

Introduction to Electrochemistry (Chapter 22)

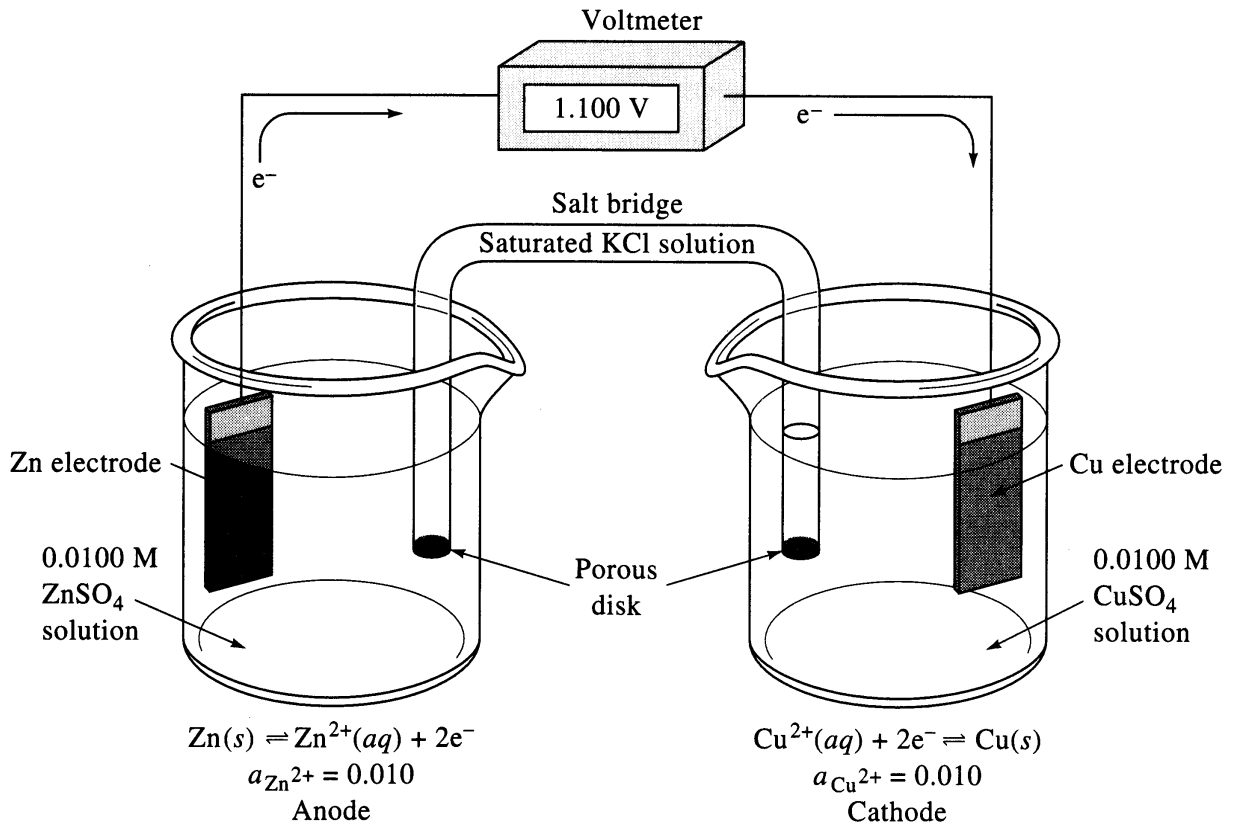
Many different **electroanalytical** methods:

- fast
- inexpensive
- in situ
- information about
 - oxidation states
 - stoichiometry
 - rates
 - charge transfer
 - equilibrium constants

Electrochemical Cells:

Oxidation and **reduction** (redox) reactions

Separate species to prevent direct reaction (Fig 22-1)



- Most contain
- external **wires** (electrons carry current)
 - **ion solutions** (ions carry current)
 - **interfaces** or junctions
- All contain
- complete **electrical circuit**
 - conducting **electrodes** (metal, carbon)

