Section 17.3
Electrodes and Cell Potentials

Michael Stogsdill

Mott Community College

Learning Objectives

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Measuring Potential

- The activity of a redox reaction can be quantified by measuring a relatively easy property called **potential** or **voltage**.
  - It is a measure of energy accompanying the transfer of charge.
- Potentials are measured in the volt unit
  - Defined as one joule of energy per one coulomb of charge, V = J/C.
- A potential reflects the driving force for the transfer of electrons between redox reactants.

Cell Potentials

- The transfer of electrons requires two half cell reactions.
  - An oxidation reaction at the anode donating electrons
  - A reduction reaction at the cathode accepting electrons
  - *Electrons flow from the anode to the cathode*
- The difference in potential between two half-cells that may be measured
  - These measured potentials are called **cell potentials, E_{cell}.**

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

Standard Cell Potentials

- **$E_{cathode}$** and **E_{anode}** are the potentials of two different half-cells functioning as specified in the subscripts.
- The **standard cell potential, E°_{cell}**, is a cell potential measured when both half-cells are under standard-state conditions
  - 1 M concentrations
  - 1 bar pressure
  - 298 K

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

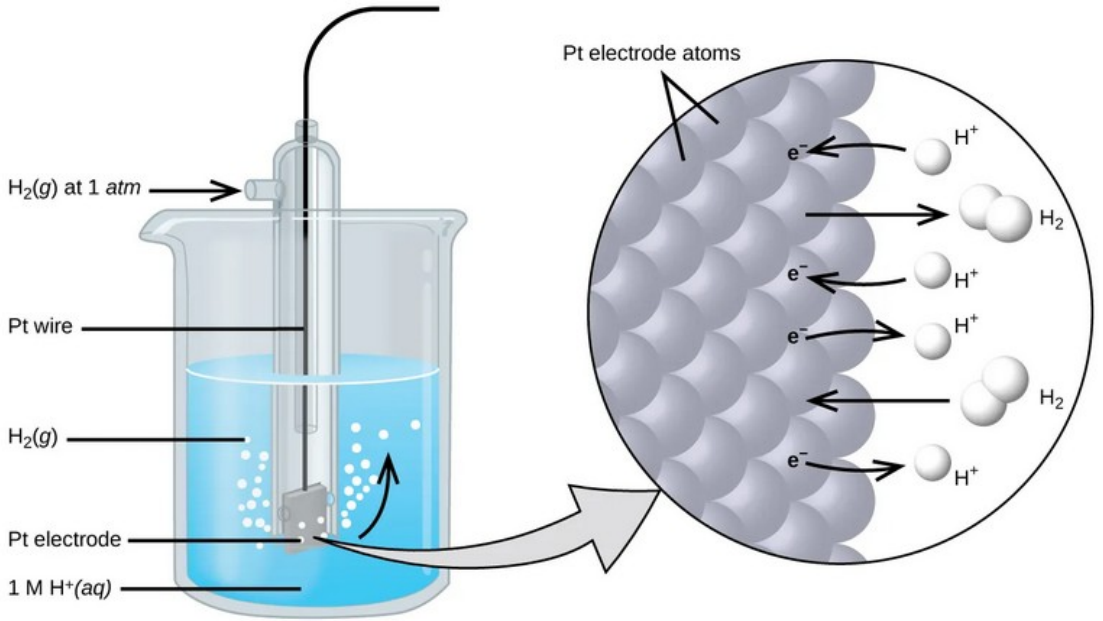
SHE

- To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements
  - Assigning it a potential of exactly 0 V.
- This half-cell is the **standard hydrogen electrode (SHE)** and it is based on half-reaction below:

$$2\mathrm{H}^+(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{H}_2(g)$$

SHE

- A typical SHE contains an inert platinum electrode immersed in precisely 1 M aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K.



