

CHE 729
Electrochemistry
Lecture 1

**Introduction and Overview of
 Electrode Processes**





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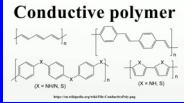
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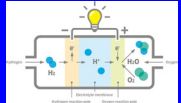
Electrochemistry

The study of chemical reactions that involve electron or charge transfer (e.g., ions).

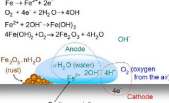



Conductive polymer



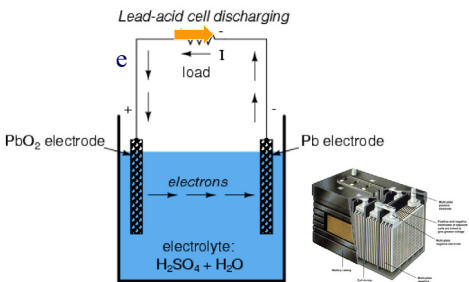


$Fe \rightarrow Fe^{2+} + 2e^-$
 $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$
 $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
 $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 2Fe_2O_3 + 4H_2O$



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Lead-acid cell discharging



At (+) electrode: $Pb(IV)O_2 + 3H^+ + HSO_4^- + 2e^- \rightarrow Pb(II)SO_4 + 2H_2O$

At (-) electrode: $Pb + HSO_4^- \rightarrow Pb(II)SO_4 + H^+ + 2e^-$

Overall cell: $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

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Electroanalytical Chemistry

A large group of analytical methods (Quantitative and Qualitative) based on electrochemistry.

For example:

Voltammetry, Potentiometry, Electrogenerated Chemiluminescence (ECL), Electrochemical Scanning Microscopy (SECM), Electrochemical Biosensors.

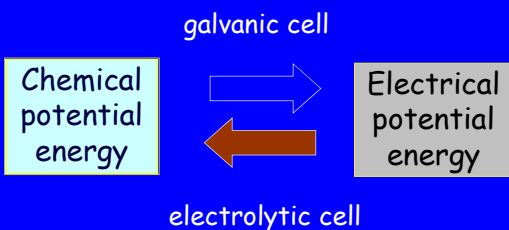
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Some Advantages of Electroanalytical Methods

- fast
- inexpensive
- in situ (pH, glucose)
- information about oxidation states
- stoichiometry
- rates of diffusion, electron transfer,
- equilibrium constants

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Energy Conversions with Cells



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(a) A galvanic electrochemical cell at open circuit; (b) a galvanic cell doing work; (c) an electrolytic cell.

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Redox Processes - electron transfer

$$Cu(s) - 2e^- \xrightleftharpoons[\text{Reduction (+e) [Electrolyte Cell]}]{\text{Oxidation (-e) [Galvanic Cell]}} Cu^{2+}(aq)$$

$$2Ag^+(aq) + 2e^- \xrightleftharpoons[\text{Oxidation (-e) [Electrolyte Cell]}]{\text{Reduction (+e) [Galvanic Cell]}} 2Ag(s)$$

$$Cu(s) + 2Ag^+(aq) \xrightleftharpoons[\text{Electrolytic Cell}]{\text{Galvanic Cell}} Cu^{2+}(aq) + 2Ag(s)$$

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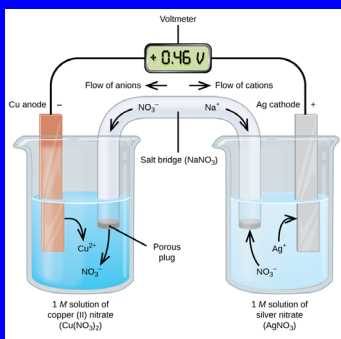
Anode vs Cathode

Anode: electrode with oxidation process
Cathode: electrode with reduction process

- Depends on the type of electrochemical cell
- Determined by the redox process

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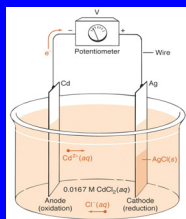
Movement of electrons and ions in a cell—Functions of salt bridge



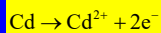
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Liquid Junction

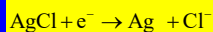
the interface between electrochemical solution and the salt bridge (liquid-liquid interface) → could develop a small junction potential



Anode (Negative electrode):



Cathode (Positive electrode):

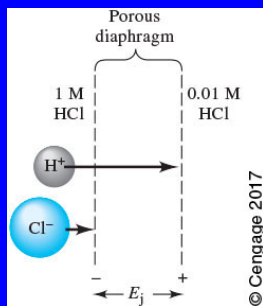


Cell without a salt bridge

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Origin of Liquid Junction Potentials

• HCl (1.0 M)|HCl (0.01 M)

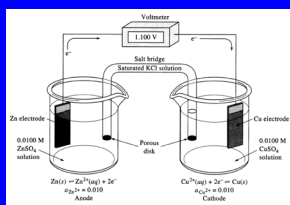


Differences in ion mobility give rise to junction potentials. Unequal distribution.