Electrons transferred at electrode surface at liquid/solid **interface**

Potential difference (voltage) is measure of tendency to move to equilibrium

Galvanic cell - cell develops spontaneous potential difference

Overall: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

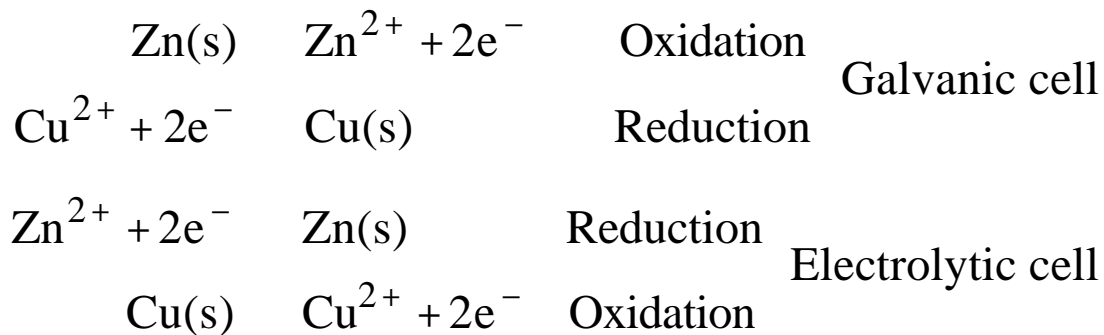
Half reactions:

| | | |
|----------------------------------|----------------------------------|-----------|
| Zn(s) | $\text{Zn}^{2+} + 2\text{e}^{-}$ | Oxidation |
| $\text{Cu}^{2+} + 2\text{e}^{-}$ | Cu(s) | Reduction |

Convention: **Reduction** at **Cathode**
 Oxidation at **Anode**

Galvanic cell - Zn **anode** (**negative**), Cu **cathode** (**positive**)

Electrolytic cells - require potential difference greater than galvanic potential difference (to drive away from equilibrium)



Electrolytic cell - Zn **cathode** (positive), Cu **anode** (negative)

Many chemically reversible cells

Short-Hand Cell notation:

Convention: **Anode** on Left

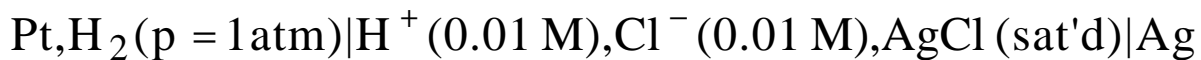
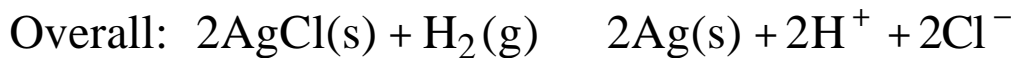
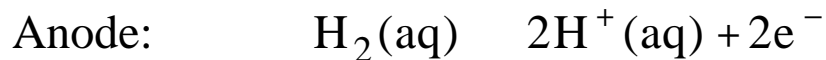
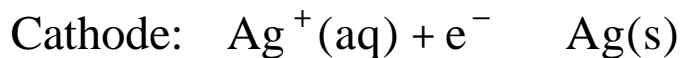
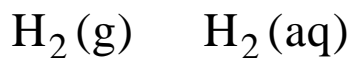
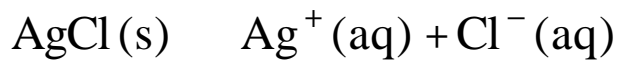
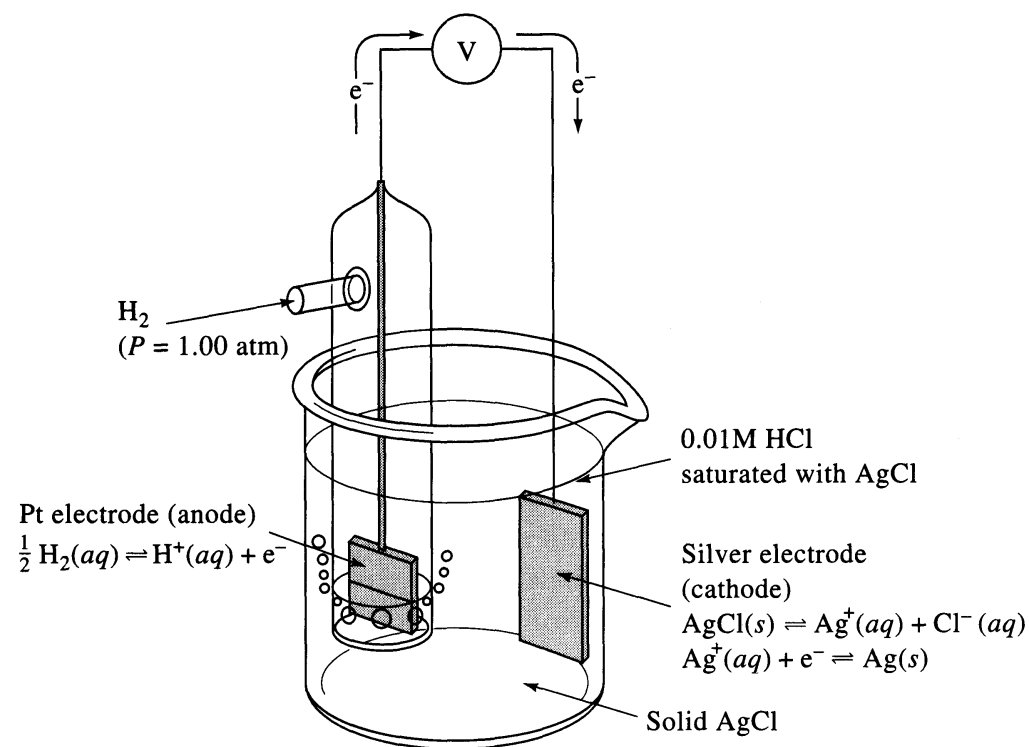