Measuring Electrode Potential

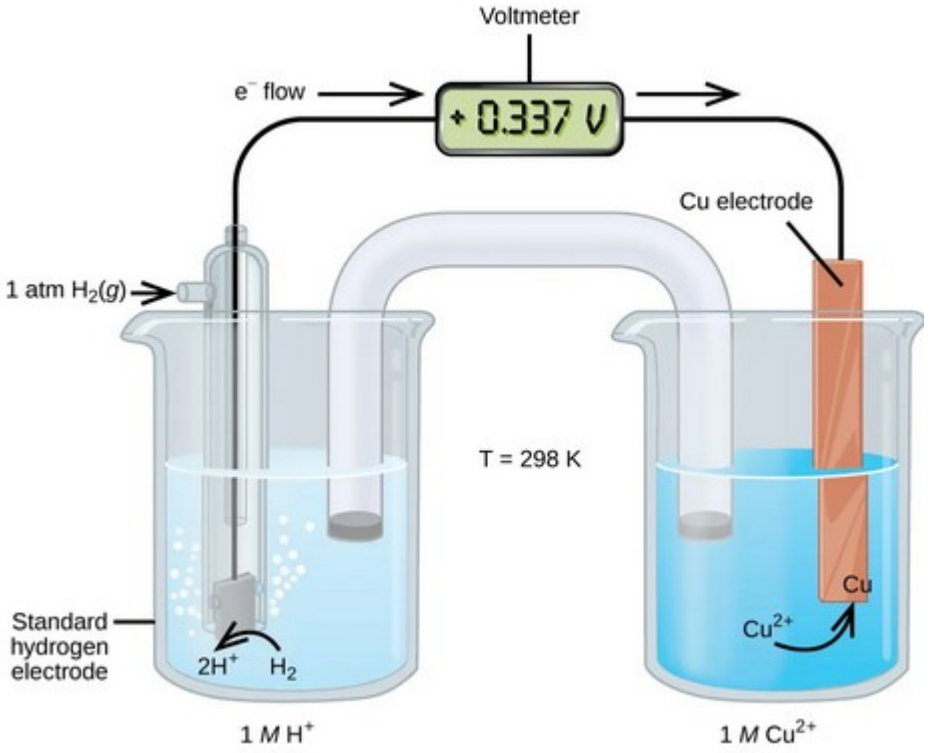
- The **electrode potential (E_X)** for a half-cell *X* is defined as the potential measured for a cell comprised of *X* acting as cathode and the SHE acting as anode:

$$E_{cell} = E_X - E_{SHE}$$
$$E_{SHE} = 0\ V\ (defined)$$
$$E_{cell} = E_X$$

- When the half-cell *X* is under standard-state conditions, its potential is the **standard electrode potential, E°_X.**

Standard Reduction Potentials

- Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called **standard reduction potentials.**
- Tabulations of E° values for half-cells measured against a SHE are available in Appendix L.



$$E^\circ_{cell} = E^\circ_{Cu} = +0.337\ V$$

Cell Potential and Spontaneity

- *Spontaneous processes have positive cell potential, $E^{\circ}_{cell} > 0$, while the nonspontaneous process have negative cell potential, $E^{\circ}_{cell} < 0$.*
- Since electrode potentials are for reduction processes, an increased value of E° corresponds to an increased driving force behind the reduction of the species
  - Stronger oxidants (oxidizing agents) have greater standard electrode potential, E°.
- Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE.

Reversible Reactions

- If a process is spontaneous in one direction, it is non-spontaneous in the opposite direction.
- The potential of a cell reaction shows a consequential relationship in its arithmetic sign.

$$\mathrm{Cu}(s) + \mathrm{Pb}^{2+}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{Pb}(s) \quad E^{\circ}_{forward} = -0.47\,\mathrm{V}\ \text{(negative, non-spontaneous)}$$

$$\mathrm{Pb}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Pb}^{2+}(aq) + \mathrm{Cu}(s) \quad E^{\circ}_{forward} = +0.47\,\mathrm{V}\ \text{(positive, spontaneous)}$$

  - Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions.