

# An Introduction to Electrochemistry

## Redox Reaction



## Outline

- 1. Review
  - Concepts: Redox Reaction, Cell, Potential
  - Balance an Equation
  - Nernst Equation
- 2. Redox Titration
- 3. Potentiometry
- 4. Voltammetry and Electrochemical Sensor

## 12.1 Balancing Oxidation-Reduction Reactions

- *Mass Balance*: the amount of each element present at the beginning of the reaction must be present at the end.
- *Charge Balance*: electrons are not lost in a chemical reaction.

### Half Reactions

- Half-reactions are a convenient way of separating oxidation and reduction reactions.

## Half Reactions

- The half-reactions for



are



- Oxidation: electrons are products.
- Reduction: electrons are reagents.

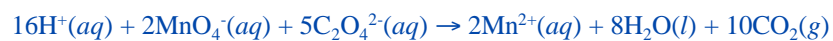
## Balancing Equations by the Method of Half Reactions

- Consider the titration of an acidic solution of  $\text{Na}_2\text{C}_2\text{O}_4$  (sodium oxalate, colorless) with  $\text{KMnO}_4$  (deep purple).

## How?

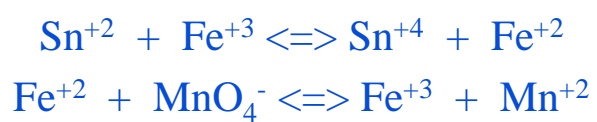
1. Write down the two half reactions.
2. Balance each half reaction:
  - a. First with elements other than H and O.
  - b. Then balance O by adding water.
  - c. Then balance H by adding H<sup>+</sup>.
  - d. Finish by balancing charge by adding electrons.
3. Multiply each half reaction to make the number of electrons equal.
4. Add the reactions and simplify.
5. Check!

## Balancing Equations by the Method of Half Reactions



Exercise:

Try to Balance:

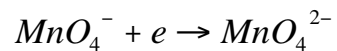
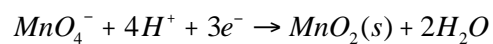
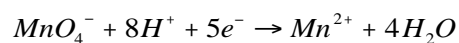




## Important Redox Titrants and the Reactions

Oxidizing Reagents (Oxidants)

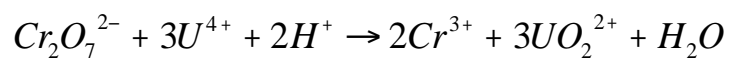
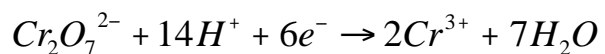
(1) Potassium Permanganate



## Important Redox Titrants and the Reactions

Oxidizing Reagents (Oxidants)

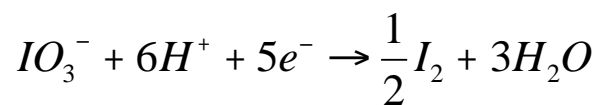
(2) Potassium Dichromate



## Important Redox Titrants and the Reactions

Oxidizing Reagents (Oxidants)

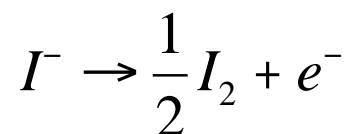
(2) Potassium Iodate



## Important Redox Titrants and the Reactions

Reducing Reagent ( Reductants )

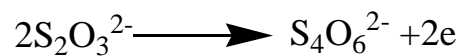
(2) Potassium Iodide



## Important Redox Titrants and the Reactions

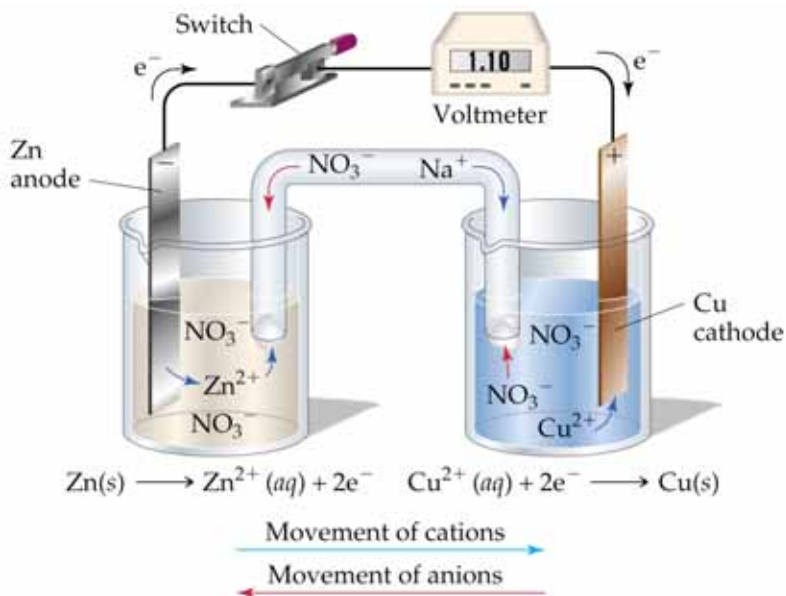
Reducing Reagent ( Reductants )

(2) Sodium Thiosulfate





## 12.2 Nernst Equation



- Voltaic cells consist of
  - **Anode:**  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
  - **Cathode:**  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu(s)}$
  - **Salt bridge** (used to complete the electrical circuit): cations move from anode to cathode, anions move from cathode to anode.
- The two solid metals are the electrodes (cathode and anode).

The salt bridge allows charge transfer through the solution and prevents mixing.

