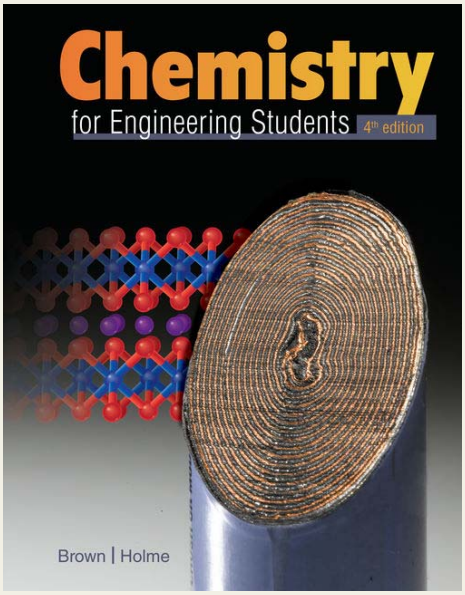
HW Assignments

- **Exam 3** will be on 30th November (Friday)
  - ✓ Covers the Chapters 8, 9, 10 and 13
  - ✓ 25 MCQs
  - ✓ I will post a practice exam for Exam 3 during the break
- Chapter 10 HW Due 26th November at 11:55 pm
- Chapter 13 HW will assign today
- Quiz 5 (Chapters 9, 10) will post on 26th (Monday) and due Wednesday before midnight



Chapter 13

Electrochemistry

Edited by Dr. Katugampola

Corrosion

- Corrosion is the degradation of metals by chemical reactions
  - ✓ Uniform corrosion occurs evenly over a large portion of the surface area of a metal
  - ✓ Galvanic corrosion occurs when two different metals contact each other in the presence of an electrolyte
  - ✓ Crevice corrosion occurs in machines

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Oxidation–Reduction Reactions and Galvanic Cells

- Reactions involving the transfer of electrons are known as oxidation–reduction or redox reactions
  - ✓ Oxidation is the loss of electrons from some chemical species

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

  - ✓ Reduction is the gain of electrons by some chemical species

$$Ag^+(aq) + 1e^- \longrightarrow Ag(s)$$

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Oxidation–Reduction and Half-Reactions

- When a clean copper wire is placed into a colorless solution of silver nitrate, it is quickly apparent that a chemical reaction occurs: Crystals of silver metal form on the copper wire, and the solution turns blue

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- The solution's blue color is indicative of Cu^{2+} ions in solution
  - ✓ Cu^{2+} is formed when a copper atom loses two electrons
  - ✓ The copper metal is oxidized

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

- The crystals formed on the surface of the copper wire are silver metal
  - ✓ Metallic silver is formed when a silver cation gains an electron
  - ✓ The silver in the solution is reduced

$$Ag^+(aq) + 1e^- \longrightarrow Ag(s)$$

Two Half-Reactions,

Oxidation: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Reduction: $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$

- The electron transfer must be balanced, so the reduction half-reaction is multiplied by 2

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$$

Oxidation–Reduction and Half-Reactions
(continued)

- Add the two half-reactions together and the electrons will cancel out, leaving the net ionic equation for the redox reaction

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$$
$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

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Oxidation–Reduction and Half-Reactions
(continued)

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

- Reducing agent: The species undergoing oxidation
  - ✓ The Cu was oxidized and is the reducing agent
- Oxidizing agent: The species undergoing reduction
  - ✓ The Ag^{+} was reduced and is the oxidizing agent

- Writing the molecular equation by adding the spectator ions (NO_3^- in this case)

$$2\,AgNO_3(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu(NO_3)_2(aq)$$

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Problem

13.5 For the following oxidation-reduction reactions, identify the half reactions and label them as oxidation or reduction.

(a) $Cu(s) + Ni^{2+}(aq) \rightarrow Ni(s) + Cu^{2+}(aq)$

(b) $2Fe^{3+}(aq) + 3Ba(s) \rightarrow 3Ba^{2+}(aq) + 2Fe(s)$

Answer:

(a) **oxidation:** $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
reduction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

(b) **oxidation:** $Ba(s) \rightarrow Ba^{2+}(aq) + 2e^-$
reduction: $Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$

