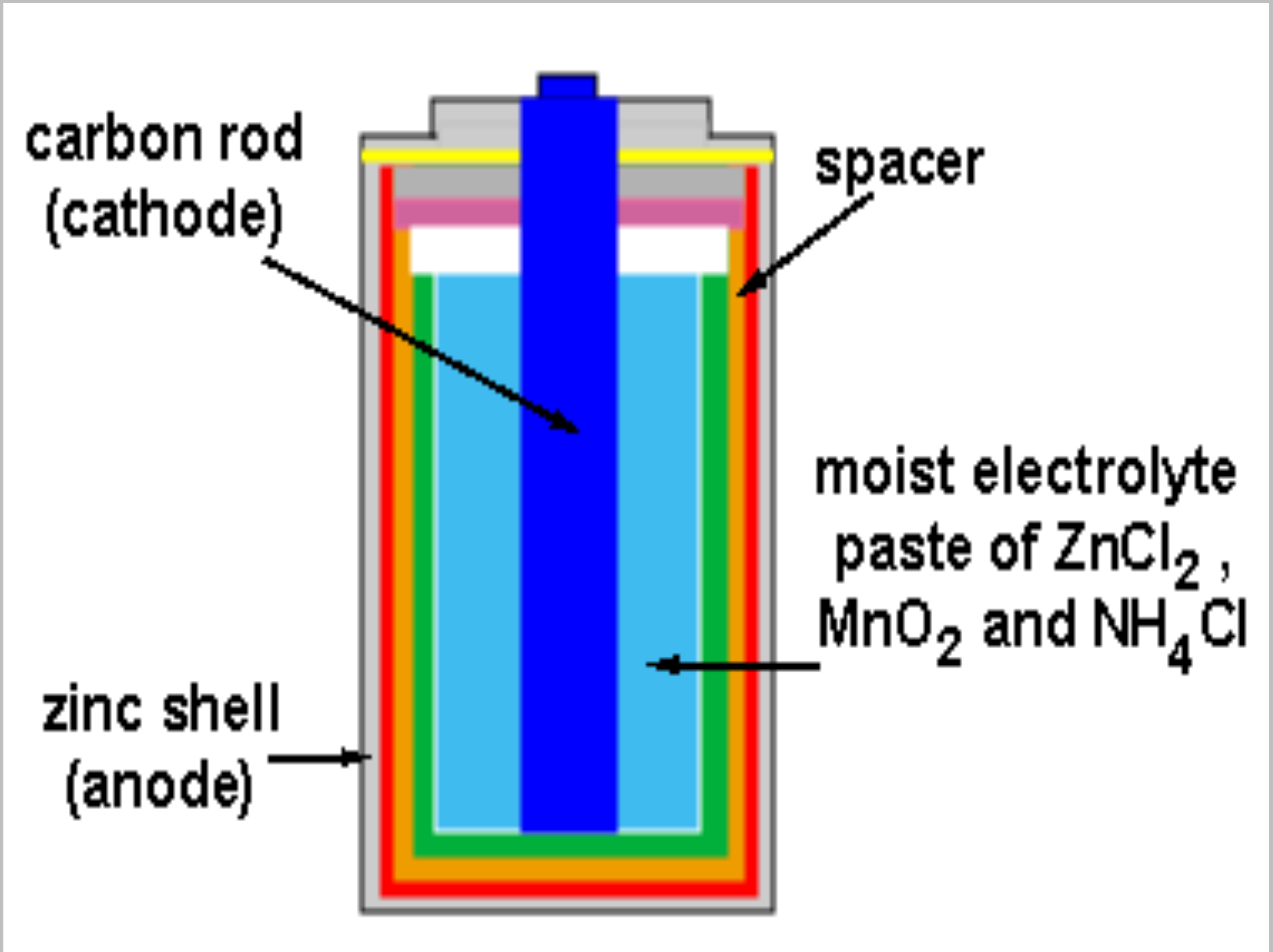
Electrochemistry - Cell Potential

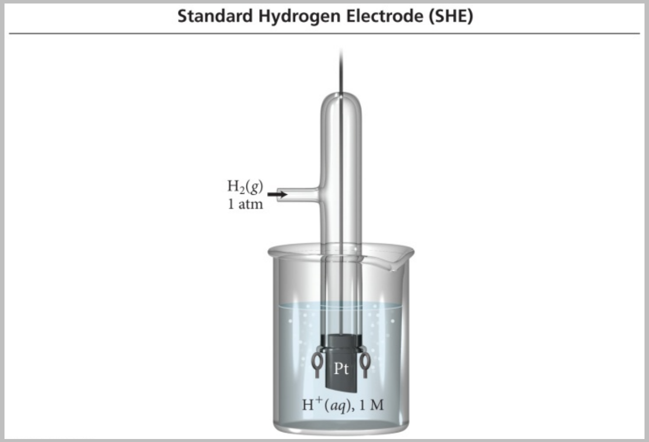


Cell Potential

- The difference in potential energy between the anode and the cathode in a voltaic cell is called the **cell potential**.
- The cell potential depends on the relative ease with which the oxidizing agent is reduced at the cathode and the reducing agent is oxidized at the anode.
- The cell potential under standard conditions is called the **standard emf, E°_{cell}**.
  - 25 °C, 1 atm for gases, 1 M concentration of solution
  - Sum of the cell potentials for the half-reactions

Standard Reduction Potential

- We cannot measure the absolute tendency of a half-reaction, we can only measure it relative to another half-reaction.
- We select as a standard half-reaction the reduction of H^+ to H_2 under standard conditions, which we assign a potential difference = 0 v.
  - **Standard hydrogen electrode, SHE**



Half-Cell Potentials

- SHE reduction potential is defined to be exactly 0 V.
- Standard reduction potentials compare the tendency for a particular reduction half-reaction to occur relative to the reduction of H^+ to H_2.
  - Under standard conditions
- Half-reactions with a stronger tendency toward reduction than the SHE have a positive value for $E°_{red}$.
- Half-reactions with a stronger tendency toward oxidation than the SHE have a negative value for $E°_{red}$.
- For an oxidation half-reaction, $E°_{oxidation} = -E°_{reduction}$.

TABLE 18.1 Standard Electrode Potentials at 25 °C

	Reduction Half-Reaction		$E°$ (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O(l)$	1.69	
	$MnO_4^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow MnO_2(s) + 2H_2O(l)$	1.68	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	1.50	
	$PbO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	1.46	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.21	
