Chemical Engineering 378

Science of Materials Engineering

Lecture 29

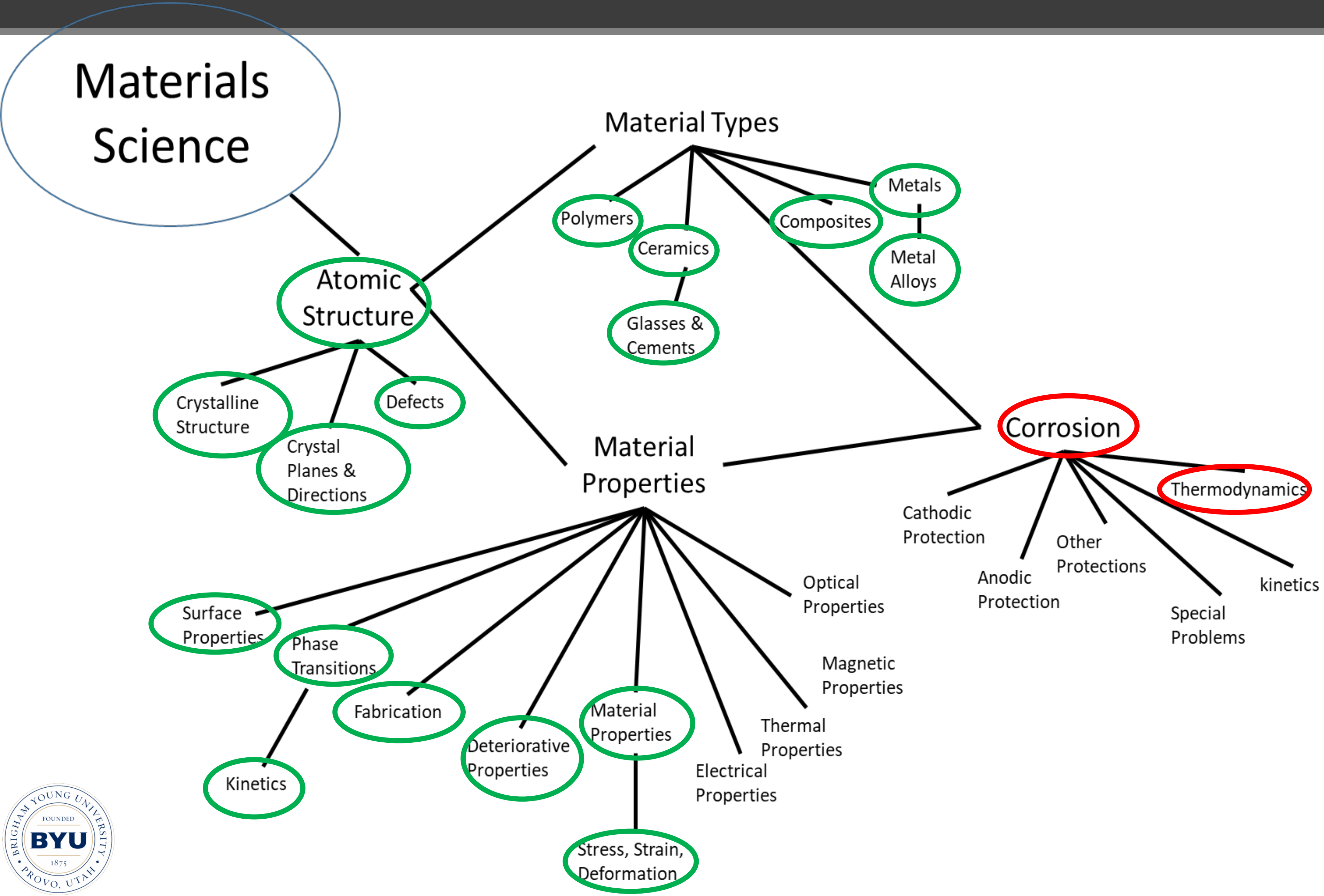
Corrosion: Thermodynamics

Spiritual Thought

We should not generalize and overlook precious opportunities to render service and thereby relieve those who are hungry, those who are sick or who have special needs. When we are willing and we express our desire to render a service, the Lord, through his Spirit, will lead us to the right people and opportunities. Every morning, we could wake up and ask ourselves, “How can I be an answer to someone’s prayer through the service I am going to render?” We render service by giving of our energy, our goods, our time and our attention.