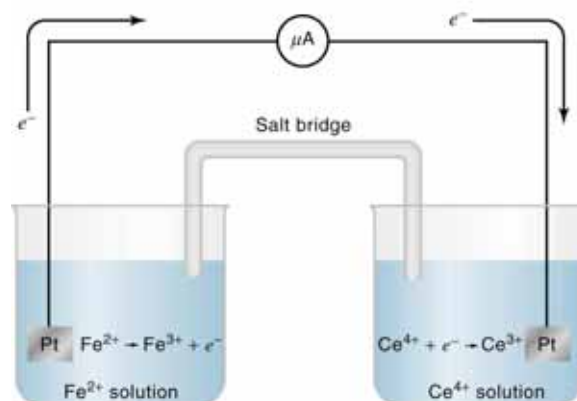
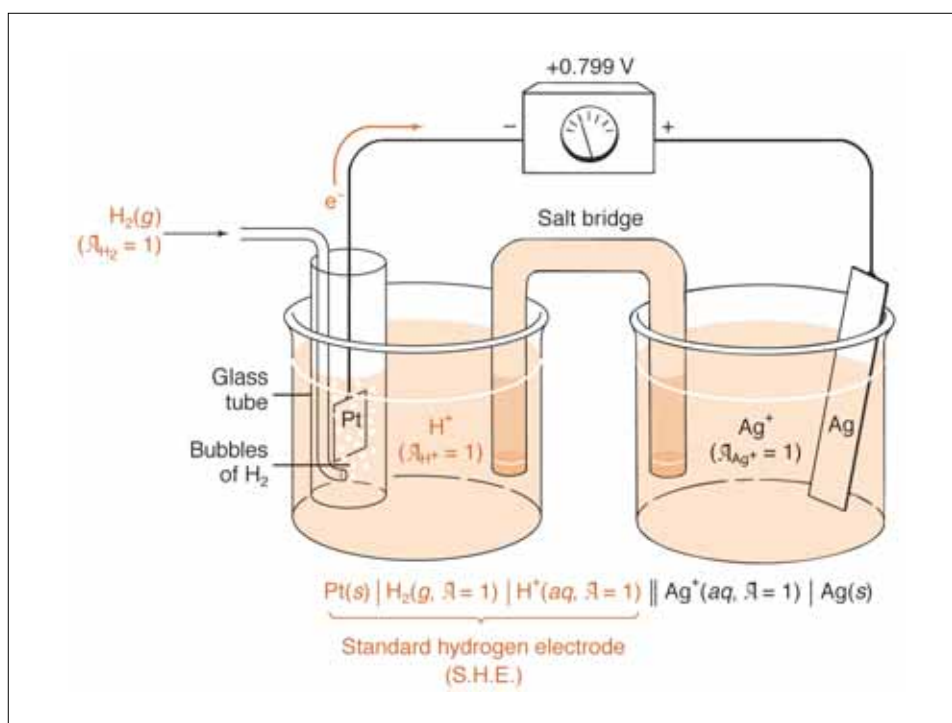
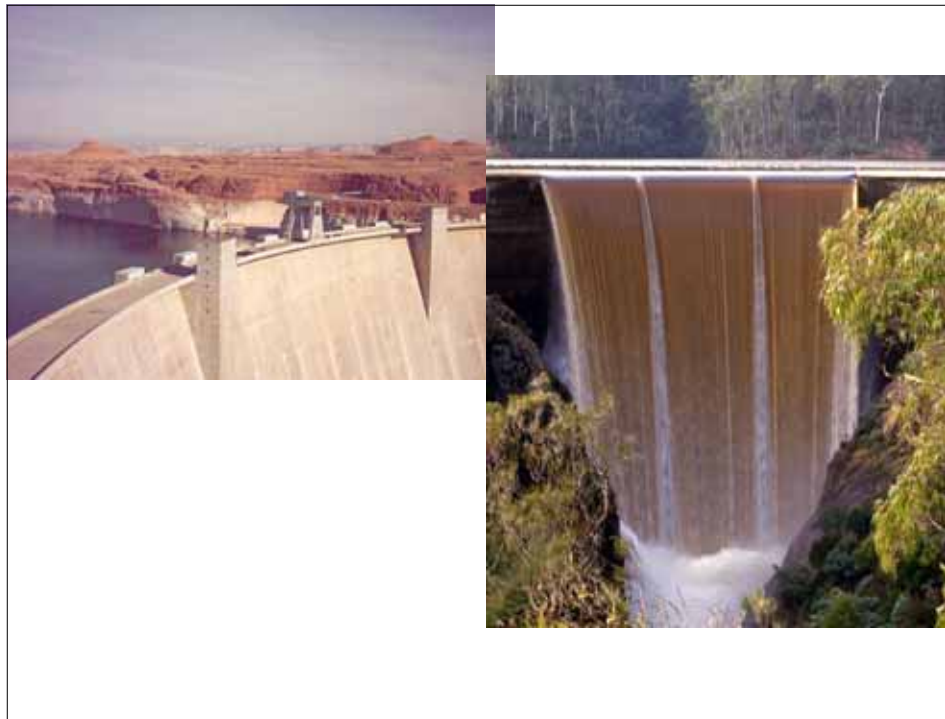
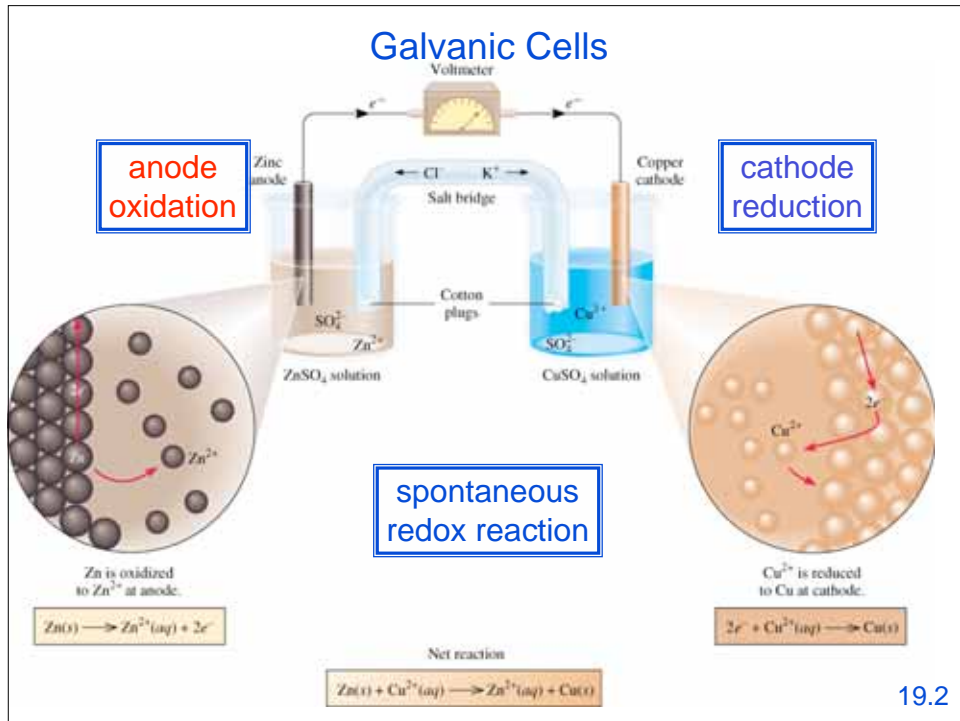


Fig. 12.1. Voltaic cell.





- This rearranges to give the **Nernst equation**:

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

- The Nernst equation can be simplified by collecting all the constants together using a temperature of 298 K:

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

- (Note that change from natural logarithm to base-10 log.)
- Remember that ***n*** is number of moles of **electrons**.

## Nernst Equation

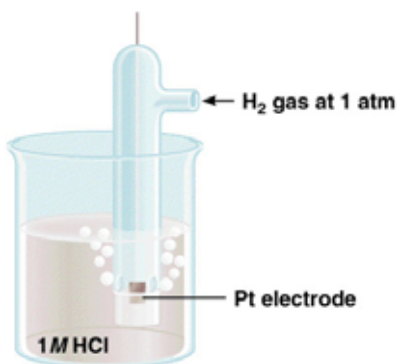


$$E = E^\circ - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{at } 25^\circ\text{C}$$

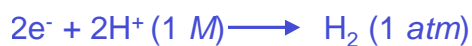
$$E = E^\circ - \frac{0.0592}{n} \log \frac{[Red]}{[Ox]}$$

## Standard Electrode Potentials

**Standard reduction potential ( $E^\circ$ )** is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1  $M$  and all gases are at 1 atm.



Reduction Reaction



$$E^\circ = 0\ V$$

Standard hydrogen electrode (SHE)

19.3

## Standard Reduction (Half-Cell) Potentials

- The **SHE** is the cathode. It consists of a Pt electrode in a tube placed in 1  $M$   $H^+$  solution.  $H_2$  is bubbled through the tube.
- For the SHE, we assign



- $E^\circ_{red}$  of zero.
- The potential of a cell can be calculated from standard reduction potentials:

$$E^\circ_{cell} = E^\circ_{red}(cathode) - E^\circ_{red}(anode)$$

## Standard Reduction (Half-Cell) Potentials

- Consider  $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$ . We measure  $E_{\text{cell}}$  relative to the SHE (cathode):

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{ox}}^{\circ}(\text{anode})$$

$$0.76 \text{ V} = 0 \text{ V} - E_{\text{red}}^{\circ}(\text{anode}).$$

- Therefore,  $E_{\text{red}}^{\circ}(\text{anode}) = -0.76 \text{ V}$ .
- Standard reduction potentials must be written as reduction reactions:



TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq)$
+1.51	$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$
+1.36	$\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$
+1.23	$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$
+1.06	$\text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq)$
+0.96	$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$
+0.80	$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$
+0.77	$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$
+0.68	$\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2\text{O}_2(aq)$
+0.59	$\text{MnO}_4^-(aq) + 2\text{H}_2\text{O}(l) + 3e^- \rightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$
+0.54	$\text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(aq)$
+0.40	$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq)$
+0.34	$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$
0	$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$
-0.28	$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$
-0.44	$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$
-0.76	$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$
-0.83	$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$
-1.66	$\text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s)$
-2.71	$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$
-3.05	$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$

## 12.3 Cell Diagram

anode//cathode  
Zn/ZnSO<sub>4</sub> (0.1 M)//CuSO<sub>4</sub> (0.2  
M)/Cu

If a cell,

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

if  $E_{\text{cell}} \Rightarrow$  positive, spontaneous as written

**Table 14-1** Ordered redox potentials

	Oxidizing agent	Reducing agent	$E^\circ$ (V)
↑ Oxidizing power increases	$F_2(g) + 2e^- \rightleftharpoons 2F^-$		2.890
	$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$		2.075
	⋮		
	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
	⋮		
	$Ag^+ + e^- \rightleftharpoons Ag(s)$		0.799
	⋮		
	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$		0.339
	⋮		
	$2H^+ + 2e^- \rightleftharpoons H_2(g)$		0.000
	⋮		
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$		-0.402	
⋮			
$K^+ + e^- \rightleftharpoons K(s)$		-2.936	
$Li^+ + e^- \rightleftharpoons Li(s)$		-3.040	

The more positive the  $E^\circ$ , the better oxidizing agent is the oxidized form (e.g.,  $MnO_4^-$ ).  
 The more negative the  $E^\circ$ , the better reducing agent is the reduced form (e.g., Zn).

