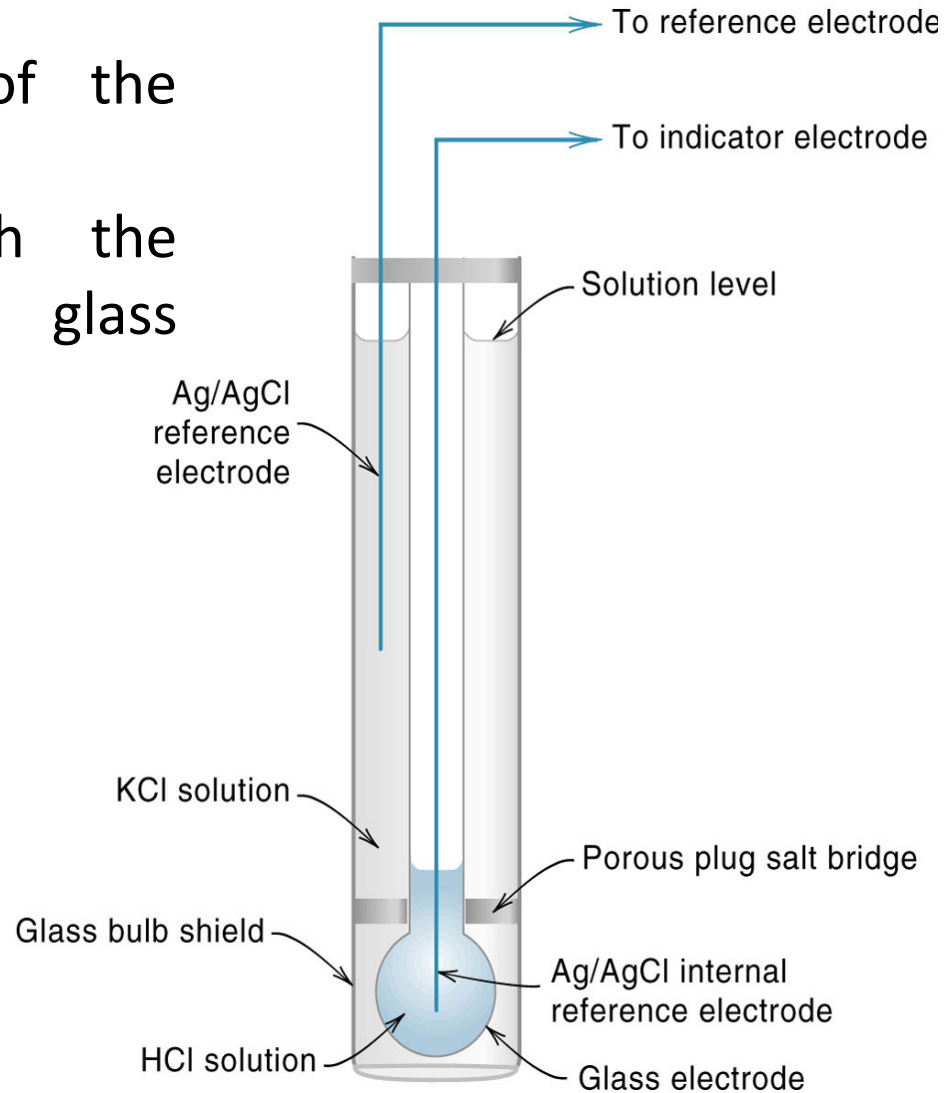
# The Combination pH Electrode

Modern pH electrodes are of the "combination" type. A single cylinder contains both the reference electrode, and a glass membrane electrode.

$\text{Ag}/\text{AgCl}(\text{s})/\text{Cl}^-//([\text{H}_3\text{O}^+]=a_1)/\text{glass membrane}/[\text{H}_3\text{O}^+]=a_2, \text{Cl}^-/\text{AgCl}(\text{s})/\text{Ag}$



Typical pH meter



**A Modern Combination pH Electrode**

# Errors in pH Measurements

- Junction potential: If ionic strengths differ between analyte and standard buffer, junction potential will differ, resulting in an error of  $\pm 0.01$
- Sodium Error: At very low  $[H^+]$ , electrode responds to  $Na^+$  and the apparent pH is lower than the true pH
- Acid Error: At high  $[H^+]$ , the measured pH is higher than actual pH, glass is saturated
- Equilibration Time: Takes  $\sim 30$ s to minutes for electrode to equilibrate with solution
- Hydration of glass: A dry electrode will not respond to  $H^+$  correctly.
- Temperature: Calibration needs to be done at same temperature of measurement
- Cleaning: Contaminates on probe will cause reading to drift until properly cleaned or equilibrated with analyte solution

# Selectivity Coefficient (K)

- The selectivity of an ion-selective electrode is determined by the reaction that brings the analyte ions into the **hydrated layer**.
- A measure of the ability of ISE to discriminate against an interfering ion
- Measure of the response of an ISE to other ions
- It is assumed that ISEs respond only to ion of interest
- In practice, no electrode responds to only one specific ion
- The glass pH electrode is among the most selective, but it also responds to high concentration of  $\text{Na}^+$ .



# Selectivity Coefficient (K)

- When an electrode is used to measure ion A, it also responds to ion X
- The **selectivity coefficient** gives the relative response of the electrode to the two different species (A, X)

$$k_{A,X} = \frac{\text{response to X}}{\text{response to A}}$$

The smaller the selectivity coefficient, the less interference by X, and the more selective is the electrode.

**K = 0** for an ideal electrode (implies no interference)

**For k > 1** (ISE responds better to interfering ion than to the target ion)

**For k = 1** (ISE responds similarly to both ions)

**For k < 1** (ISE responds more selectively to the target ion)

The potential of most ion-selective electrodes is described by the general equation

$$E = Q + \frac{0.0592}{z_A} \log [A] + K_{B/A} [B]^{z_A/z_B} + K_{C/A} [B]^{z_A/z_C} + \dots$$

$$E = Q + \frac{0.0592}{z_A} \log ([A] + \sum K_{X/A} [X]^{z_A/z_X})$$

**A** represents the analyte ion

**X** represents the interfering ions

**$z_A$**  and  **$z_X$**  are the charges on those ions.

**Example:** A nitrate-ion electrode in  $1.64 \times 10^{-4}$  M  $\text{KNO}_3$  has an electrode potential of 0.017 V, enough potassium nitrite is added to the solution to make its concentration  $4.76 \times 10^{-2}$  without changing the volume. The new potential is -0.049 V. calculate the selectivity of the electrode for nitrate over nitrite ions