-Elder Eustache Ilunga

Materials Roadmap



Materials Science

Atomic Structure

Crystalline Structure

Crystal Planes & Directions

Defects

Material Types

Polymers

Ceramics

Glasses & Cements

Composites

Metals

Metal Alloys

Material Properties

Surface Properties

Phase Transitions

Kinetics

Fabrication

Deteriorative Properties

Material Properties

Stress, Strain, Deformation

Electrical Properties

Thermal Properties

Magnetic Properties

Optical Properties

Corrosion

Cathodic Protection

Anodic Protection

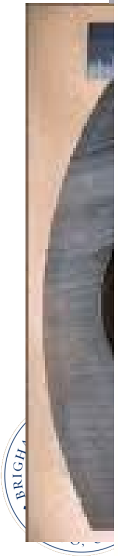
Other Protections

Special Problems

Thermodynamics

kinetics

Davis Besse Plant



GREAT LAKES REGION NUCLEAR FACILITIES

LEGEND **ONLY FACILITIES SPECIFICALLY RELATED TO NUCLEAR POWER GENERATION ARE ON THIS MAP**

- ▲ Uranium Mining and Mill Tailings
- ● Operating Nuclear Power Reactors*
- ☒ Closed Nuclear Power Reactors*
- ▭ Nuclear Fuel Waste
- ▯ Low-and/or Intermediate-Level Radioactive Waste (L&ILRW) Sites**
- ● Uranium Processing & Fuel Fabrication
- ▬ Deep Geological Repository (DGR)
- ♨ Incinerator

* Number in brackets ( ) indicates the number of reactors **These wastes are also stored at all nuclear power reactor sites

- Original production by Irene Koch, 1990-91, Nuclear Awareness Project.
- Updated by Anna Tilman (annatilman@sympatico.ca) and John Jackson (jjackson@web.ca), May 1, 2013.
- Funded by the Citizens' Clearinghouse on Waste Management and Great Lakes United.

OEP #9

Group work okay, Due 11/27/23 at beginning of class

(Don't be afraid to "Google" for reasonable assumptions; just provide references!)

Davis Besse Plant “Near” Accident

Rather than a movie, we have a real life open-ended problem, which illustrates the challenge of corrosion. The Boric acid primary coolant leaked out through a faulty control rod drive shaft seal, then evaporated leaving concentrated boric acid on the carbon steel reactor pressure vessel. Over the course of 6 years (3 fuel cycles, the duration of inspection periods), this acid had completely eaten through the 6 inches of carbon steel, leaving only the 3/8” of the stainless steel liner left. Since the pressure in a reactor pressure vessel is 2250 psi, this could have easily resulted in a catastrophic accident had the shutdown and inspection been delayed by only a couple of weeks. Considering the significance of this near-miss situation, I want you to calculate a couple of things: 1) what was the corrosion penetration rate for this accident? 2) What concentration does the boric acid need to reach in order for this corrosion to be spontaneous?

THE COST OF CORROSION

- Corrosion:
  -- the destructive electrochemical attack of a material.
  -- Ex: Rusting of automobiles and other equipment

© EHStock/iStockphoto

- Cost:
  -- 4 to 5% of the Gross National Product (GNP)*
  -- in the U.S. this amounts to just over $400 billion/yr**