**Table 12.1**

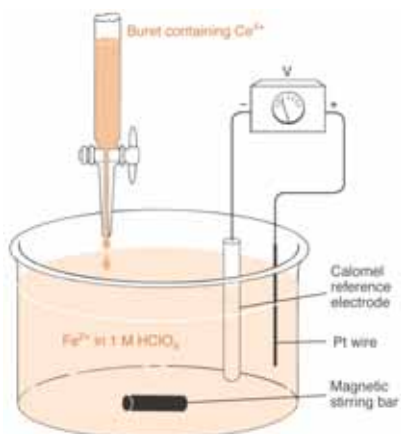
Some Standard Potentials

Half-Reaction	$E^\circ$ (V)
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	1.695
$Ce^{4+} + e^- = Ce^{3+}$	1.61
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.51
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.23
$2IO_3^- + 12H^+ + 10e^- = I_2 + 6H_2O$	1.20
$H_2O_2 + 2e^- = 2OH^-$	0.88
$Cu^2 + I^- + e^- = CuI$	0.86
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$O_2 + 2H^+ + 2e^- = H_2O_2$	0.682
$I_2(aq) + 2e^- = 2I^-$	0.6197
$H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O$	0.559
$I_3^- + 2e^- = 3I^-$	0.5355
$Sn^{4+} + 2e^- = Sn^{2+}$	0.154
$S_2O_8^{2-} + 2e^- = 2S_2O_8^{2-}$	0.08
$2H^+ + 2e^- = H_2$	0.000
$Zn^{2+} + 2e^- = Zn$	-0.763
$2H_2O + 2e^- = H_2 + 2OH^-$	-0.828

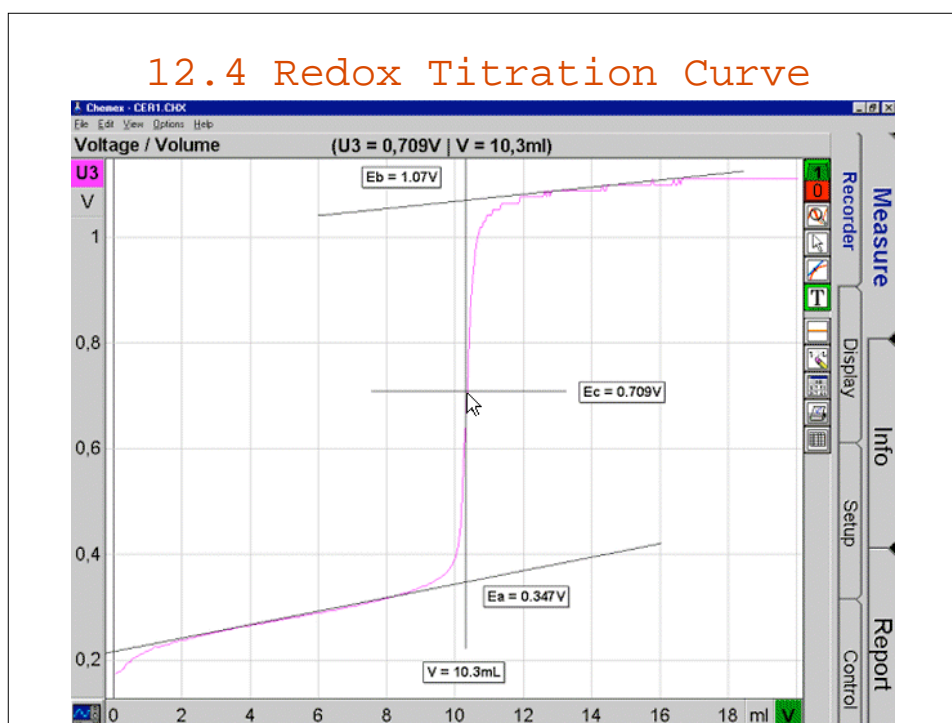
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## 12.4 Redox Titration Curve



## 12.4 Redox Titration Curve



## 12.4 Redox Titration Curve

Derivation of a titration curve



**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M  $\text{Fe}^{+2}$  with 0.1000 M  $\text{Ce}^{+4}$  in a medium that is 1.0 M in  $\text{H}_2\text{SO}_4$ .

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M  $\text{Fe}^{+2}$  with 0.1000 M  $\text{Ce}^{+4}$  in a medium that is 1.0 M in  $\text{H}_2\text{SO}_4$ .

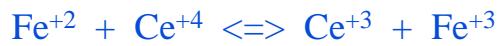


$$E = E^\circ - (0.0592/n) \log([\text{red}]/[\text{ox}])$$

At 0.00 mL of  $\text{Ce}^{+4}$  added, initial point

no  $\text{Ce}^{+4}$  present; minimal, unknown  $[\text{Fe}^{+3}]$ ;  
thus, insufficient information to calculate E

Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>2+</sup> with 0.1000 M Ce<sup>4+</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 15.00 mL of Ce<sup>4+</sup> added,  $V_{\text{Fe}}M_{\text{Fe}} > V_{\text{Ce}}M_{\text{Ce}}$

$$\begin{aligned} [\text{Fe}^{3+}] &= \frac{V_{\text{Ce}} M_{\text{Ce}}}{V_{\text{Fe}} + V_{\text{Ce}}} = \frac{(15.00 \text{ mL})(0.1000 \text{ M})}{(50.00 + 15.00) \text{ mL}} \\ &= 2.308 \times 10^{-2} \text{ M} \end{aligned}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>2+</sup> with 0.1000 M Ce<sup>4+</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 15.00 mL of Ce<sup>4+</sup> added,  $V_{\text{Fe}}M_{\text{Fe}} > V_{\text{Ce}}M_{\text{Ce}}$

$$[\text{Fe}^{3+}] = 2.308 \times 10^{-2} \text{ M}$$

$$[\text{Fe}^{2+}] = \frac{V_{\text{Fe}} M_{\text{Fe}} - V_{\text{Ce}} M_{\text{Ce}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 15.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Fe}}M_{\text{Fe}} > V_{\text{Ce}}M_{\text{Ce}}$

$$[\text{Fe}^{+3}] = 2.308 \times 10^{-2} \text{ M}$$

$$[\text{Fe}^{+2}] = \frac{(50.00 \text{ mL})(0.0500 \text{ M}) - (15.00 \text{ mL})(0.1000 \text{ M})}{(50.00 + 15.00) \text{ mL}}$$

$$= 1.54 \times 10^{-2} \text{ M}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 15.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Fe}}M_{\text{Fe}} > V_{\text{Ce}}M_{\text{Ce}}$

$$[\text{Fe}^{+3}] = 2.308 \times 10^{-2} \text{ M} \quad [\text{Fe}^{+2}] = 1.54 \times 10^{-2} \text{ M}$$

$$\text{for } \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} \quad E^{\circ} = 0.69 \text{ v}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 15.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Fe}}M_{\text{Fe}} > V_{\text{Ce}}M_{\text{Ce}}$

$$[\text{Fe}^{+3}] = 2.308 \times 10^{-2} \text{ M} \quad [\text{Fe}^{+2}] = 1.54 \times 10^{-2} \text{ M}$$

for  $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3} \quad E^{\circ} = 0.69 \text{ v}$

$$E_{\text{cell}} = 0.68 \text{ v} - \frac{0.0592}{1} \log \frac{1.54 \times 10^{-2}}{2.31 \times 10^{-2}} \quad \text{v} = 0.69 \text{ v}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 25.00 mL of Ce<sup>+4</sup> added,

$V_{\text{Fe}}M_{\text{Fe}} = V_{\text{Ce}}M_{\text{Ce}}$ , equivalence point

$$E_{\text{cell}} = \frac{n_{\text{Fe}} E_{\text{Fe}}^{\circ} + n_{\text{Ce}} E_{\text{Ce}}^{\circ}}{n_{\text{Fe}} + n_{\text{Ce}}} = \frac{1(1.44) + 1(0.68)}{1 + 1} \text{ v}$$

$$= 1.06 \text{ v}$$

### Determination of the equivalence point

$$E_{\text{eq}} = \frac{n_A E_A^\circ + n_B E_B^\circ}{n_A + n_B}$$

This expression is only valid for simple REDOX expressions.

Only  $A_{\text{ox}}$ ,  $A_{\text{red}}$ ,  $B_{\text{ox}}$  and  $B_{\text{red}}$  are involved in the reaction.

No other concentration dependent species are involved.

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M  $\text{Fe}^{+2}$  with 0.1000 M  $\text{Ce}^{+4}$  in a medium that is 1.0 M in  $\text{H}_2\text{SO}_4$ .