## Solution

Using the electrode potential with respect to the nitrate and nitrite

$$E = Q + \frac{0.0592}{-1} \log ([\text{NO}_3^-] + K_{\text{NO}_2^-/\text{NO}_3^-} [\text{NO}_2^-]^{-1/-1})$$

The value of Q can be calculate form this equation using the electrode measured **with no nitrite present**:

$$0.017 = Q + \frac{0.0592}{-1} \log [1.64 \times 10^{-4} + K(0)] = Q + 0.224$$

$$Q = 0.017 - 0.224 = -0.207V$$

Using the data for the mixture, we obtain

$$-0.049 = -0.207 + \frac{0.0592}{-1} \log [(1.64 \times 10^{-4}) + K_{NO_2^- / NO_3^-} (4.76 \times 10^{-2})^{-1/-1}]$$

$$\log [(1.64 \times 10^{-4}) + K_{NO_2^- / NO_3^-} (4.76 \times 10^{-2})] = \frac{-0.049 + 0.207}{-0.0592} = -2.67$$

Taking the antilog of both sides gives us

$$1.64 \times 10^{-4} + K_{NO_2^- / NO_3^-} (4.76 \times 10^{-2}) = 10^{-2.67} = 2.1 \times 10^{-3}$$

*and*

$$K_{NO_2^- / NO_3^-} = \frac{2.1 \times 10^{-3} - 1.64 \times 10^{-4}}{4.76 \times 10^{-2}} = 0.041$$

# Asymmetry potential

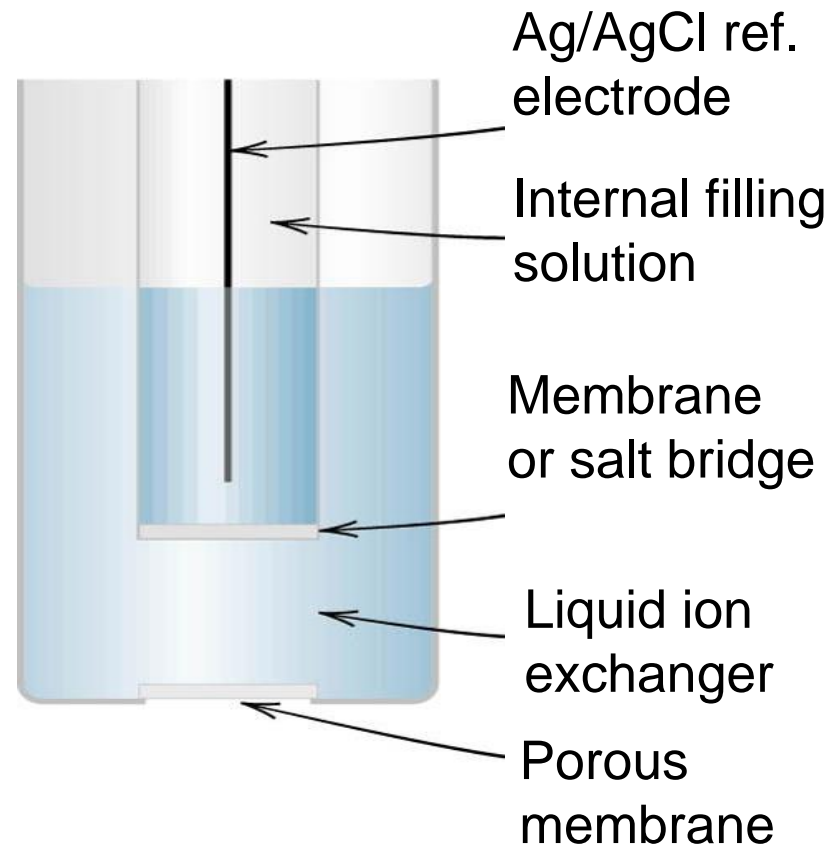
- When **identical solutions** & **reference electrodes** are placed on both sides of a glass membrane, the potential difference equals zero.
- However, a small asymmetry potential always exists.
- Asymmetry potential results from the fact that the two surfaces of the membrane are **not identical on a microscopic scale**.
- The responsible factors are surface imperfections and mechanical strains that occur during manufacturing along with mechanical attack and contamination of the outer surface occur during use.
- The asymmetry potential effects can be corrected by periodic calibration of the electrode with a standard pH buffer.

# Glass membrane electrode: Types

- Glass electrodes are fabricated in a variety of **sizes and shapes**.
- Semi micro electrodes will fit inside small test tubes and require as little as 0.2 mL of sample solution.
- Spear tip electrodes are designed to penetrate and measure the pH of various **semisoft materials such as bread, cheese and fruit**.
- Most of the pH electrodes are available physically combined with an external Ag-AgCl reference electrode, all encased in a single tube.

# Liquid Membrane Electrodes

- Employ **water-immiscible substances** (liquid ion exchanger) impregnated in a **polymeric membrane** (polyvinyl chloride PVC)
- For measurement of polyvalent cations and some anions
- The inner solution is a saturated solution of the target ion
- Hydrophilic complexing agents (e.g. EDTA) are added to inner solutions to improve detection limits
- Inner wire is Ag/AgCl