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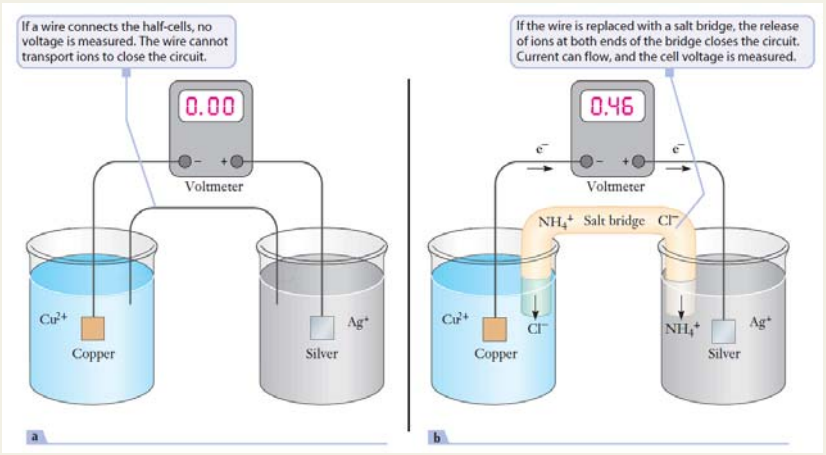
Galvanic Cell



- The salt bridge contains a strong electrolyte that allows either cations or anions to migrate into the solution where they are needed to maintain charge neutrality. Also, it closes the circuit.

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Terminology for Galvanic Cells

- Electrodes
  - ✓ The electrode where oxidation occurs is the anode
  - ✓ The electrode where reduction occurs is the cathode
- Cell notation: A shorthand notation for representing the specific chemistry of an electrochemical cell
  - Cell notation lists the metals and ions involved in the reaction
  - A single vertical line, |, denotes a phase boundary
  - A double vertical line, ||, denotes a salt bridge
  - The anode is written on the left, the cathode on the right

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Terminology for Galvanic Cells (continued)

- General form of cell notation

  anode | anode electrolyte || cathode electrolyte | cathode

- For the previous example of copper and silver

  $$Cu(s)\,|\,Cu^{2+}(aq)\ (1\ M)\,||\,Ag^{+}(aq)\ (1\ M)\,|\,Ag$$

  - The electrolyte concentration is also given

- An electrochemical cell is at its standard state when the electrolyte concentrations are 1 M
- For half-cells that generate or consume a gas, a partial pressure of 1 atm is required for the standard state

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- Maximum work that can be obtained from an electrochemical cell

  $$w_{max} = qE$$

  ✓ q is the charge
  ✓ E is the cell potential or electromotive force (EMF)

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Problem

In a classroom demonstration of the reaction between copper metal and silver ions, silver plates out on the copper wire. Which is the oxidizing agent in this reaction?

- Silver metal
- Silver ions
- Copper metal
- Copper ions

Answer: Silver ions

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Problem

In a galvanic cell, where does oxidation occur?

- In the electrolyte
- At the anode
- At the cathode
- In the salt bridge

Answer: At the anode

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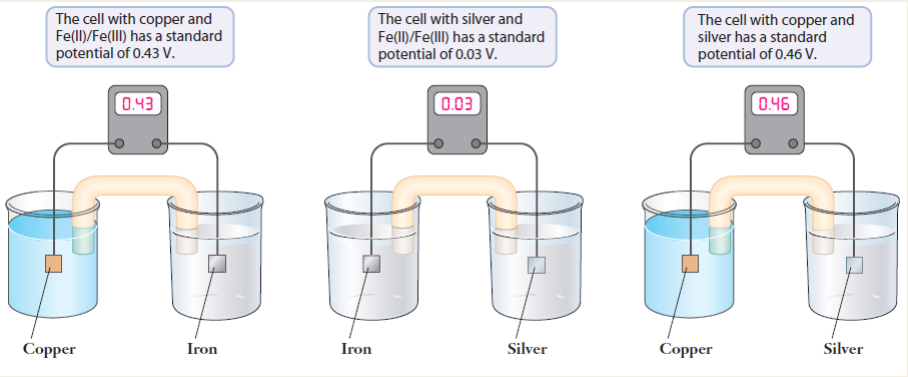
Measuring cell potential



- Measurement of standard cell voltages for various combinations of the same half-reactions suggests that a characteristic potential can be associated with a particular half-reaction