At 26.00 mL of  $\text{Ce}^{+4}$  added,  $V_{\text{Ce}} M_{\text{Ce}} > V_{\text{Fe}} M_{\text{Fe}}$

$$\begin{aligned} [\text{Ce}^{+3}] &= \frac{V_{\text{Fe}} M_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}} = \frac{(50.00 \text{ mL})(0.0500 \text{ M})}{(50.00 + 26.00) \text{ mL}} \\ &= 3.29 \times 10^{-2} \text{ M} \end{aligned}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 26.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Ce}}M_{\text{Ce}} > V_{\text{Fe}}M_{\text{Fe}}$

$$[\text{Ce}^{+3}] = 3.29 \times 10^{-2} \text{ M}$$

$$[\text{Ce}^{+4}] = \frac{V_{\text{Ce}} M_{\text{Ce}} - V_{\text{Fe}} M_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 26.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Ce}}M_{\text{Ce}} > V_{\text{Fe}}M_{\text{Fe}}$

$$[\text{Ce}^{+3}] = 3.29 \times 10^{-2} \text{ M}$$

$$[\text{Ce}^{+4}] = \frac{(26.00 \text{ mL})(0.1000 \text{ M}) - (50.00 \text{ mL})(0.0500 \text{ M})}{(50.00 + 26.00)\text{mL}}$$

$$= 1.32 \times 10^{-3} \text{ M}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



At 26.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Ce}}M_{\text{Ce}} > V_{\text{Fe}}M_{\text{Fe}}$

$$[\text{Ce}^{+3}] = 3.29 \times 10^{-2} \text{ M} \quad [\text{Ce}^{+4}] = 1.32 \times 10^{-3} \text{ M}$$

for Ce<sup>+4</sup> → Ce<sup>+3</sup> E° = 1.44 v

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Ce}^{+3}]}{[\text{Ce}^{+4}]}$$

**EXAMPLE:** Derive the titration curve for 50.00 mL of 0.0500 M Fe<sup>+2</sup> with 0.1000 M Ce<sup>+4</sup> in a medium that is 1.0 M in H<sub>2</sub>SO<sub>4</sub>.



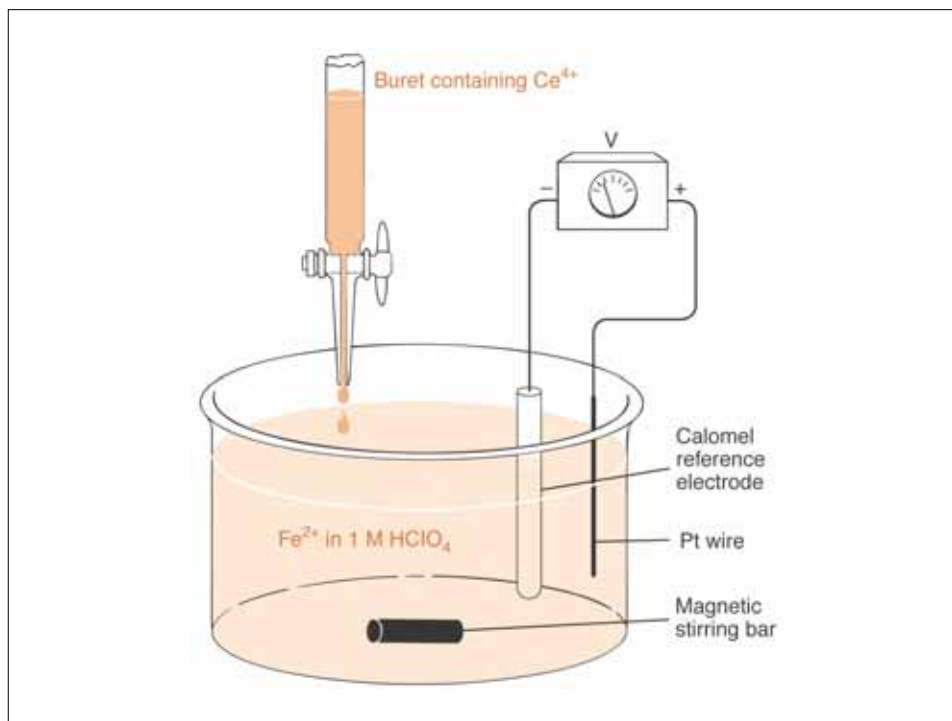
At 26.00 mL of Ce<sup>+4</sup> added,  $V_{\text{Ce}}M_{\text{Ce}} > V_{\text{Fe}}M_{\text{Fe}}$

$$[\text{Ce}^{+3}] = 3.29 \times 10^{-2} \text{ M} \quad [\text{Ce}^{+4}] = 1.32 \times 10^{-3} \text{ M}$$

for Ce<sup>+4</sup> → Ce<sup>+3</sup> E° = 1.44 v

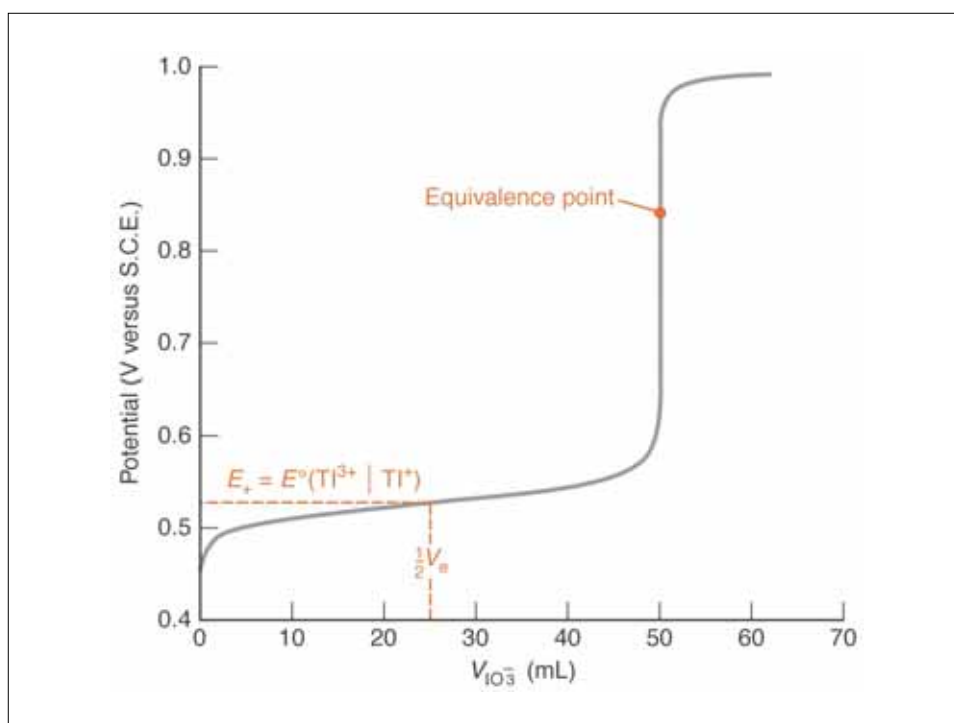
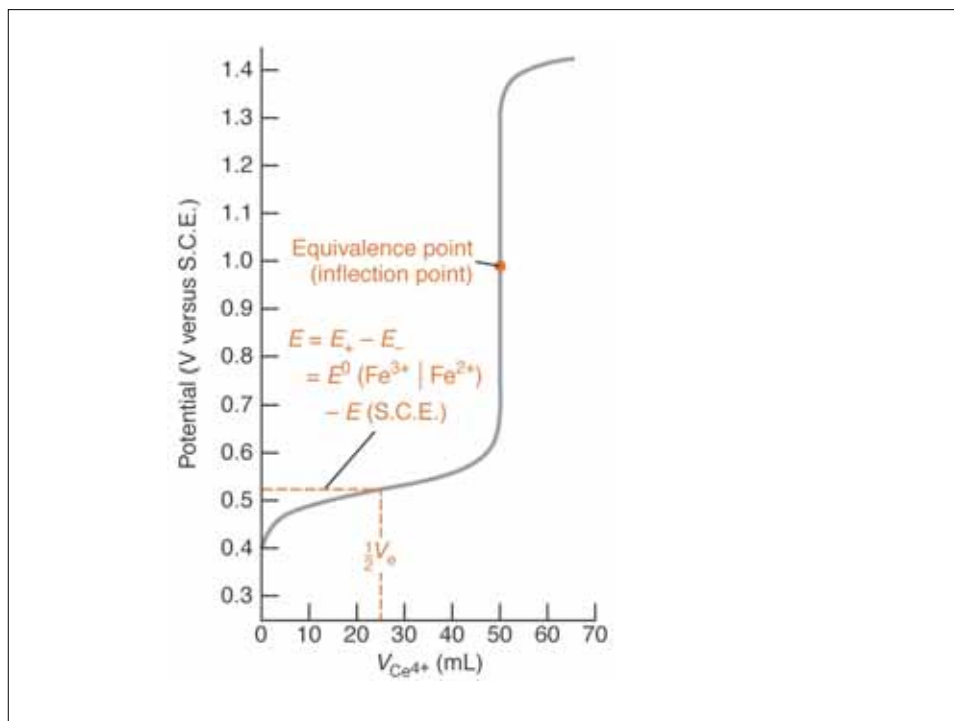
$$E_{\text{cell}} = 1.44 \text{ v} - \frac{0.0592}{1} \log \frac{3.29 \times 10^{-2}}{1.32 \times 10^{-3}} \text{ v} = 1.39 \text{ v}$$