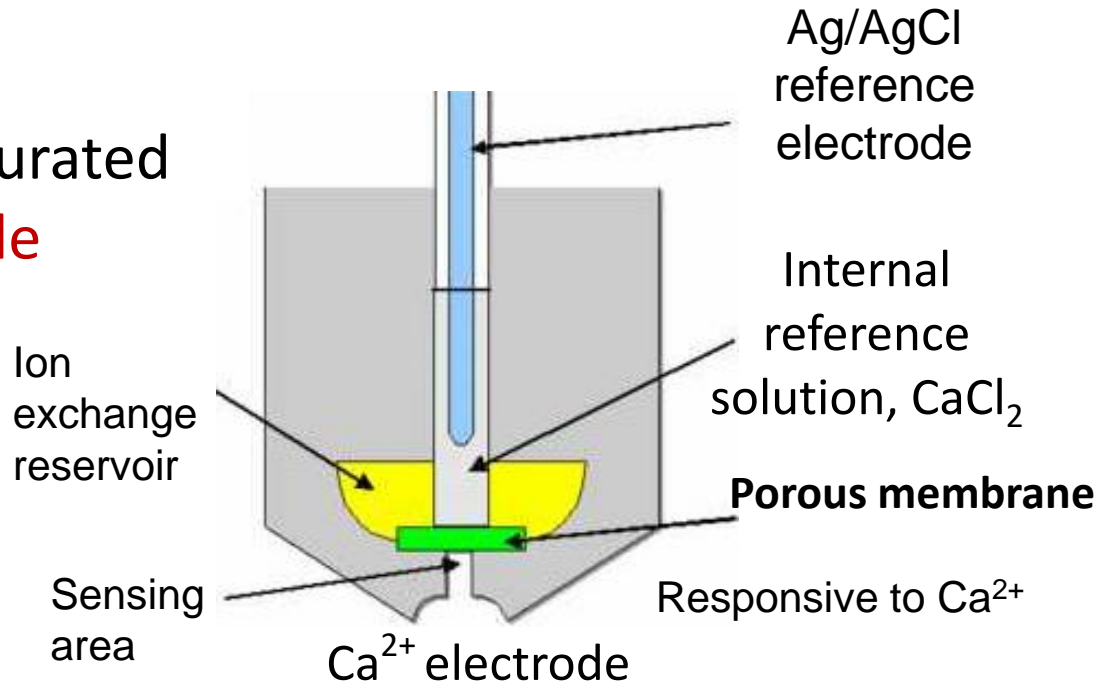
**Liquid-membrane electrode**

# Liquid Membrane Electrode for $\text{Ca}^{2+}$

- Similar to a pH electrode except that the membrane is **an organic polymer saturated with a liquid ion exchanger**
- The potential develops across the interface between the analyte and a **liquid cation-exchanger of high affinity** for calcium ions (diester of phosphoric acid)
- Phosphate ions form stable complex with calcium ions

- Inner solution is a saturated solution of **calcium chloride**

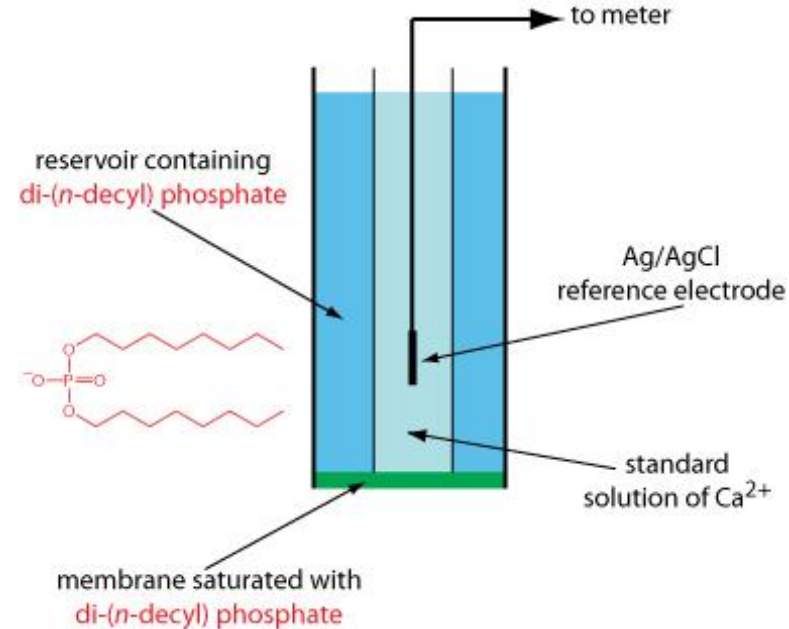
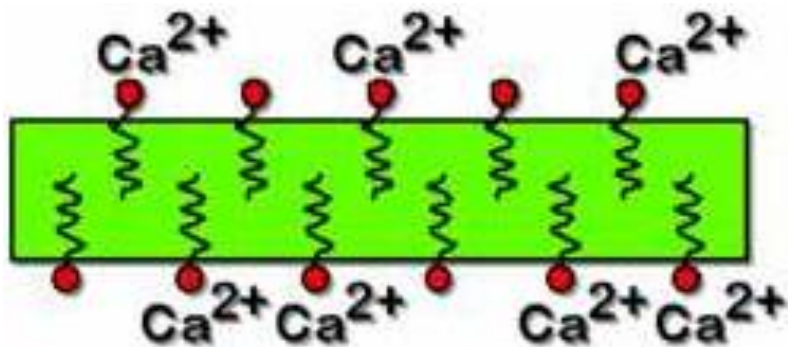
Calcium dialkyl phosphate insoluble in water but binds  $\text{Ca}^{2+}$  strongly





# Liquid Membrane Electrode for $\text{Ca}^{2+}$

- A polymer membrane electrode selective for calcium ion is similar to the glass pH electrode
- It contains an internal  $\text{Ag}/\text{AgCl}$  and an **internal reference solution of fixed composition.**
- The membrane consists of liquid calcium di(*n*-decyl) phosphate,  $[\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{O}]_2\text{PO}_2\text{Ca}$ , immobilized in **a thin disk of polyvinyl chloride** that can not be penetrated by water.

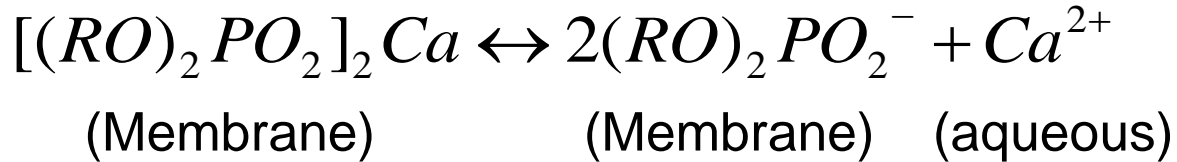


**Calcium di(*n*-decyl) phosphate**

# Liquid Membrane Electrode for Ca<sup>2+</sup>

At membrane surface, the calcium compound establishes an equilibrium with its ions:

R= n-decyl hydrocarbon chain



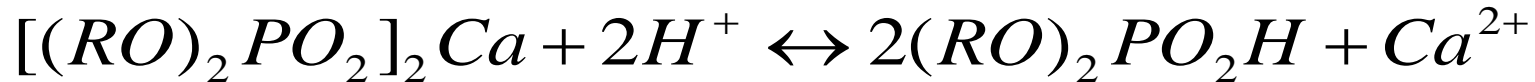
- The didecylphosphate anion is a fixed part of the non-aqueous liquid membrane.
- The concentration of anions at each membrane is different, giving rise to a potential described by the equation

$$E = E_{AgCl/Ag^+}^o - \frac{0.0592}{1} \log [Cl^-] + \frac{0.0592}{2} \log \frac{[Ca^{2+}]_{outside}}{[Ca^{2+}]_{inside}}$$

Collecting constants into a single term

$$E = Q + \frac{0.0592}{2} \log [Ca^{2+}]_{outside}$$

- The selectivity is determined by the ability of **the di(n-decyl) phosphate anion** in the membrane to bind specifically to  $Ca^{2+}$  ions.
- Interference from  $H^+$  ion occurs below a pH of 5, due to the replacement of  $Ca^{2+}$  with  $H^+$  ions on the (di(n-decyl) phosphate):



The electrode becomes sensitive to  $Ca^{2+}$  as well as  $H^+$  ions.