liquid-liquid interface

Galvanic cell as written

Electrolytic cell if reversed

Not all cells have liquid-liquid junctions (Fig 22-3)



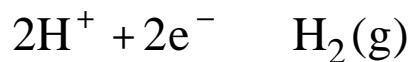
Electrode Potentials:

- Cell potential is **difference** between **anode** and **cathode** potential

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

when half-reactions written as reductions

Example:



electrons on left

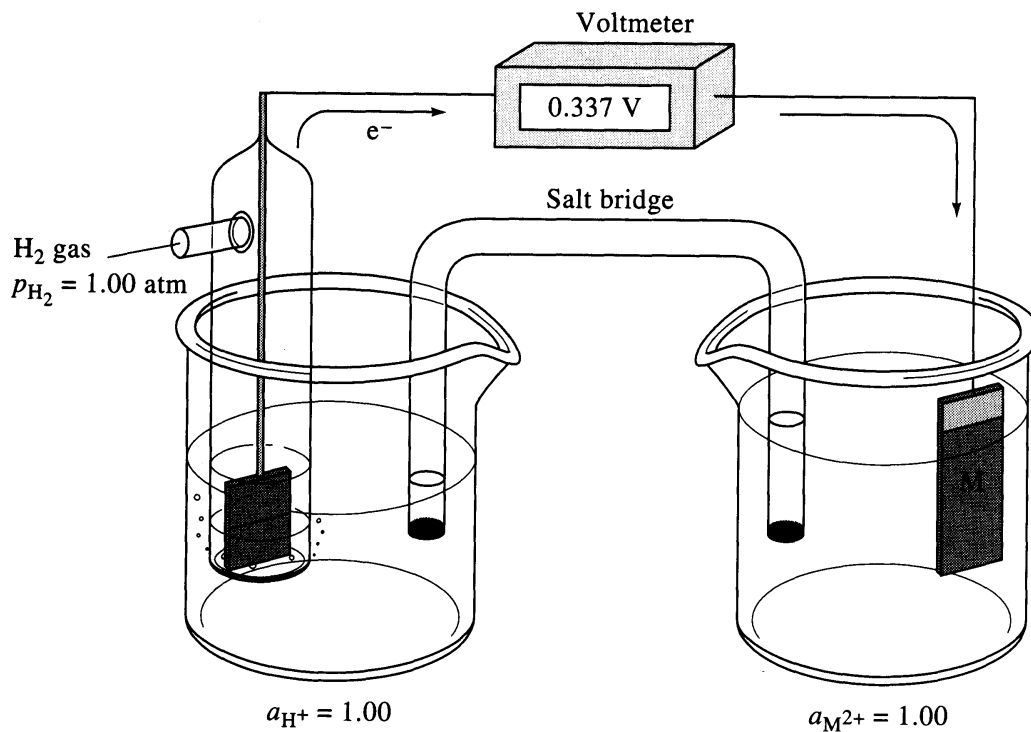
Galvanic cell $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.46 \text{ V}$