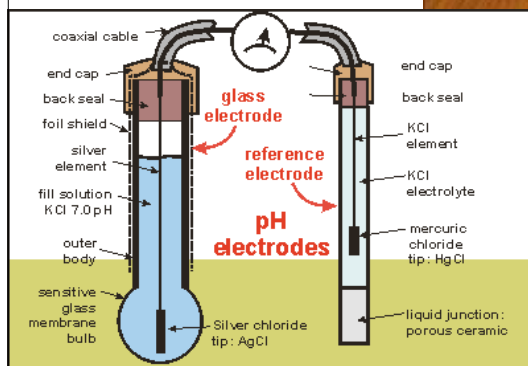
**Table 16-2** Redox indicators

Indicator	Color		$E^\circ$
	Oxidized	Reduced	
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4'-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2'-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2'-bipyridine)ruthenium	Pale blue	Yellow	1.29



## Electrochemical Methods: Potentiometry

- Reference Electrodes
- Indicator Electrodes
  - pH Electrodes
  - Ion-Selective Electrodes

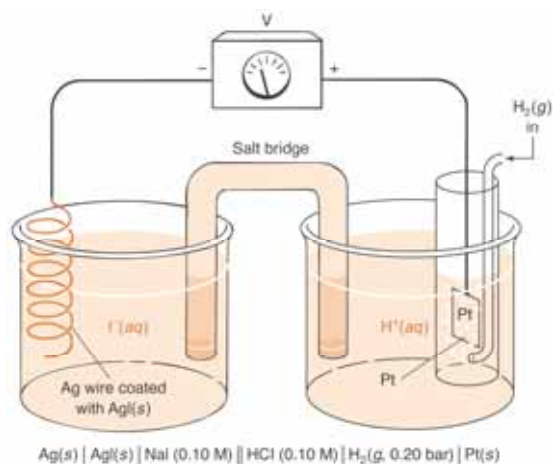


## Reference Electrodes

- A half-cell with a constant potential that is used as a comparison for other measurements.
- Made of some stable chemical species, is readily available and usually simple to use.
- Should be non-toxic if you are going to use it in a biological system.
- Should be rugged and portable if you are going to use it in the field!
- Several Varieties:
  - S.H.E
  - Ag/AgCl
  - Calomel

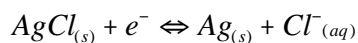
## S.H.E. (again)

- Cell made with hydrogen gas and hydrogen ion using a Pt electrode
- Not practical for regular use due to the hydrogen gas
- 



## Ag/AgCl

- Constructed of a silver wire, coated with silver chloride, in a solution containing silver chloride
  - Sometimes AgCl is in solution saturated with KCl
  - Saturated KCl keeps the chloride activity constant and helps keep the electrode stable

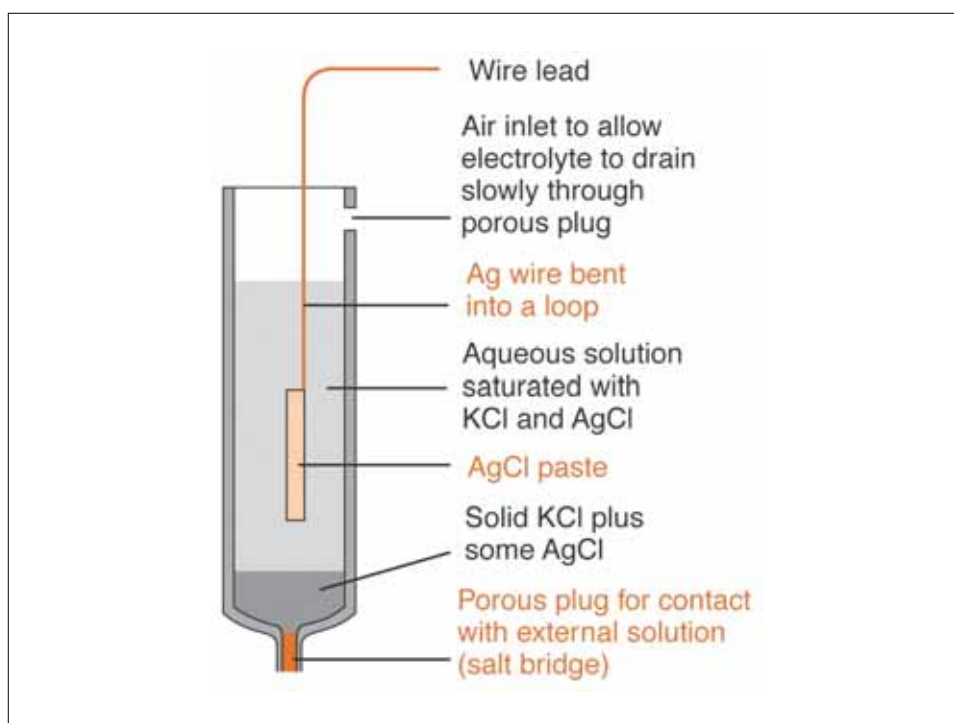
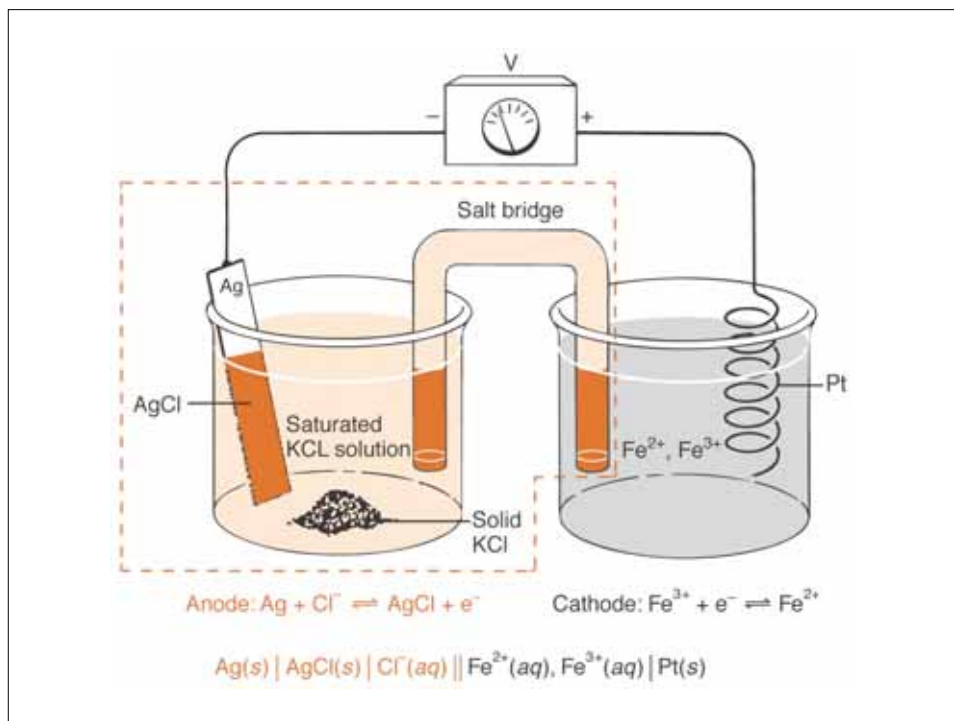


$$E^\circ = 222\text{mV (Relative to S.H.E.)}$$

$$E (\text{sat. KCl}) + 197 \text{ mV (relative to S.H.E.)}$$

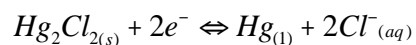
$$E = E^\circ - \frac{RT}{nF} \ln[\text{Cl}^-] \quad \frac{RT}{nF} = 0.05916 @ 25^\circ\text{C}$$

IF we replace ln with base ten log!