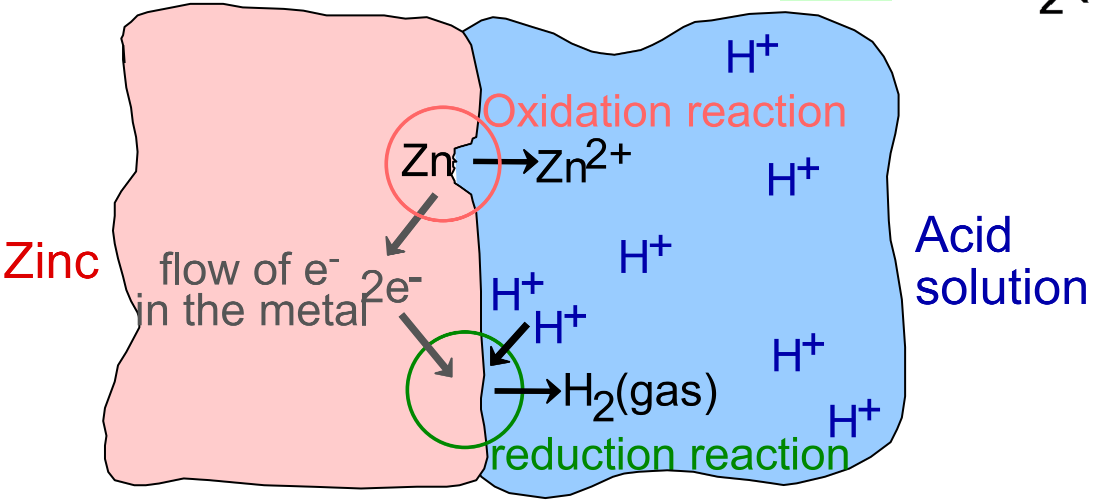
* H.H. Uhlig and W.R. Revie, *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, 3rd ed., John Wiley and Sons, Inc., 1985.

**Economic Report of the President (1998).

ELECTROCHEMICAL CORROSION

Ex: consider the corrosion of zinc in an acid solution

- Two reactions are necessary:
  - -- oxidation reaction: $Zn \rightarrow Zn^{2+} + 2e^-$
  - -- reduction reaction: $2H^+ + 2e^- \rightarrow H_2(gas)$



- Other reduction reactions in solutions with dissolved oxygen:
  - -- acidic solution
  - -- neutral or basic solution

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$$

CORROSION REQUIREMENTS

Corrosion Occurs with 4 basic components:

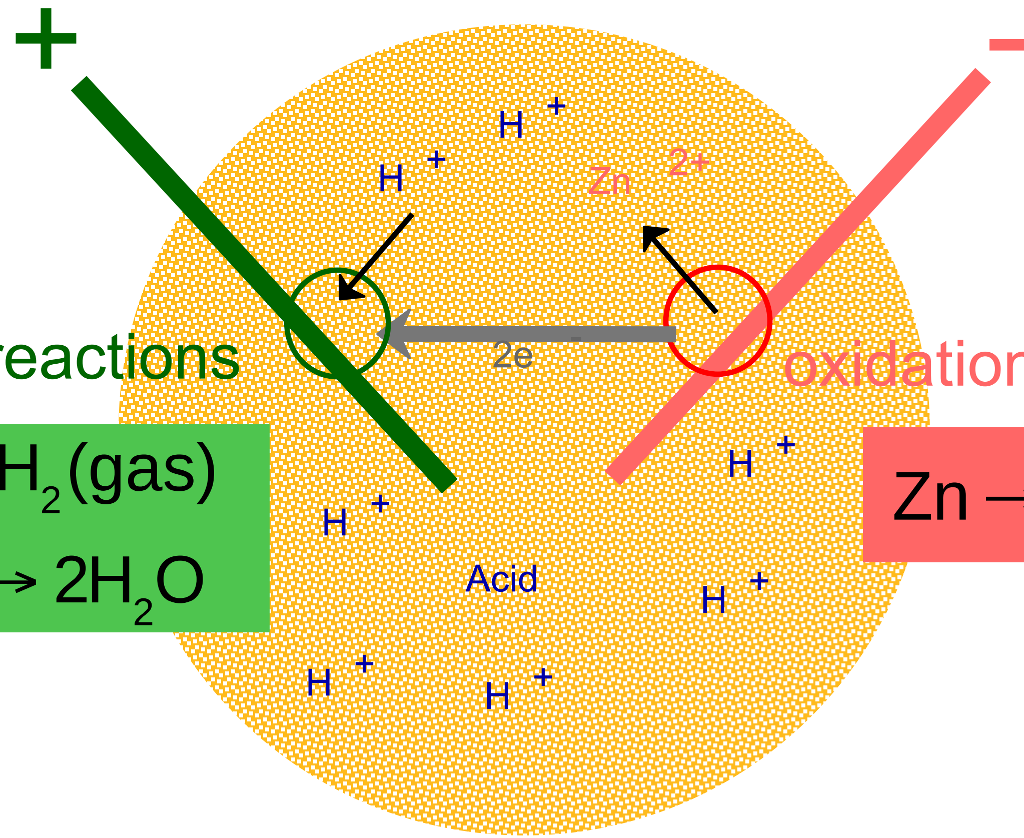
- Anode
- Cathode
- Electron Conductor (metal contact)
- Ion Conductor (aqueous environment)

- Is this always true?