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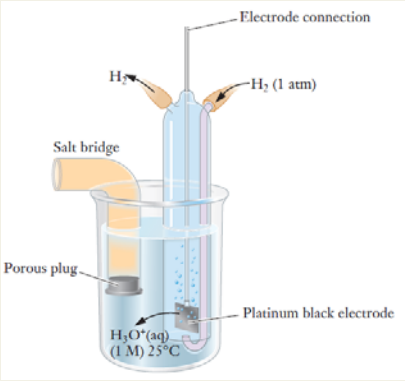
Standard component in cell potential measurements

- Standard hydrogen electrode or SHE
- The cell is constructed using a platinum wire or foil as the electrode
  - The electrode is immersed in a 1 M HCl solution, and H_2 gas is bubbled over the electrode at a pressure of 1 atm
- chosen as the reference point for the scale of standard reduction potentials and assigned a potential of exactly zero volts



Half-reaction,

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$

Half-cell notation,

$$Pt(s)\,|\,H_2(g, 1\,atm)\,|\,H^+(1\,M)$$

Measuring Cell Potential

- For some galvanic cells, the SHE acts as the anode, and for other galvanic cells, the SHE acts as the cathode (anode is the site of oxidation and cathode is the site of reduction)

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Standard Reduction Potentials

Here we list standard reduction potentials for several of the half-reactions involved in the cells discussed in the text. A more extensive table of potentials appears in Appendix I.

Half-Reaction	Standard Reduction Potential (V)
$Zn^{2+} + 2\ e^- \rightarrow Zn$	−0.763
$Fe^{2+} + 2\ e^- \rightarrow Fe$	−0.44
$2\ H^+ + 2\ e^- \rightarrow H_2$	0.000
$Cu^{2+} + 2\ e^- \rightarrow Cu$	+0.337
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$Ag^+ + e^- \rightarrow Ag$	+0.7994

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Standard Reduction Potentials (continued 1)

- ✓ A large, positive value for the standard reduction potential implies the substance is reduced readily and is a good oxidizing agent
- ✓ A large, negative value for the standard reduction potential implies the substance is oxidized readily and is a good reducing agent

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Standard Reduction Potentials (continued 2)

- For a galvanic cell,
  - ✓ the half-reaction with the **more positive reduction potential** will be the cathode
  - ✓ The half-reaction with the **more negative reduction potential** will be the anode
- The standard cell potential for any pair of half-reactions (E°_{cell})

$$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$$

- ✓ E°_{red} is the standard reduction potential of the cathode
- ✓ E°_{ox} is the standard reduction potential of the anode

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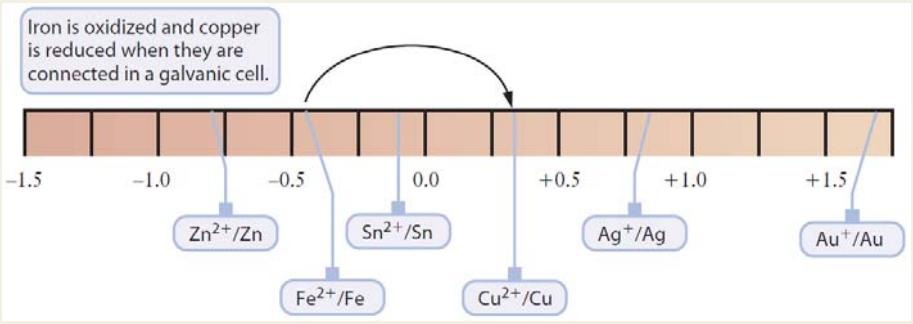
Standard Reduction Potentials (continued 3)



- Arranging standard reduction potentials horizontally enables easy identification of the anode and cathode in a galvanic cell
- The reduction potential farthest to the left is the anode
- The reduction potential farthest to the right is the cathode

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Example Problem

1) Using standard reduction potentials, identify the anode and the cathode and determine the cell potential for a galvanic cell composed of copper and iron. Assume standard conditions

$$\mathrm{Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)} \qquad E^\circ = -0.44\ \mathrm{V}$$
$$\mathrm{Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)} \qquad E^\circ = 0.337\ \mathrm{V}$$

Iron must be oxidized,

$$\mathrm{Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)} \qquad E^\circ_{\mathrm{cell}} = ?$$

By using, $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{red}} - E^\circ_{\mathrm{ox}}$

$$E^\circ_{\mathrm{cell}} = 0.337\ \mathrm{V} - (-0.44\ \mathrm{V}) = 0.78\ \mathrm{V}$$

Copper is the cathode, because it is reduced
Iron is the anode, because it is oxidized

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