## Calomel (S.C.E)

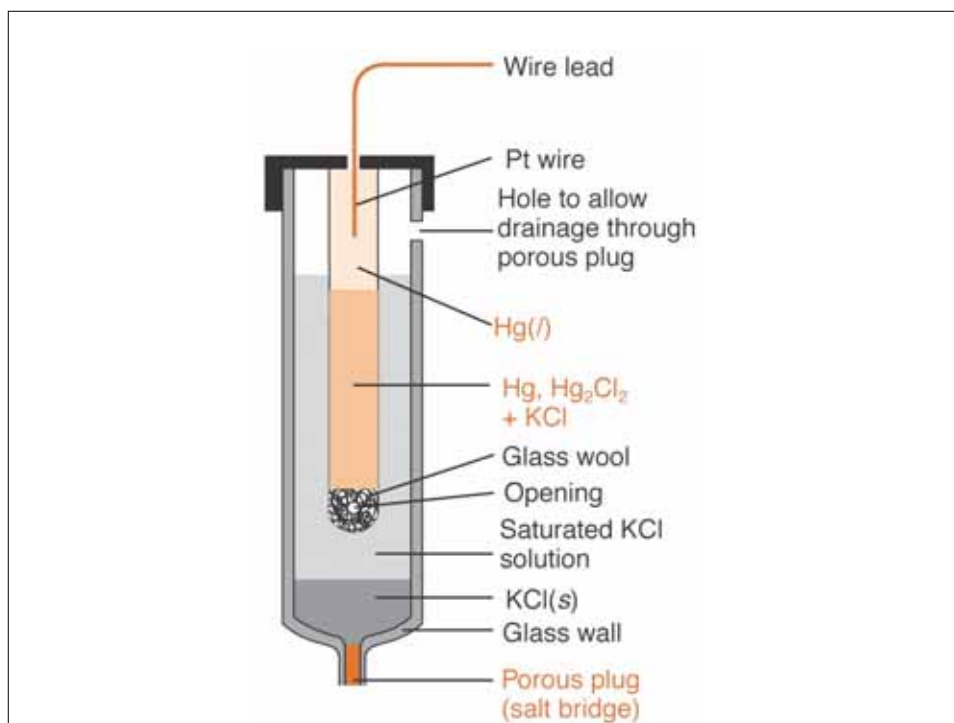
- Calomel is mercury (I) chloride
- One of the most common reference electrodes



$E^\circ = 268 \text{ mV}$  (relative to S.H.E.)

$E$  (sat. KCl) = 241 mV (relative to S.H. E.)

$$E = E^\circ - \frac{RT}{nF} \ln[\text{Cl}^-]^2$$



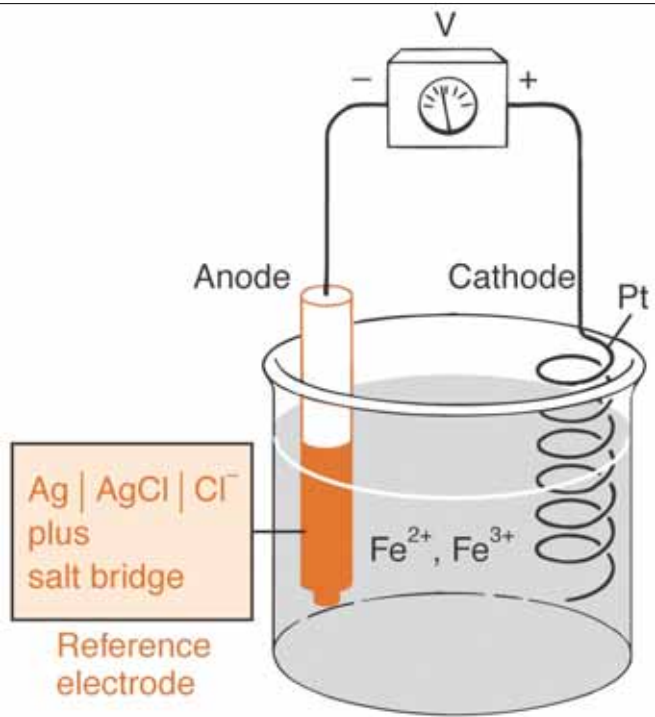
## Conversions among different scales (different electrodes)

- **The reduction potential for iron (III) under standard conditions is ? (look it up)**
  - What is it if measured compared to the Ag/AgCl reference electrode?
  - A saturated calomel electrode?

## Indicator Electrodes

- **Used for indicating the potential caused by some chemical species as compared to the reference electrode.**
- **Usually connected to the + (cathode) side of the potentiometer**
- **Made of a variety of often allegedly, but never actually, inert materials.**
- **Metal Electrodes**
  - Gold
  - Platinum
  - Carbon
    - ?
    - Solid carbon
    - Carbon Paste
  - Analyte of Interest
- **Ion Selective**
  - Glass membrane
  - Crystalline
    - Solid State
  - Liquid Membrane

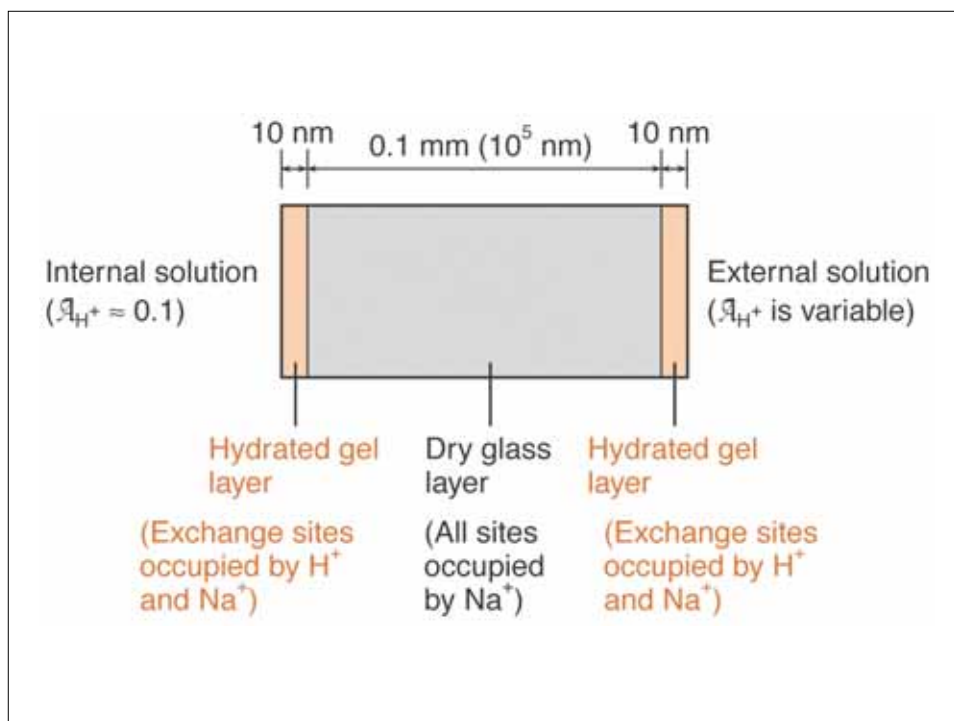
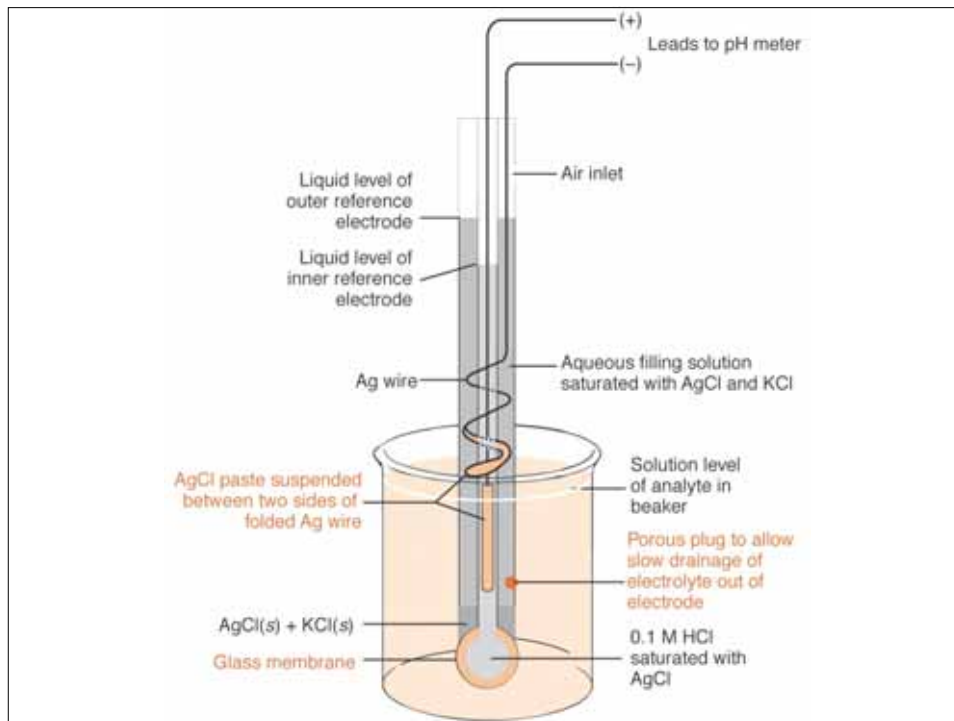
## Typical Metal Electrode Arrangement