CORROSION IN A GRAPEFRUIT

Cu (cathode)

Zn (anode)



reduction reactions

$$2H^+ + 2e^- \rightarrow H_2(gas)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

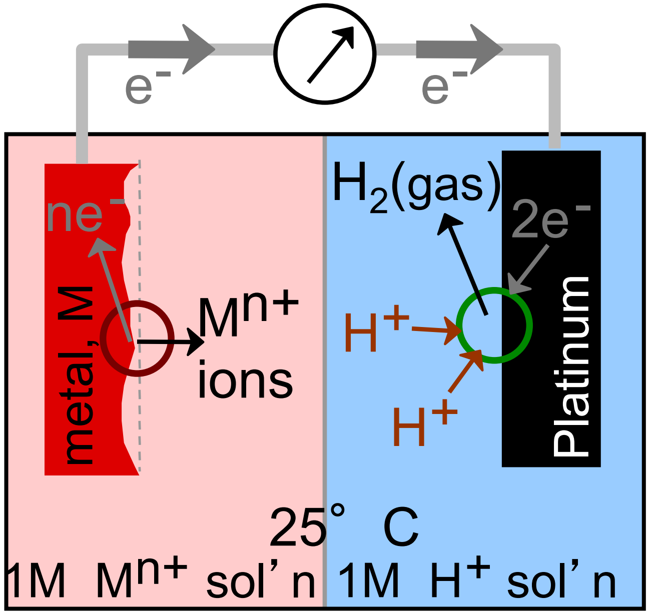
oxidation reaction

$$Zn \rightarrow Zn^{2+} + 2e^-$$

STANDARD HYDROGEN ELECTRODE

- Two outcomes:

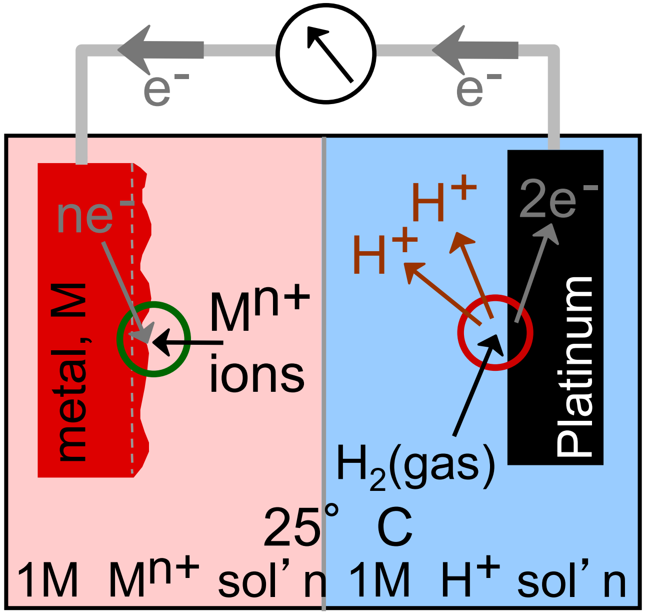
-- Corrosion



-- Metal is the anode (-)

$$V^o_{metal} < 0 \quad \text{(relative to Pt)}$$

-- Electrodeposition



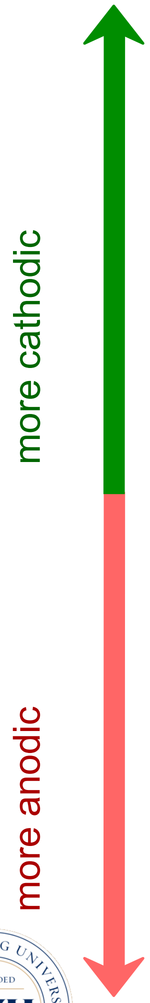
-- Metal is the cathode (+)

$$V^o_{metal} > 0 \quad \text{(relative to Pt)}$$

Standard Electrode Potential

STANDARD EMF SERIES

- EMF series



metal	V^o_{metal}
Au	+1.420 V
Cu	+0.340
Pb	- 0.126
Sn	- 0.136
Ni	- 0.250
Co	- 0.277
Cd	- 0.403
Fe	- 0.440
Cr	- 0.744
Zn	- 0.763
Al	- 1.662
Mg	- 2.363
Na	- 2.714
K	- 2.924

$\Delta V^o =$ 0.153V

Data based on Table 17.1, *Callister 10e*.