## Characteristics of $Ca^{+2}$ ISE

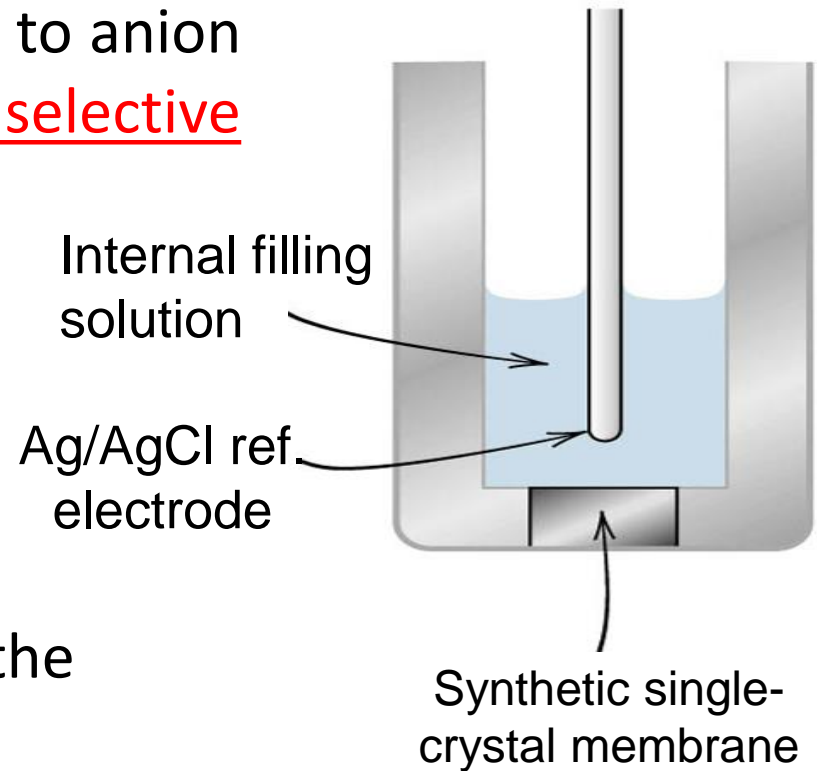
- Relatively high sensitivity
- Low LOD
- Working pH range: 6.0 – 11
- Relevant in studying physiological processes

# Characteristics of selected liquid membrane electrodes

Analyte ion	Active membrane material	Concentration range (M)	Recommended pH range	Selectivity coefficient
$\text{NH}_4^+$	Nonctin/monactin	$10^{-1}$ - $10^{-5}$	0-8	$\text{K}^+=0.12$ , $\text{Na}^+=0.002$ , $\text{Li}^+=0.0042$
$\text{Ca}^{2+}$	Calcium di(n-decyl) phosphate	$10$ - $10^{-6}$	6-10	$\text{Zn}^{2+}=3.2$ , $\text{Fe}^{2+}=0.8$ , $\text{Mg}^{2+}=0.14$
$\text{Ca}^{2+}+\text{Mg}^{2+}$ (divalent )	Similar to $\text{Ca}^{2+}$ electrode	$10^{-2}$ - $10^{-5}$	6-10	$\text{Zn}^{2+}=3.2$ , $\text{Fe}^{2+}=0.8$ ,
$\text{K}^+$	Valinomycin	$10$ - $10^{-6}$	3-10	$\text{NH}_4^+=0.013$ , $\text{H}^+=0.01$
$\text{Cl}^-$	Dimethyl dioctadecyl ammonium chloride	$10$ - $10^{-5}$	3-10	$\text{I}^-=17$ , $\text{NO}_3^-=4.2$
$\text{ClO}_4^-$	Tris(substutated 1,10 phenanthroline) iron (II) per hlorate	$10$ - $10^{-5}$	4-10	$\text{I}^-=17$ , $\text{NO}_3^-=4.2$
$\text{NO}_3^-$	Tridodecylhexadecyl-ammonium nitrate	$10$ - $10^{-5}$	3-8	$\text{I}^-=17$ , $\text{NO}_3^-=4.2$

# Crystalline Membrane Electrodes

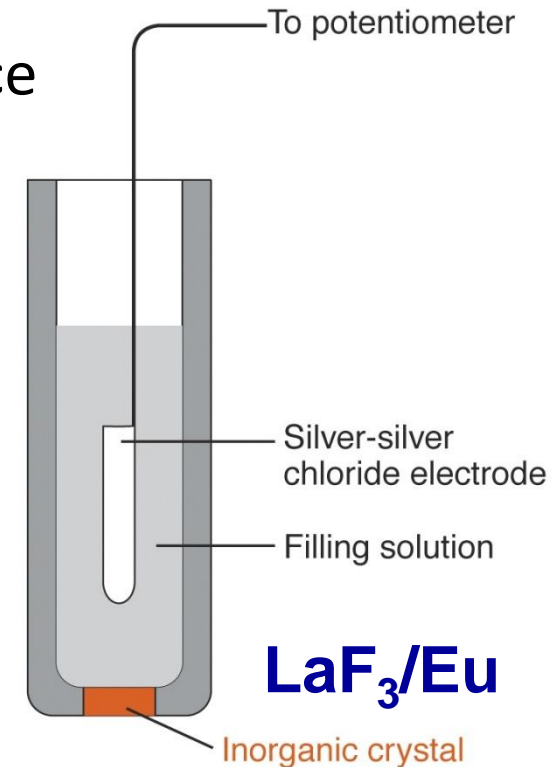
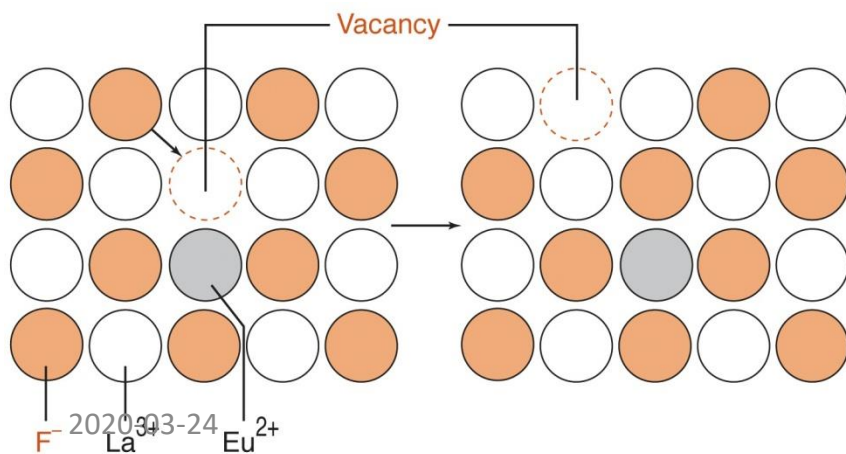
- These electrodes differ from glass electrode only in that they are constructed with a **crystalline** rather than **glass membrane**.
- Could be designed to be responsive to anion by using a membrane containing selective anionic sites.
- The **fluoride-ion electrode** was the first such electrode developed.