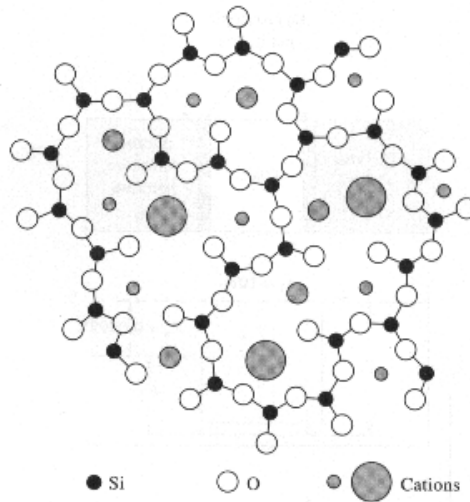


## pH (Glass Membrane) Electrodes

- One of the simpler ion-selective electrodes (ISE)
- Hydrogen Ion imparts a charge across a hydrated glass membrane
- Generally include an internal reference electrode (Ag/AgCl) and a separate Ag/AgCl electrode for sensing the charge imparted by the hydrogen ions
- Not as simple to use as you think!







**Figure 23-5** Cross-sectional view of a silicate glass structure. In addition to the three Si—O bonds shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. (Adapted with permission from G. A. Perley, *Anal. Chem.*, **1949**, 21, 395. Copyright 1949 American Chemical Society.)

### Basic Nernst Equation of a pH Electrode (only the pH sensing cell, not the reference electrode)....

$$E_{pH \text{ cell}} = \text{constant} + \beta \times 0.05916 \times \log \left( \frac{A_{H^+ \text{ outside}}}{A_{H^+ \text{ inside}}} \right)$$

The constant is cancelled out by calibration in similar  
Ionic strength solutions  
 $\beta$  is an efficiency factor that cancels out by calibration in similar  
Ionic strength solutions.

So, what really matters are the activities of hydrogen ions!  
Don't forget, electrodes respond to ACTIVITIES, even if we pretend  
That they are concentrations to simplify our calculations.

# Ionic Activity and Concentration

Debye and Huckel in 1923

Ionic Activity

$$a_i = r_i C$$

Activity coefficient

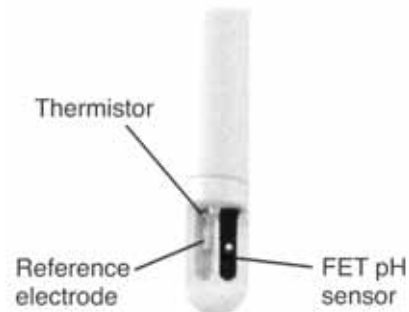
$$\log r_i = \frac{-0.51z^2\sqrt{I}}{1 + \sqrt{I}}$$

Ionic Strength

$$I = \frac{1}{2} \sum C_i z_i^2$$

## ISFET pH electrode

(Ion Selective Field Effect Transistor)



## What does 0.05916 mean?

- It is a constant, if there is a one-electron reaction
- It can be considered as the equivalent of a constant of 59.16 mV
- A pH meter is a high-impedance potentiometer (measures voltage)
- A pH change of “1” imparts a change in 59.16 mV to the potential recorded by the pH meter!
- 1 pH unit change = 59.16 mV

mV (relative readings)	pH
100.00	2.00
159.16	3.00
218.32	4.00
277.48	5.00
336.64	6.00
395.80	7.00

## Errors in pH Measurement....

1. **Junction potential** due to the salt bridge and differences in junction potentials over time due to contamination of the junction
  - Overcome by regular recalibration
2. **Sodium Error** will result in high concentration of sodium solutions. The sodium can also impart a charge across the glass membrane.
3. **Acid error** (strong acids) can saturate or contaminate the membrane with hydrogen ion!
4. **Equilibration Error** is overcome by letting the electrode equilibrate with the solution
5. **Dried out** glass membrane (ruins electrode)
6. **Temperature.** Since temperature affects activities, it is best to have all solutions at the same, constant temperature!
7. **Strong bases.** Strongly basic solutions (>pH 12) will dissolve the glass membrane!
8. **Uncertainty** in your buffer pH due to normal weighing, diluting errors.

## Ion Selective Electrodes.....

- **Selectivity Coefficient**

- Defines how an ISE responds to the species of interest versus some interfering species
  - Interferences cause a signal (voltage) to be imparted on the electrode that is NOT the result of the ion or chemical species of interest
- You want the selectivity coefficient to be as SMALL as possible

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

Where X is the interference and A is the analyte

$$E = \text{constant} + \beta \frac{0.05916}{n} \log(A_A + \sum(k_{(A,X)} \times A_X))$$

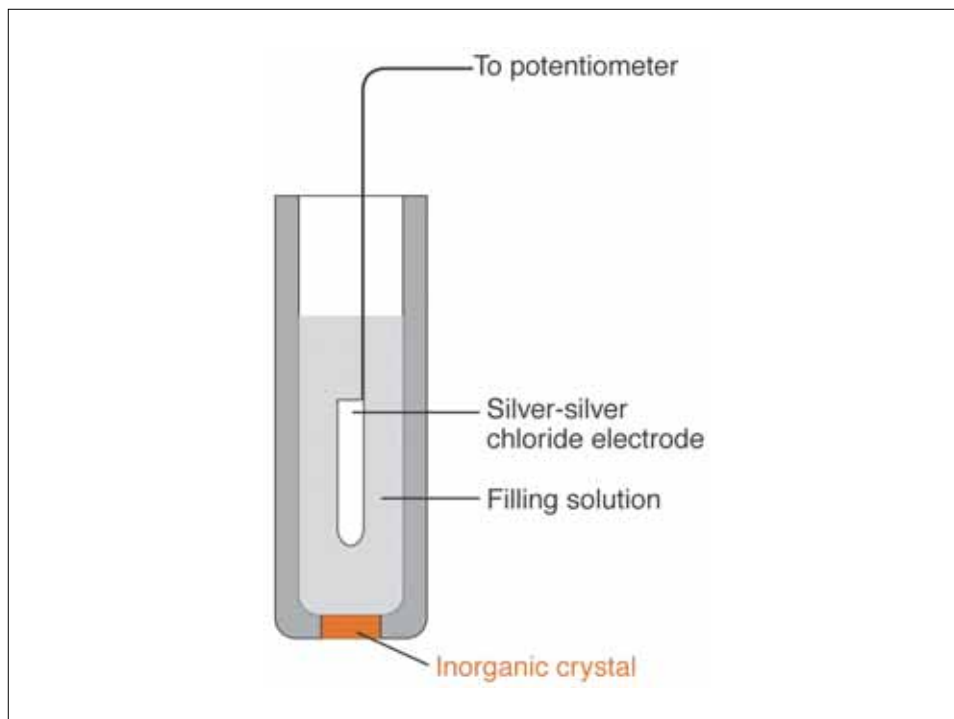
## Examples of Electrodes / Interferences