- Metal with smaller V^o_{metal} corrodes.
- Ex: Cd-Ni cell

$V^o_{Cd} < V^o_{Ni}$ ∴ Cd corrodes

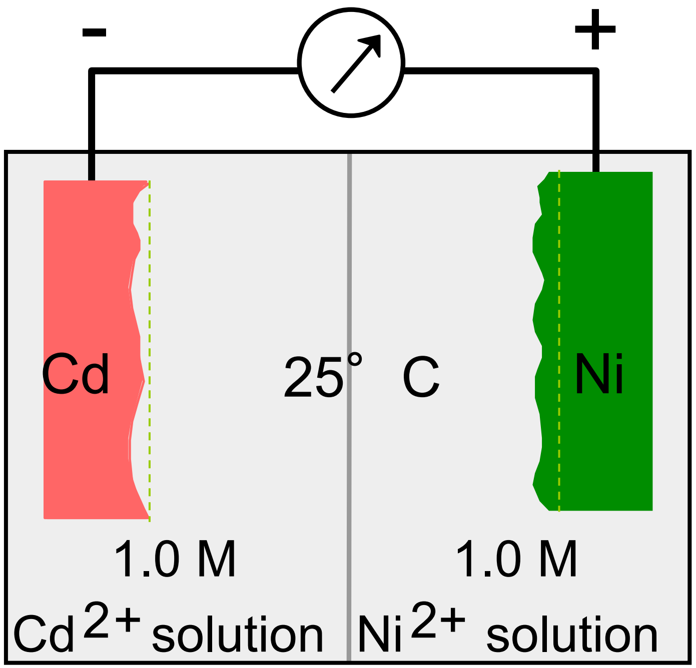


Fig. 17.2, *Callister & Rethwisch 10e*.

Nernst/Gibbs Equations

- Gibbs energy is of interest here:
  - Negative Gibbs – spontaneous reaction
  - $\Delta G = -nF\Delta E°$
- How do we find Δ E °?
  - From EMF Charts?
    - Only ideal conditions at 1M concentrations
  - From Other Charts?
    - May not apply
- Nernst Equation

$$\Delta E° = \Delta V = (V_2^o - V_1^o) - \frac{RT}{nF} ln \frac{[a_1]}{[a_2]}$$

Activities

$a_i = C_i/C_i^o$ for species in solution,

where C_i^o = 1M at standard state

$a_i = P_i/P_i^o$ for gas phase species

where P_i^o = 1 atm at standard state

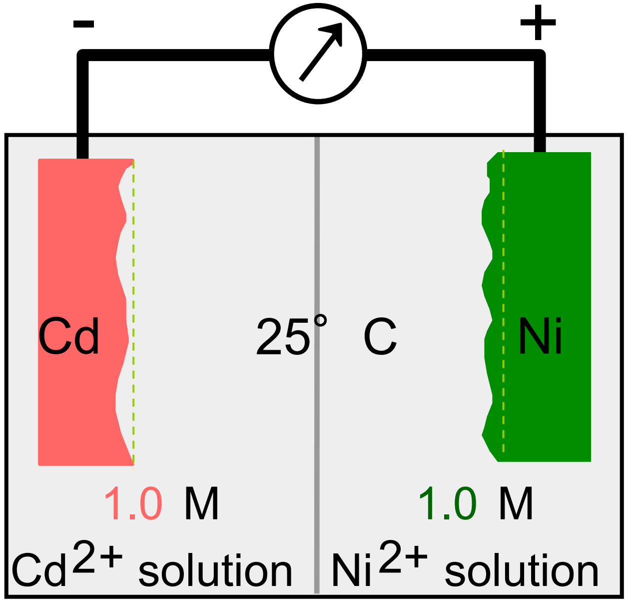
$a_i = 1$ for solids

$$\Delta E^\circ = \Delta V = (V_2^o - V_1^o) - \frac{RT}{nF} ln \frac{[M_1^{n+}]}{[M_2^{n+}]}$$