# Crystalline Membrane Electrode for Fluoride

- The membrane consists of a single crystal of lanthanum fluoride,  $\text{LaF}_3$  doped with  $\text{Eu(II)}$  to increase conductivity (to generate the crystal defects necessary for its electrical conductivity).
- The potential caused by charge imbalance from migrating ion across membrane

**$\text{F}^-$  migrates across crystal by “jumping” into crystal vacancies caused by  $\text{Eu}^{2+}$**



**$\text{F}^-$  electrode:  $\text{LaF}_3$  crystal doped with  $\text{Eu}^{2+}$**

# Crystalline Membrane Electrode for Fluoride



membrane    membrane    aqueous

Potential caused by charge imbalance from migrating ion across membrane

$$E = Q + \frac{0.0592}{-1} \log[F^-]_{\text{outside}} = Q - 0.0592 \log [F^-]_{\text{outside}}$$

- The electrode is at least 1000 times more selective for fluoride ion than other common anions with exception of **hydroxide**.
- $F^-$  and  $OH^-$  are about the **same size and same charge**,  $LaF_3/Eu^{2+}$  doped crystal selects for size and charge, so,  $OH^-$  develops a response.
- **At low pH**,  $F^-$  ion is converted to the weak acid HF ( $pK_a=3.17$ ) to which the electrode is insensitive.

- Many insoluble crystalline salts exhibit good selectivity toward **both cation and anion exchange**, but they are not conductive to be useful membranes in ion-selective electrodes.
- Upon mixing silver salts or sulfide salts (1:1 molar ratio) with silver sulfide and pressed into a thin disk, will produce good electrical conductors due to the mobility of the  $\text{Ag}^+$  ion in the sulfide matrix.
- Thus membranes of  **$\text{Ag}_2\text{S}$  with  $\text{AgBr}$  or  $\text{CuS}$**  are used to make a bromide-ion or  $\text{Cu}^{2+}$  ion electrode.

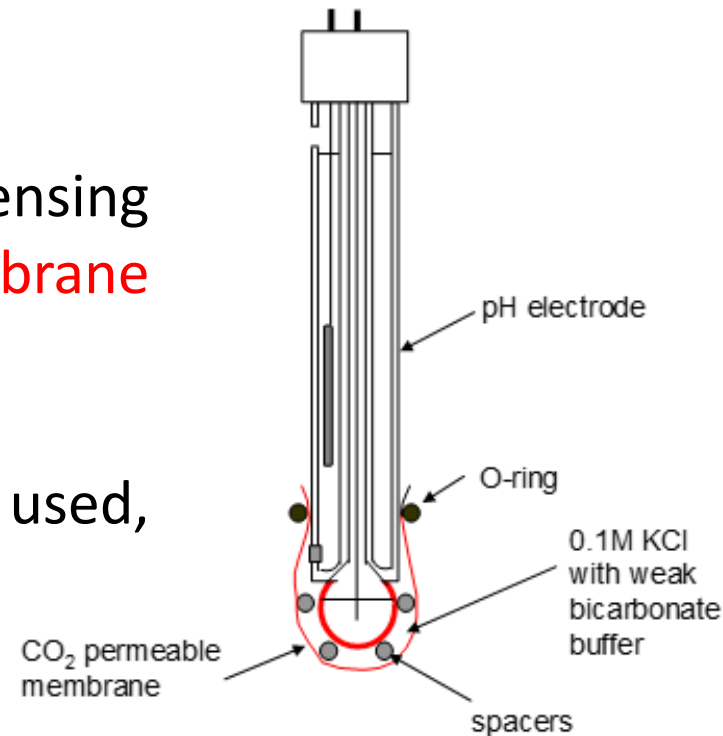


# Characteristics of selected crystalline membrane electrodes

Analyte ion	membrane composition	Concentration range (M)	Recommended pH range
F <sup>-</sup>	LaF <sub>3</sub>	10 <sup>-1</sup> -10 <sup>-5</sup>	5-8
Cl <sup>-</sup>	AgCl/Ag <sub>2</sub> S	10-10 <sup>-4</sup>	2-11
Br <sup>-</sup>	AgBr/Ag <sub>2</sub> S	10 <sup>-2</sup> -10 <sup>-5</sup>	2-12
I <sup>-</sup>	AgI/Ag <sub>2</sub> S	10-10 <sup>-7</sup>	3-12
CN <sup>-</sup>	AgCN/Ag <sub>2</sub> S	10-10 <sup>-6</sup>	11-13
S <sup>2-</sup>	Ag <sub>2</sub> S	10-10 <sup>-5</sup>	13-14
Ag <sup>+</sup>	Ag <sub>2</sub> S	10-10 <sup>-7</sup>	2-9
Cu <sup>2+</sup>	CuS/Ag <sub>2</sub> S	10-10 <sup>-8</sup>	3-7
Cd <sup>2+</sup>	CdS/Ag <sub>2</sub> S	0.1-10 <sup>-7</sup>	3-7
Pb <sup>2+</sup>	PbS/Ag <sub>2</sub> S	0.1-10 <sup>-6</sup>	3-7

# Gas-sensing electrode

- Measure the concentration of various gases in solution and in the gas phase such as  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$
- Used for environmental monitoring, clinical and industrial applications
- Highly sensitive and selective
- Selectivity is obtained by using the sensing electrode with **thin gas-permeable membrane** (microporous, hydrophobic polymer).
- Two types of polymeric materials are used, microporous and Homogeneous
- Membrane thickness is  $\sim 0.01 - 0.10$  mm