Solution: salt bridge containing a high concentration of KCl or NaNO₃

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Shorthand Cell Notation

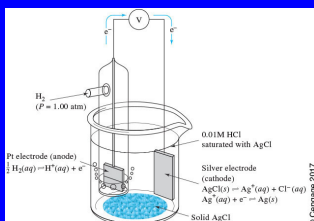
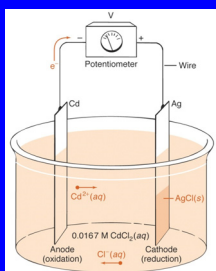


Convention

- Anode—on the left
- Cathode—right
- |—interface
- ||—salt bridge (two liquid-liquid interfaces)
- Activity/concentration/pressure included

$\text{Zn}|\text{ZnSO}_4(a_{\text{Zn}^{2+}} = 0.0100 \text{ M})||\text{CuSO}_4(a_{\text{Cu}^{2+}} = 0.0100 \text{ M})|\text{Cu}$
 (Anode, negative) (salt bridge) (cathode, positive)

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(Anode, -) $\text{Cd}|\text{CdCl}_2(0.0167 \text{ M})|\text{AgCl}|\text{Ag}$ (Cathode, +)
 $\text{Pt}, \text{H}_2(p = 1 \text{ atm})|\text{H}^+(0.01 \text{ M}), \text{Cl}^-(0.01 \text{ M}), \text{AgCl}(\text{sat'd})|\text{Ag}$

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Electrode Potentials—Nernst Equation

$\text{Ox} + n\text{e} = \text{Red}$ ("half cell" reaction)

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}} \quad \left\{ \text{Ln} b = \log_e b = \frac{\log_{10} b}{\log_{10} e} \right\}$$

$$= E^0 + \frac{8.316 \cdot 298.15}{n \cdot 96485.31 \cdot \log 2.718} \log \frac{a_{\text{Ox}}}{a_{\text{Red}}} = E^0 + \frac{0.05918}{n} \log \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

where E^0 is the standard potential (i.e., when $a_{\text{Ox}} = a_{\text{Red}} = 1$)

R is the gas constant ($8.316 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K),

n is the number of electrons transferred, F Faraday constant $96485.31 \text{ C mol}^{-1}$

$$a_X = \gamma_X [X]$$

γ_X is the activity coefficient of solute X .

γ_X varies with the presence of other ions (ionic strength)

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Formal/Conditional Potentials

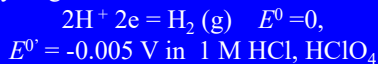
$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{OX}}}{a_{\text{Red}}} = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{\text{OX}}[\text{OX}]}{\gamma_{\text{Red}}[\text{Red}]}$$

$$= \left\{ E^0 + \frac{RT}{nF} \ln \frac{\gamma_{\text{OX}}}{\gamma_{\text{Red}}} \right\} + \frac{RT}{nF} \ln \frac{[\text{OX}]}{[\text{Red}]}$$

$$= E^{0'} + \frac{RT}{nF} \ln \frac{[\text{OX}]}{[\text{Red}]} = E^{0'} - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{OX}]}$$

($E^{0'}$ – formal/conditional potential)

e.g., Hydrogen



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Examples

Write Nernst expressions for the following half-cell reactions:

- (1) $\text{Zn}^{2+} + 2\text{e} = \text{Zn}(\text{s})$
- (2) $\text{Fe}^{3+} + \text{e} = \text{Fe}^{2+}(\text{s})$
- (3) $2\text{H}^+ + 2\text{e} = \text{H}_2(\text{g})$
- (4) $\text{MnO}_4^- + 5\text{e} + 8\text{H}^+ = \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- (5) $\text{AgCl}(\text{s}) + \text{e} = \text{Ag}(\text{s}) + \text{Cl}^-$

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$$(1) E = E^0 + \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Zn}]} = E^0 + \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{1}$$

$$(2) E = E^0 + \frac{0.0592}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$(3) E = E^0 + \frac{0.0592}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$$

$$(4) E = E^0 + \frac{0.0592}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}][\text{H}_2\text{O}]^4} = E^0 + \frac{0.0592}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

$$(5) E = E^0 + \frac{0.0592}{1} \log \frac{[\text{AgCl}(\text{s})]}{[\text{Ag}(\text{s})][\text{Cl}^-]} = E^0 + \frac{0.0592}{1} \log \frac{1}{[\text{Cl}^-]}$$

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Electrochemical Cell Potentials —Nernst Equation