EFFECT OF SOLUTION CONCENTRATION AND TEMPERATURE

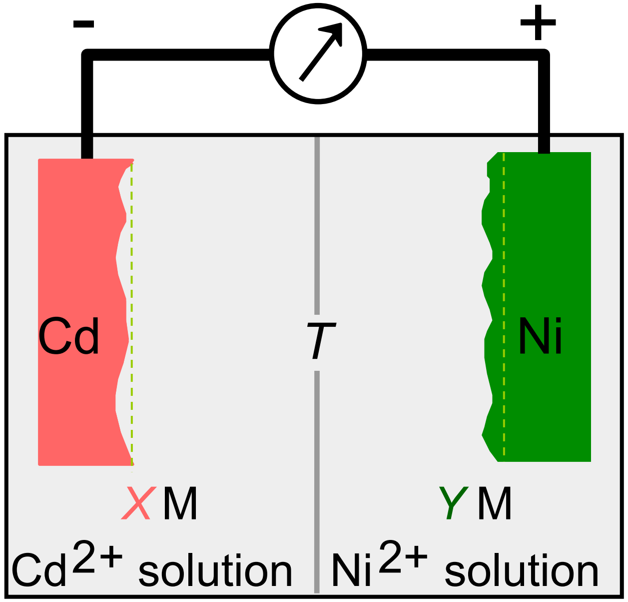
- Ex: Cd-Ni cell with standard 1 M solutions

$$V^{o}_{Ni} - V^{o}_{Cd} = 0.153\text{ V}$$



- Ex: Cd-Ni cell with non-standard solutions

$$V_{Ni} - V_{Cd} = V^{o}_{Ni} - V^{o}_{Cd} - \frac{RT}{nF}\ln\frac{X}{Y}$$



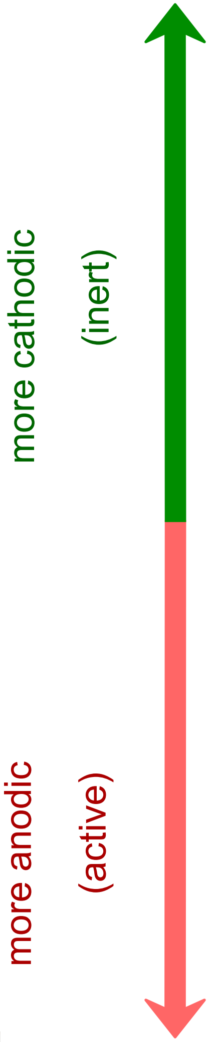
n = #e- per unit oxid/red reaction (= 2 here)

F = Faraday's constant = 96,500 C/mol.

- Reduce V_{Ni} - V_{Cd} by
  - -- increasing *X*
  - -- decreasing *Y*
  - -- increasing *T*

GALVANIC SERIES

- Ranking of the reactivity of metals/alloys in seawater



Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel (passive)
Nickel 200 (passive)
Copper
Nickel 200 (active)
Tin
Lead
316 Stainless Steel (active)
Cast Iron/Low-carbon Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

Table 17.2, *Callister & Rethwisch 9e*.
Source is Davis, Joseph R. (senior editor), ASM Handbook, Corrosion, Volume 13, ASM International, 1987, p. 83, Table 2.

Corrosion Penetration Rate

- Rate at which corrosion penetrates into a metal object

- Complex function of
  - – Mass transport
  - – Shape
  - – Reaction Rate
  - – Corrosion Method
- Simple Estimate:

$$CPR = \frac{KW}{\rho A t}$$

Example

Is corrosion of Zn Predicted thermodynamically in a dilute acid (pH=2) solution in the absence of air at 25° C?

Assume the solution already contains 0.1 ppm zinc, and the hydrogen gas concentration is maximally equal to half the hydrogen ion concentration.