# Gas-sensing electrode

- Gas permeable membrane (teflon, polyethylene) is immobilized on a pH electrode or ion-selective electrode
- Electrolyte solution is placed between electrode and membrane (fixed amount,  $\sim 0.1$  M), Inbuilt reference electrode
- The target analyte diffuses through the membrane and comes to equilibrium with the internal electrolyte solution
- Electrode response is directly related to the concentration of gas in the sample
- The target gas then undergoes chemical reaction and the resulting ion is detected by the ion-selective electrode

# CO<sub>2</sub>-sensing electrode

- pH electrode covered by a CO<sub>2</sub> selective membrane (silicon)
- NaHCO<sub>3</sub>-NaCl solution is placed between electrode and membrane
- As CO<sub>2</sub> passes through membrane and dissolves in solution, pH changes.
- pH change is an indirect measure of CO<sub>2</sub> concentration
- Inner glass electrode senses changes in pH
- Overall potential is determined by CO<sub>2</sub> concentration in sample

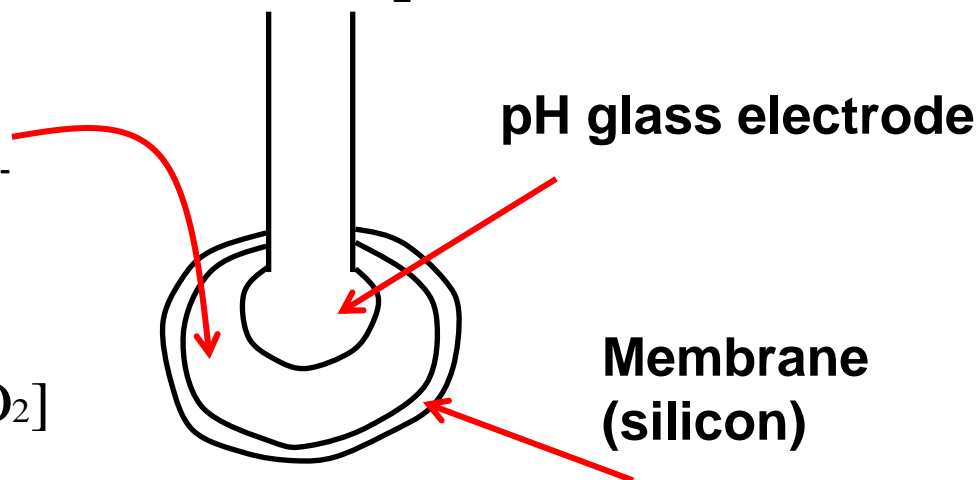
HCO<sub>3</sub><sup>-</sup> solution



H<sup>+</sup> lowers pH

$$E = K + \frac{0.0592}{z} \log[\text{CO}_2]$$

2020-03-24



- Gases ( $\text{SO}_2$  and  $\text{NO}_2$ ) that dissolve to yield acidic solutions can be detected in the same manner.
- The extent of gas to penetrate the gas –permeable membrane will determine the extent of interference with other gases
- Gas-sensing electrodes are commercially available for  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$  and  $\text{NH}_3$

# NH<sub>3</sub> Sensor

- Consists of pH electrode covered by NH<sub>3</sub> selective membrane (teflon or polyethylene)
- Electrolyte between electrode and membrane is NH<sub>4</sub><sup>+</sup>-KCl solution
- NH<sub>3</sub> goes through membrane and raises pH
- Inner glass electrode senses changes in pH
- Increase in pH is proportional to amount of NH<sub>3</sub> in sample

# Other Gas Sensing Devices

**NO<sub>2</sub> and SO<sub>2</sub>** :Makes use of modified pH electrode

**H<sub>2</sub>S-**:Makes use of S<sup>2-</sup> ISE or modified pH electrode

**HF**: Makes use of F<sup>-</sup> ISE or modified pH electrode

# Other Gas Sensing Devices

**NO<sub>2</sub> and SO<sub>2</sub>** :Use of modified pH electrode

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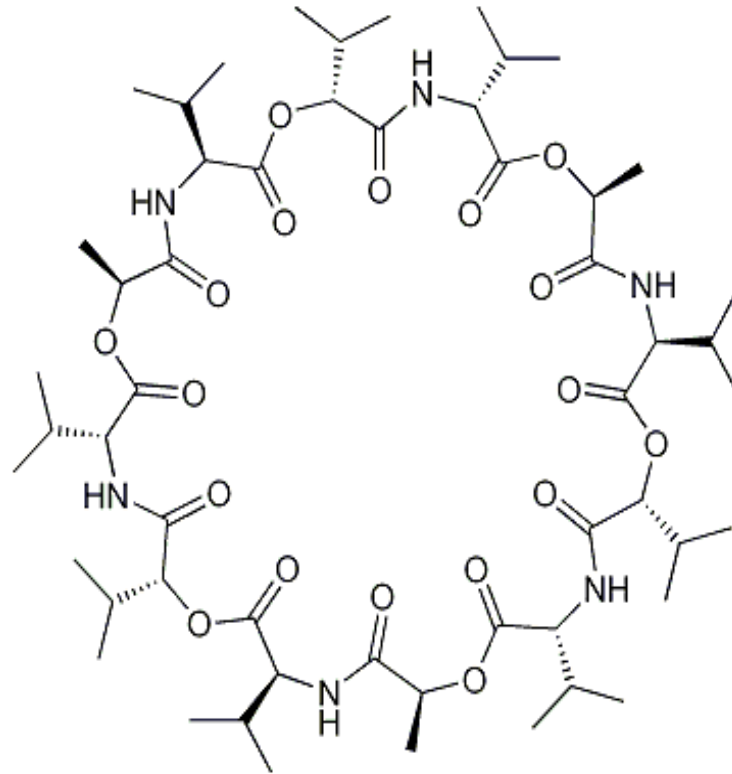


# Ions measured using ion specific electrode

Species detected	Typical sample
$\text{NH}_3/\text{NH}_4^+$	Industrial wastewater, seawater
$\text{CO}_2/\text{HCO}_3^-$	Blood, groundwater
$\text{F}^-$	Groundwater, Drinking water, Urine, Soil, industrial stack gases
$\text{Br}^-$	Grain, plant tissue
$\text{I}^-$	Milk, pharmaceuticals
$\text{NO}_3^-$	Soil, fertilizer, drinking water
$\text{K}^+$	Blood serum, soil, wine
$\text{H}^+$	Laboratory solution, soil, natural waters

# A K<sup>+</sup>-selective electrode

Sensitive membrane consists of valinomycin, an antibiotic



# Potentiometric Measurement

1. Calibration Method

2. Standard Addition Method

(overcome the interferences (matrix effect), the main reason for systematic errors)