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

Standard reference electrode is usually standard hydrogen electrode (SHE)



Fig 22-5



SHE:

- assigned 0.000 V
- can be anode or cathode
- Pt does not take part in reaction
- Pt electrode coated with fine particles (Pt black) to provide large surface area
- cumbersome to operate

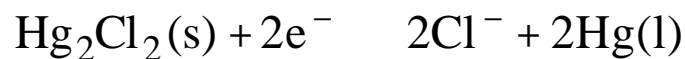
Alternative reference electrodes:

- Ag/AgCl electrode



$$E_{\text{cell}} = +0.20 \text{ V vs. SHE}$$

- Calomel electrode



$$E_{\text{cell}} = +0.24 \text{ V vs. SHE}$$

Electrode and Standard Electrode Potentials (E and E⁰):

How do we know which way reaction will go spontaneously?

Use **electrode potentials**, E (potential of electrode versus SHE) to find **E_{anode}** and **E_{cathode}**. Then find **E_{cell}**.

But electrode potential varies with activity of ion (appendix 2)

activity

activity coefficient

$$a_X = \gamma_X [X]$$

concentration

γ_X varies with presence of other ions (ionic strength)

$$\mu = \frac{1}{2} ([X]Z_X^2 + [Y]Z_Y^2 + \dots)$$

concentration

charge

Note: activity of pure liquid or solid in excess=1.00

Note: use pressure (atm) for gases

If $a=1.00$ M, the electrode potential, E, becomes *standard* electrode potential, E⁰

Appendix 3:

| | | |
|----------------------------------|------------------------|--------------------------|
| $\text{Cu}^{2+} + 2\text{e}^{-}$ | Cu(s) | $E^0 = +0.337 \text{ V}$ |
| $2\text{H}^{+} + 2\text{e}^{-}$ | $\text{H}_2(\text{g})$ | $E^0 = +0.000 \text{ V}$ |
| $\text{Cd}^{2+} + 2\text{e}^{-}$ | Cd(s) | $E^0 = -0.403 \text{ V}$ |
| $\text{Zn}^{2+} + 2\text{e}^{-}$ | Zn(s) | $E^0 = -0.763 \text{ V}$ |

Cell containing Cu/Cu^{2+} and Cd/Cd^{2+}

called couple

- (1) $\text{Cu}^{2+} + 2\text{e}^{-}$ Cu spontaneously **forward**
 $\text{Cd}^{2+} + 2\text{e}^{-}$ Cd spontaneously **backward** ($\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^{-}$)
- (2) e^{-} flow towards Cu electrode (**cathode/positive** electrode)
 e^{-} flow away from Cd electrode (**anode/negative** electrode)
- (3) Cu^{2+} good **electron acceptor** (**oxidizing agent**)
Cd good **electron donor** (**reducing agent**)

The most positive E or E^0 spontaneously **forward** forming **cathode**

Calculation of Cell Potentials, E_{cell} :

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

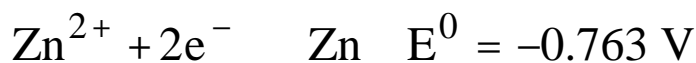
when written as reductions

Example:



anode

cathode



Zn reaction spontaneously **backward** - forms **negative electrode** -
place of oxidation - **anode**

If $a=1.00 \text{ M}$, $E=E^0$:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= +0.337 - (-0.763) \\ &= +1.100 \text{ V} \end{aligned}$$

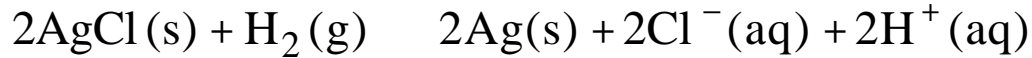
Spontaneous reaction is galvanic $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$