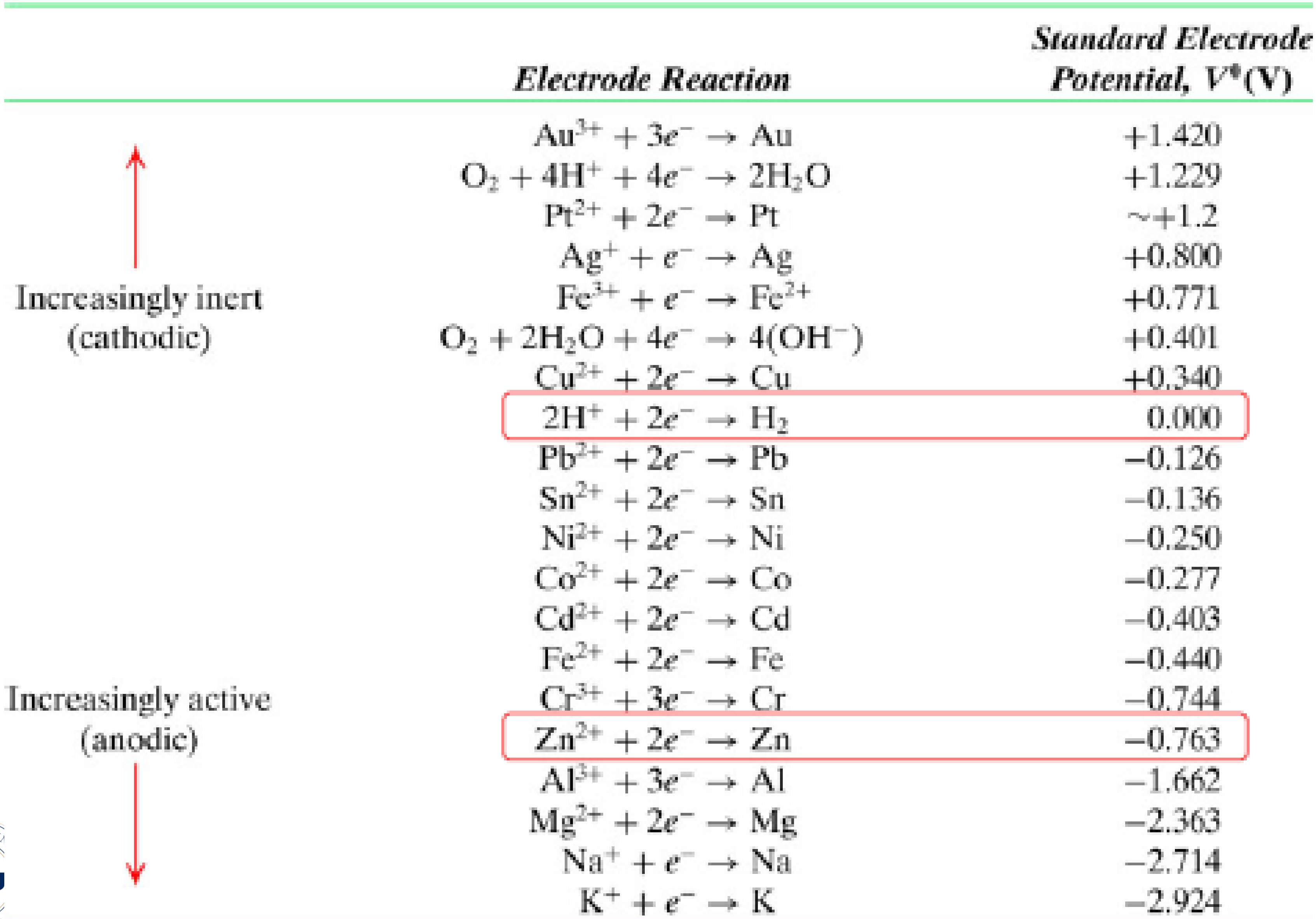
Data: T = 25° C, $C_{H+} = 1x10^{-2}$ M, $C_{H2} = 1/2\ C_{H+}$,