	$IO_3^-(aq) + 6H^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3H_2O(l)$	1.20	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$VO_2^+(aq) + 2H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
	$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O(l)$	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20	
	$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$\boxed{2H^+(aq) + 2e^-}$	$\boxed{\longrightarrow H_2(g)}$	$\boxed{0}$	
	$Fe^{3+}(aq) + 3e^-$	$\longrightarrow Fe(s)$	−0.036	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.14	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.23	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50	
	$Cr^{3+}(aq) + 3e^-$	$\longrightarrow Cr(s)$	−0.73	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Mn^{2+}(aq) + 2e^-$	$\longrightarrow Mn(s)$	−1.18	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
	$Ca^{2+}(aq) + 2e^-$	$\longrightarrow Ca(s)$	−2.76	
	$Ba^{2+}(aq) + 2e^-$	$\longrightarrow Ba(s)$	−2.90	
Weaker oxidizing agent	$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92	Stronger reducing agent
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

Calculating Cell Potentials under Standard Conditions

- $E°_{\text{cell}} = E°_{\text{oxidation}} + E°_{\text{reduction}}$
- When adding $E°$ values for the half-cells, ***do not multiply*** the half-cell $E°$ values, even if you need to multiply the half-reactions to balance the equation.

Tendencies from the Table of Standard Reduction Potentials

- A redox reaction will be spontaneous when there is a strong tendency for the oxidizing agent to be reduced and the reducing agent to be oxidized.
  - Higher on the table of standard reduction potentials = stronger tendency for the reactant to be reduced
  - lower on the table of standard reduction potentials = stronger tendency for the product to be oxidized