# Potentiometric Titrations

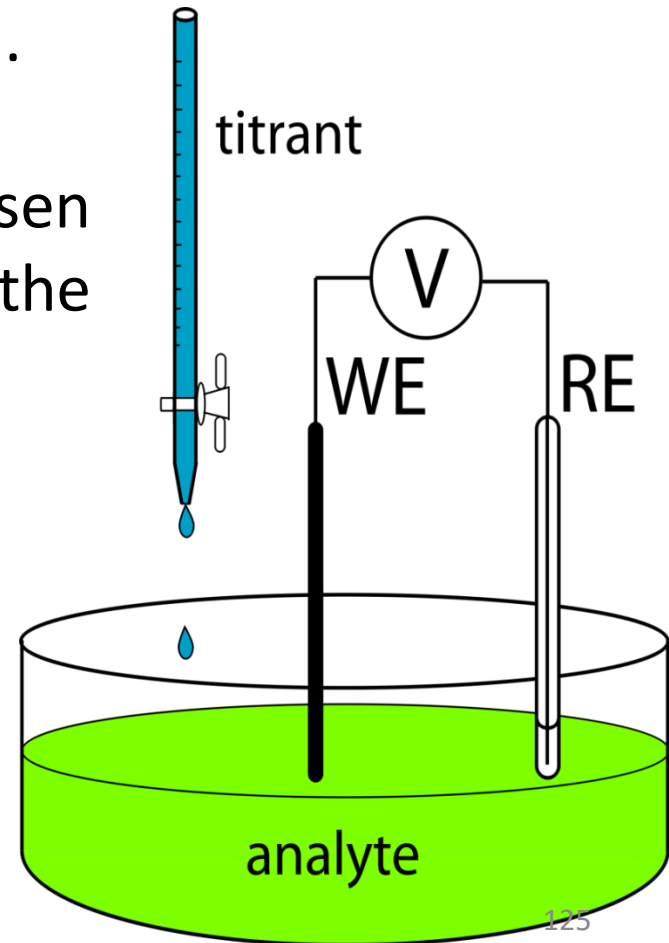
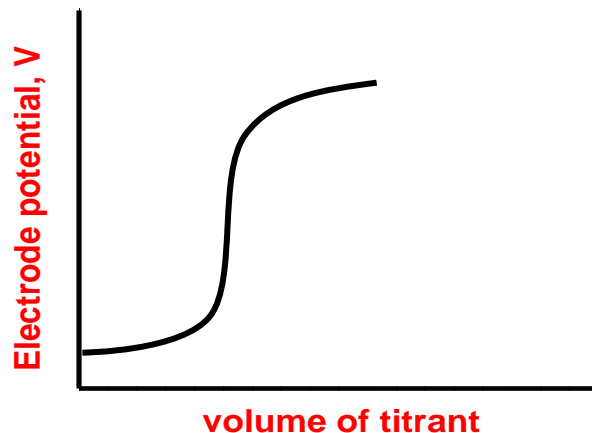
- Measuring the potential of a suitable indicator electrode as a function of titrant volume
- Useful with colored and turbid solutions
- May be automated
- **More time consuming**

# Potentiometric titrations

- Appropriate **indicator and reference electrodes** are placed in the **sample solution** and record the **cell voltage** as increasing amounts of titrant are added.
- Selectivity comes from the titrant (chosen for its ability to react only with the analyte).

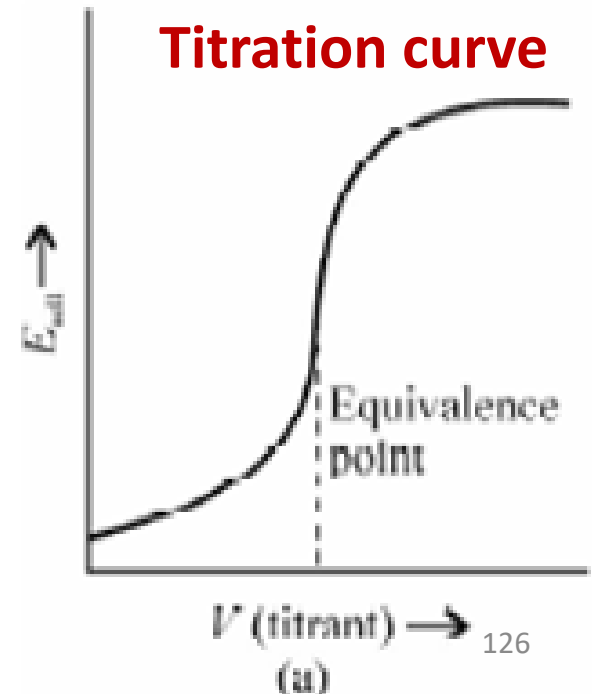
V (mL)	E Cell

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# Finding the end point

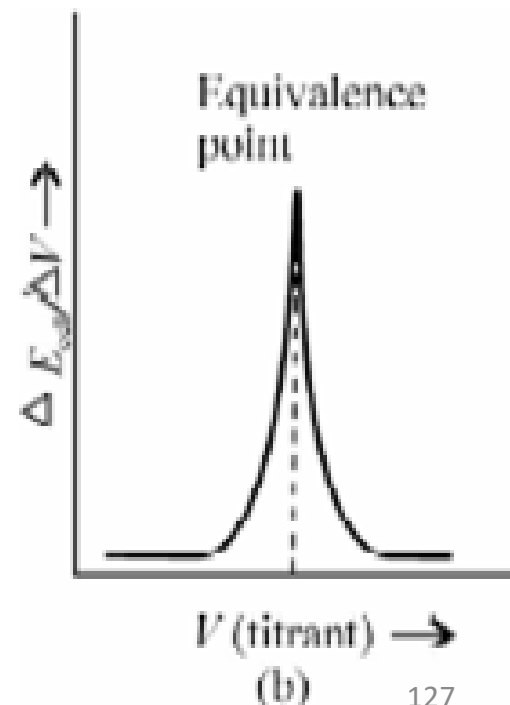
- There are several ways to graph potentiometric titration data so, that the end point can be determined.
- The most common method is to **plot the cell voltage versus the volume of titrant added.**
- The end point is taken as the inflection point (point of maximum slope)



# Finding the end point: First derivative curve

- Another approach to find the end point
- The plot of **slop of the curve versus the volume of the titrant added.**
- The endpoint is the extrapolated intersection of the rising and falling portions of the curve.