E_{cell} indicates if reaction is spontaneous as written

E_{cell} **positive** - reaction **forward**

E_{cell} **negative** - reaction **backwards**

Electrode potential is related to **position of equilibrium**



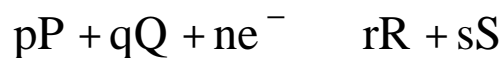
$$K_{\text{eq}} = \frac{a_{\text{Ag}}^2 a_{\text{Cl}^-}^2 a_{\text{H}^+}^2}{a_{\text{AgCl}}^2 P_{\text{H}_2}}$$

$$K_{\text{eq}} = \frac{a_{\text{Cl}^-}^2 a_{\text{H}^+}^2}{P_{\text{H}_2}}$$

If reaction is long way from thermodynamic equilibrium, K will change with time

Eventually, **concentrations reach equilibrium values** and K stops changing (true equilibrium constant K_{eq})

In general:

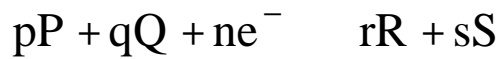


$$E = E^0 - \frac{0.0592}{n} \log K_{\text{eq}}$$

$$E = E^0 - \frac{0.0592}{n} \log \frac{(a_{\text{R}})^r (a_{\text{S}})^s}{(a_{\text{P}})^p (a_{\text{Q}})^q}$$

Nernst Equation

In principle, can calculate E and E_{cell} from E^0 for any activity from Nernst equation:



$$E = E^0 - \frac{0.0592}{n} \log \frac{(a_R)^r (a_S)^s}{(a_P)^p (a_Q)^q}$$

- $E = E^0$ when log quotient in Nernst equation is unity
- E^0 is relative to SHE
- E^0 is measure of driving force for half-cell reduction

Limitations of Standard Electrode Potentials:

- (1) E^0 is temperature dependent
- (2) Substitution of concentration for activity always introduces error. Error is worse at high ionic strength
- (3) Formation of complexes, association, dissociation alter E^0

Formal potentials (E^0') apply for specific reactions when specifying ALL concentrations (Appendix 3)

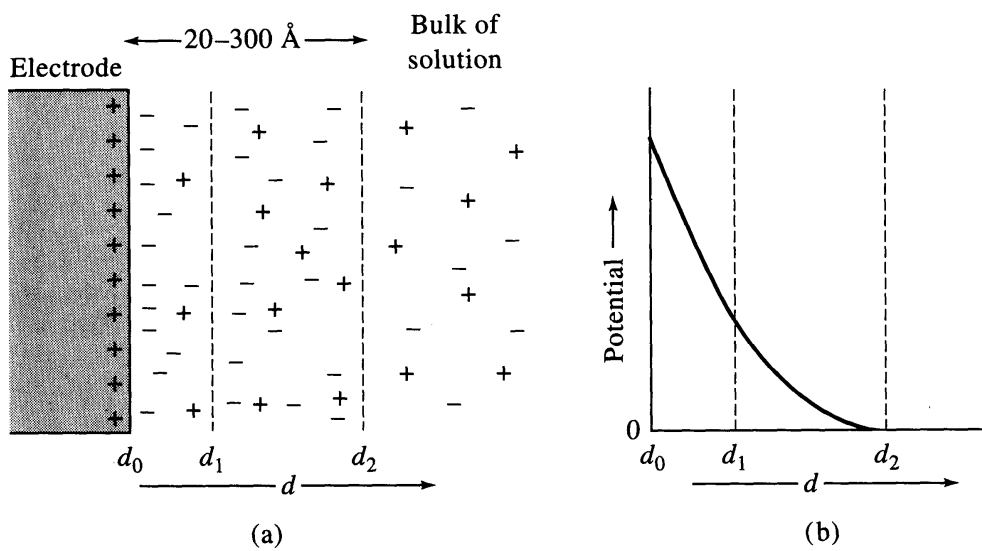
What happens at electrode surface?

Electrons transferred at electrode surface by **redox reactions**

- occur at liquid/solid interface (solution/electrode)

Electrical double layer formed (Fig 22-2)

- (i) **Tightly** bound **inner** layer
- (ii) **Loosely** bound **outer** layer



Faradaic currents:

proportional to species concentration
due to redox reaction

Non-faradaic currents:

charging of double layer (capacitance)
not due to redox reactions

Redox reactions happen close to electrode surface (inner part of double layer - $<10 \text{ \AA}$)

Continual **mass transport** of ions to electrode surface by

- (i) **convection** (stirring, liquid currents)
- (ii) **diffusion** (concentration gradient)
- (iii) **migration** (electrostatic force)

Types of Electroanalytical Techniques:

Fig 22-9