$P_{H2} = 0.122$atm, $C_{Zn2+} = 1x10^{-7}$ M

$$Zn \rightarrow Zn^{2+} + 2e\text{-}$$

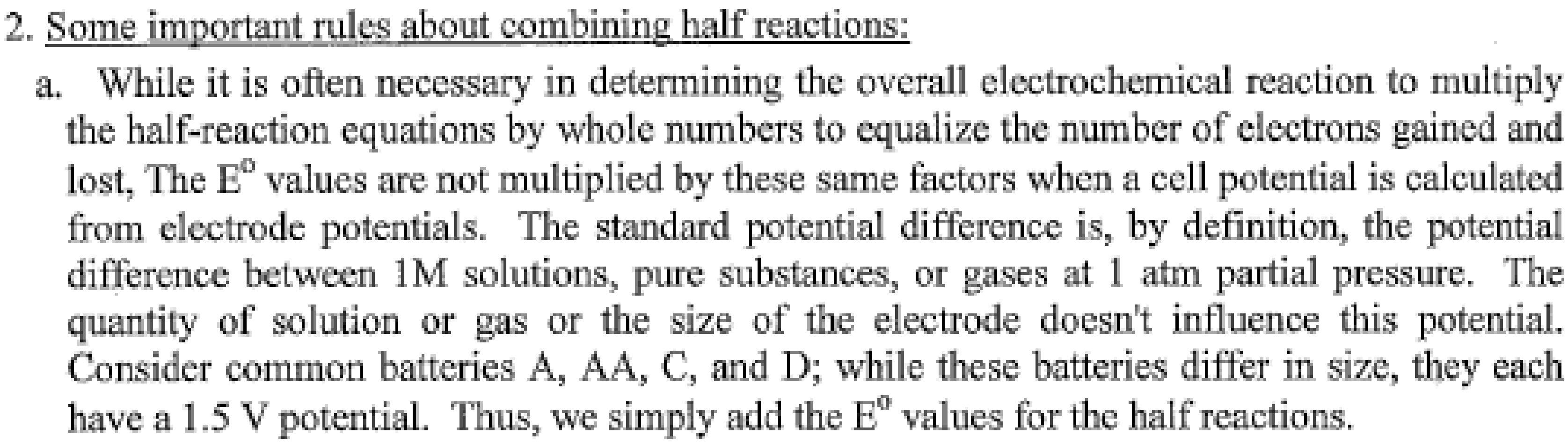
$$2H^{+} + 2e^{-} \rightarrow H_2$$

$$V_{Zn} = V_{Zn}^{o} - \frac{RT}{nF}\ln\left(\frac{a_{Zn}}{a_{Zn^{+}}}\right) \quad V_H = V_H^{o} - \frac{RT}{nF}\ln\left(\frac{a_{H_2}}{\left(a_{H^{+}}\right)^{2}}\right)$$



	Electrode Reaction	*Standard Electrode Potential, V°(V)*
↑	$Au^{3+} + 3e^- \rightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \rightarrow Pt$	~+1.2
	$Ag^+ + e^- \rightarrow Ag$	+0.800
Increasingly inert (cathodic)	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.340
	$2H^+ + 2e^- \rightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \rightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440
Increasingly active (anodic)	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744
	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \rightarrow Al$	−1.662
	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.363
	$Na^+ + e^- \rightarrow Na$	−2.714
↓	$K^+ + e^- \rightarrow K$	−2.924

From ST3



2. Some important rules about combining half reactions:

a. While it is often necessary in determining the overall electrochemical reaction to multiply the half-reaction equations by whole numbers to equalize the number of electrons gained and lost, The E^o values are not multiplied by these same factors when a cell potential is calculated from electrode potentials. The standard potential difference is, by definition, the potential difference between 1M solutions, pure substances, or gases at 1 atm partial pressure. The quantity of solution or gas or the size of the electrode doesn't influence this potential. Consider common batteries A, AA, C, and D; while these batteries differ in size, they each have a 1.5 V potential. Thus, we simply add the E^o values for the half reactions.

Example

Is corrosion of Zn Predicted thermodynamically in a dilute acid (pH=2) solution in the absence of air at 25° C?

Assume the solution already contains 0.1 ppm zinc, and the hydrogen gas concentration is maximally equal to half the hydrogen ion concentration.

Data: T = 25° C, $C_{H+} = 1x10^{-2}$ M, $C_{H2} = 1/2\ C_{H+}$,
$P_{H2} = 0.122$atm, $C_{Zn2+} = 1x10^{-7}$ M

$$Zn \rightarrow Zn^{2+} + 2e\text{-}$$

$$\underline{2H^{+} + 2e^{-} \rightarrow H_2}$$

$$V_{Zn} = V_{Zn}^{o} - \frac{RT}{nF}\ln\left(\frac{a_{Zn}}{a_{Zn^{+}}}\right) \quad V_H = V_H^{o} - \frac{RT}{nF}\ln\left(\frac{a_{H_2}}{\left(a_{H^{+}}\right)^2}\right)$$

$E° = 0.879$V $\Delta G =$-nF$E°$ $\Delta G = -170kJ/mol$