- The Nernst equation can be derived from the equation linking free energy changes to the reaction quotient:

$$\Delta G = \Delta G^0 + RT \ln Q \quad \text{where } Q \text{ is the reaction quotient}$$

$$\therefore \Delta G = -nF\Delta E \quad \Delta E \text{ is the electrochemical cell potential}$$

$$\Delta G^0 = -nF\Delta E^0 \quad \Delta E^0 \text{ is the standard electrochemical cell potential}$$

$$\therefore \Delta E = \Delta E^0 - \frac{RT}{nF} \ln Q$$

$$= \Delta E^0 - \frac{0.0592}{n} \log Q \text{ at } 298 \text{ K (} 25^\circ \text{C)}$$

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$\Delta E \text{ (or } E_{\text{cell}}) = E_{\text{cathode}(+)} - E_{\text{anode}(-)}$

For $aA + bB + \dots = pP + sS + \dots$
(n electrons involved)

$$Q = \frac{a_p^p \cdot a_s^s \dots}{a_A^a \cdot a_B^b \dots}$$

When the reaction reaches equilibrium

$\therefore \Delta G = 0 \text{ } (\Delta E = 0), Q = K_{\text{eq}}$

$\therefore \Delta G^0 = -RT \ln K_{\text{eq}}$

or $-nF\Delta E^0 = -RT \ln K_{\text{eq}}$

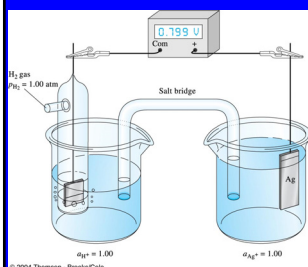
$$\ln K_{\text{eq}} = \frac{nF\Delta E^0}{RT}$$

or $\lg K_{\text{eq}} = \frac{n\Delta E^0}{0.0592} \text{ (at } 298\text{K)}$

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Standard (Normal) Hydrogen Electrode (SHE/NHE)

Can't measure potential on each electrode independently — only differences



$2\text{H}^+ (a = 1.00 \text{ M}) + 2\text{e}^- = \text{H}_2 (\text{g}, p = 1.00 \text{ atm})$
 $\text{Pt}, \text{H}_2 (\text{g}, p = 1.00 \text{ atm}) | \text{H}^+ (a = 1.00 \text{ M}) || \dots$
 Assigned 0.000 V at any Temperature.
 Can be anode or cathode.
 Pt-electron carrier, does not take part in rxn.
 Cumbersome to operate.

$$\Delta E_{\text{cell}} = E_{\text{M}} - E_{\text{SHE}}$$

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Practical Reference Electrodes (Secondary Ref. Electrodes)

Aqueous

- SCE (Saturated Calomel Electrode)
- Ag/AgCl (KCl, x M)
- Ferrocene methanol--Fc-CH₂OH--water soluble,
→ added directly to the analyte solution.

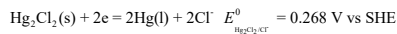
Non-aqueous

- Ag/Ag⁺ (x M AgNO₃)
- Pseudo (Quasi) references
 - Pt, Ag wires
- Ferrocene--Internal standard potential ref.
→ added directly to the analyte solution.

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Saturated Calomel Electrodes (SCE)

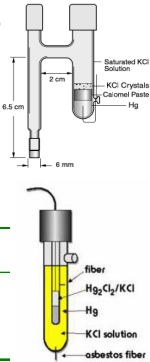
- Hg(l)|Hg₂Cl₂(s)|KCl(Sat'd)
- E⁰ = 0.241 V vs. SHE @ 25°C



$$E_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-} = E_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-}^0 + \frac{RT}{2F} \ln \frac{1}{(a_{\text{Cl}^-})^2} = 0.268 - 0.0592 \lg a_{\text{Cl}^-}$$

(Saturated KCl, [Cl⁻] = 4.5 M)

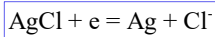
Electrode	Acronym	Potential vs. SHE
Hg(l)/Hg ₂ Cl ₂ (s)/KCl (0.1 M)		0.3337
Hg/Hg ₂ Cl ₂ (s)/KCl (1 M)	NCE	0.2801
Hg(l)/Hg ₂ Cl ₂ (s)/KCl (sat'd)	SCE	0.2412
Hg(l)/Hg ₂ Cl ₂ (s)/NaCl (sat'd)	SSCE	0.2360



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Ag/AgCl (x M KCl)

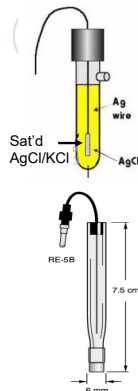
- Ag wire coated with AgCl(s), immersed in NaCl or KCl solution
- E⁰ = 0.222 V vs. SHE @ 25°C



$$E_{\text{Ag}/\text{AgCl}} = E^0 + 0.0592 \lg \frac{1}{a_{\text{Cl}^-}}$$

$$= E^0 - 0.0592 \lg a_{\text{Cl}^-}$$

$$a_{\text{Cl}^-} \uparrow, E_{\text{Ag}/\text{AgCl}} \downarrow.$$



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