**Table 15-5** Properties of solid-state ion-selective electrodes

Ion	Concentration range (M)	Membrane material	pH range	Interfering species
F <sup>-</sup>	10 <sup>-6</sup> -1	LaF <sub>3</sub>	5-8	OH <sup>-</sup> (0.1 M)
Cl <sup>-</sup>	10 <sup>-4</sup> -1	AgCl	2-11	CN <sup>-</sup> , S <sup>2-</sup> , I <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , Br <sup>-</sup>
Br <sup>-</sup>	10 <sup>-5</sup> -1	AgBr	2-12	CN <sup>-</sup> , S <sup>2-</sup> , I <sup>-</sup>
I <sup>-</sup>	10 <sup>-6</sup> -1	AgI	3-12	S <sup>2-</sup>
SCN <sup>-</sup>	10 <sup>-5</sup> -1	AgSCN	2-12	S <sup>2-</sup> , I <sup>-</sup> , CN <sup>-</sup> , Br <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>
CN <sup>-</sup>	10 <sup>-6</sup> -10 <sup>-2</sup>	AgI	11-13	S <sup>2-</sup> , I <sup>-</sup>
S <sup>2-</sup>	10 <sup>-5</sup> -1	Ag <sub>2</sub> S	13-14	

## Solid State Electrodes

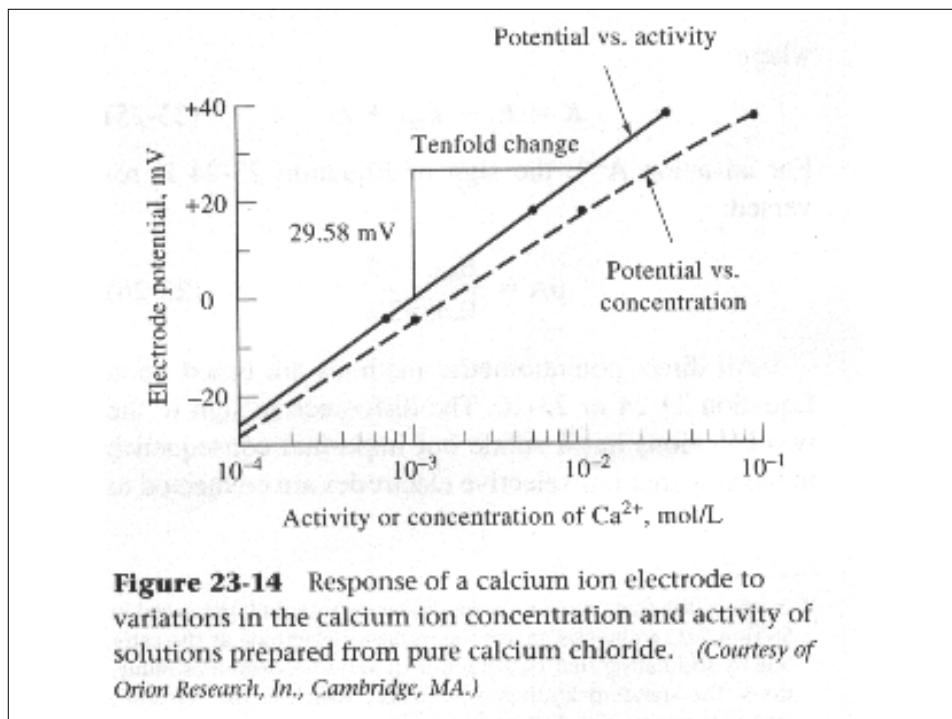
- Uses a small amount of a doped crystal to transport charge from the solution to an inner electrode
- The inner (sensing) electrode can be a Ag/AgCl electrode, and a separate Ag/AgCl electrode can be present
  - Combination electrode
- You can use a separate reference electrode also.



- Typical equation (Fluoride Electrode):

$$E = \text{constant} - \beta \times 0.05916 \times \log(A_{F^- \text{ outside}})$$

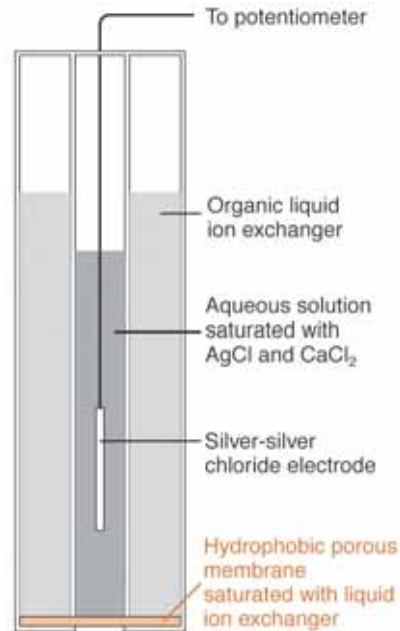
- Use:
  - Prepare calibration and sample solutions to similar ionic strengths and temperatures
  - Connect ISE and reference electrode to potentiometer (pH meter in mV mode)
  - Record potentials of calibration solutions
  - Prepare calibration curve
  - Measure potential of sample solutions and calculate fluoride activity!



**Figure 23-14** Response of a calcium ion electrode to variations in the calcium ion concentration and activity of solutions prepared from pure calcium chloride. (Courtesy of Orion Research, Inc., Cambridge, MA.)

## Liquid Membrane ISE's

- Replace the solid state crystal with a liquid ion-exchanger filled membrane
- Ions impart a charge across the membrane
- The membrane is designed to be **SELECTIVE** for the ion of interest.....



**Table 15-6** Properties of liquid-based ion-selective electrodes

Ion	Concentration range (M)	Carrier	Solvent for carrier	pH range	Interfering species
Cu <sup>2+</sup>	10 <sup>-5</sup> -1	Calcium didecylphosphate	Diocetylphenylphosphonate	6-10	Zn <sup>2+</sup> , Pb <sup>2+</sup> , Fe <sup>2+</sup> , Cu <sup>2+</sup>
K <sup>+</sup>	10 <sup>-6</sup> -1	Valinomycin	Diocetylsebacate	4-9	Rb <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>
NO <sub>3</sub> <sup>-</sup>	10 <sup>-5</sup> -1	Tridodecylhexadecylammonium nitrate	Octyl-2-nitrophenyl ether	3-8	ClO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , Br <sup>-</sup> , HS <sup>-</sup> , CN <sup>-</sup>
ClO <sub>4</sub> <sup>-</sup>	10 <sup>-5</sup> -1	Tris(substituted 1,10-phenanthroline) iron(II) perchlorate	<i>p</i> -Nitrocymene	4-10	I <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , Br <sup>-</sup>
BF <sub>4</sub> <sup>-</sup>	10 <sup>-5</sup> -1	Tris(substituted 1,10-phenanthroline) nickel(II) tetrafluoroborate	<i>p</i> -Nitrocymene	2-12	NO <sub>3</sub> <sup>-</sup>



# Voltammetry

Voltammetry can be used to

- Study electroactivity of ions and molecules at the electrode/solution interface
- Probe coupled chemical reactions and measure electron transfer rates
- Examine electrode surfaces

An electrochemical cell consists of a working (analyzing) electrode, an auxiliary (counter) electrode, and a reference electrode. The control device is a potentiostat.

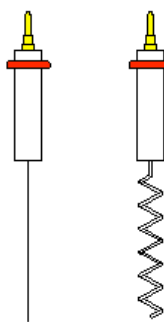
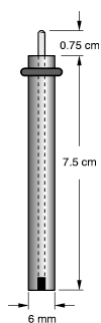
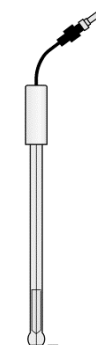
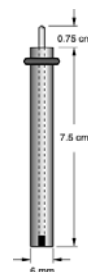
Clarifications of disk electrodes:

In quiescent solutions,

Conventional-sized (>mm)	Microelectrode (>25 μm)	Ultramicroelectrode (0.1-25 μm)	Nanode (nm)
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In flowing or agitated solutions,

Rotating disk electrode, channel electrode, wall-jet electrode, and flow-through tubular electrode.

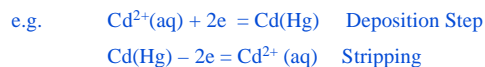


**Disk Working Electrode  
Imbedded In Teflon or Kel-F**

**Pt/Au wire or coil auxiliary electrode**

## Stripping Analysis

In **anodic stripping voltammetry (analysis)**, analytes are reduced and deposited onto an electrode. They are reoxidized during the stripping step.



In the deposition step, solution is stirred or the electrode is rotated.

In **cathodic stripping voltammetry**, typically anions are oxidized and deposited onto an electrode with subsequent stripping via a negative potential scan.



Because sample analytes are preconcentrated from a large-volume dilute solution onto a small-volume electrode under forced convection, trace analysis (enhanced sensitivity) can be realized.

## Tissue-based biosensor (voltammetric)