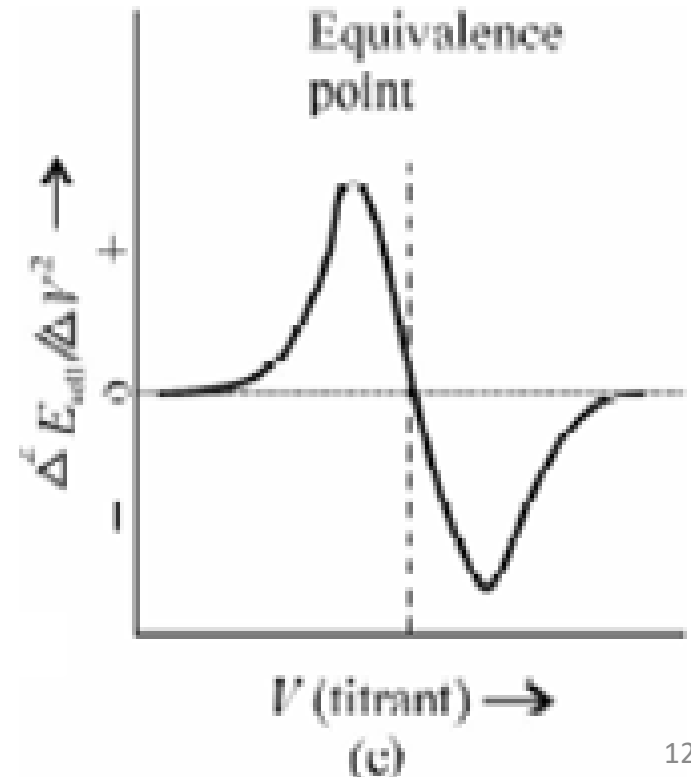
V mL	E Cell	$\Delta V$	$\Delta E$	$(\Delta E / \Delta V)$



# Finding the end point: Second derivative curve

- It is possible to prepare a second derivative curve by plotting the slope of the first derivative versus the volume of titrant added
- The point where the line passes through zero on the vertical axis is taken as the end point

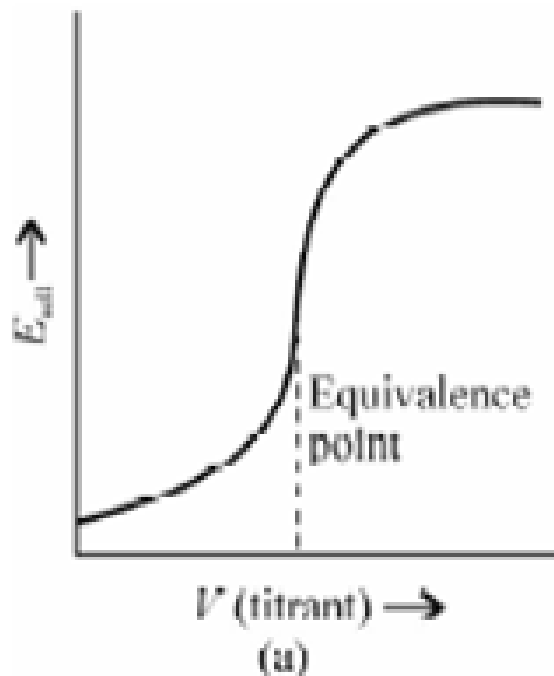
V mL	E Cell	$(\Delta E / \Delta V)$	$\Delta(\Delta E / \Delta V) / \Delta V$



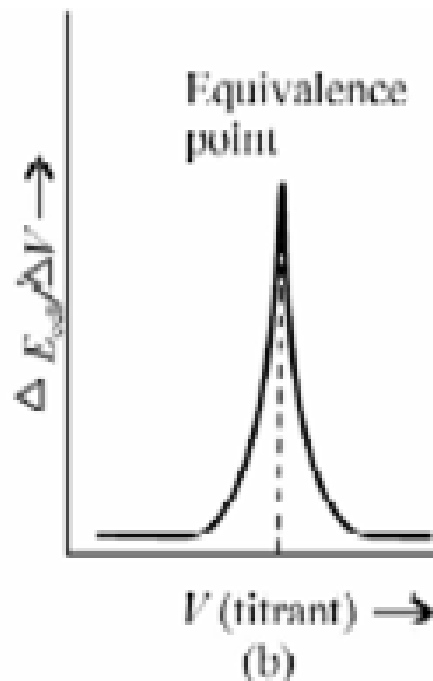


# Finding the End Point

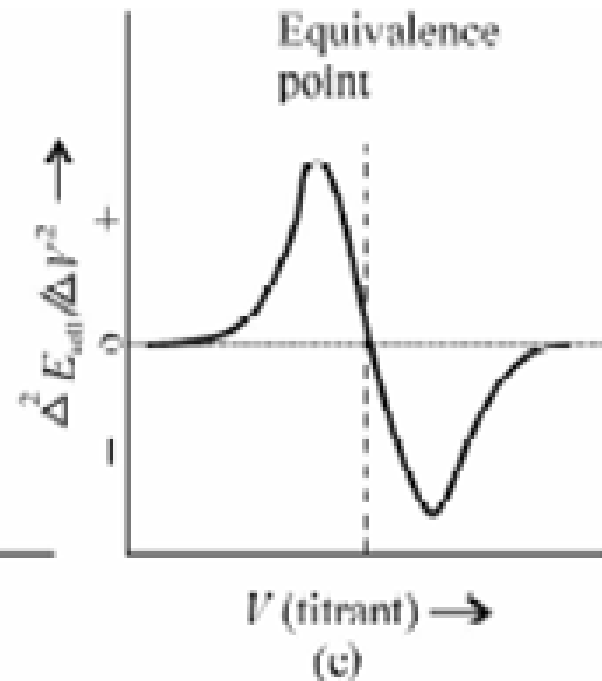
**Titration curve**



**First derivative curve**



**Second derivative curve**



# Experiments

1. Potentiometric Titration of an Unknown Monoprotic Weak Acid
2. Determination of Chloride Using Potentiometry
3. Fluoride Ion by Direct Potentiometry/Standard Addition

# References

1. Daniel Harris, (2007), “Quantitative Chemical Analysis” 7th Edition, New York, Chapter 15, electrodes and potentiometry.
2. Wang, J. *Analytical Electrochemistry*, 3<sup>rd</sup> ed.; Wiley: Hoboken, NJ 2006, pp. 165-200.
3. Skoog, D.A., Holler, F.J., Crouch, S.R., *Principles of Instrumental Analysis*, 6<sup>th</sup> ed.; Thomson Brooks/Cole: Belmont, CA, 2007.