

Electrochemistry

Cell Potential: Output of a Voltaic Cell

Free Energy and Electrical Work







Since the overall cell reaction involves the oxidation of zinc, we reverse the Zn reaction, and change the sign to get the cell potential:

$$\begin{array}{ccc} Zn_{(s)} & & \longrightarrow Zn^{2*}_{(aq)} + 2 \ e^- & & -E^o_{zinc}(-E^o_{anode}) & [oxidation] \\ Cu^{2*}_{(aq)} + 2e^- & & & Cu_{(s)} & & & P^o_{copper}(-E^o_{cathode}) & [reduction] \end{array}$$
The overall redox reaction is the sum of these two:

 $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

 $E^{o}_{cell} = E^{o}_{copper} + (-E^{o}_{zinc}) = E^{o}_{copper} - E^{o}_{zinc}$

 $E^0_{\ cell} = E^o_{\ cathode} - E^o_{\ anode}$



| Standard Electrode (Half-Cell) Potential | s (298 K) |
|--|----------------|
| Halt-Reaction | $E^{\circ}(V)$ |
| $F_2(g) + 2e^- \Longrightarrow 2F^-(aq)$ | +2.87 |
| $O_3(g) + 2H^*(aq) + 2e^- = O_2(g) + H_2O(I)$ | +2.07 |
| $Co^{3+}(aq) + e^{-} = Co^{2+}(aq)$ | +1.82 |
| $H_2O_2(aq) + 2H'(aq) + 2e^- = 2H_2O(I)$ | +1.77 |
| $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \implies PbSO_4(s) + 2H_2O(l)$ | +1.70 |
| $Ce^{4+}(aq) + e^{-} \Longrightarrow Ce^{3+}(aq)$ | +1.61 |
| $MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} = Mn^{2+}(aq) + 4H_2O(I)$ | +1.51 |
| $Au^{3+}(aq) + 3e^{-} = Au(s)$ | +1.50 |
| $Cl_2(g) + 2e^- \Longrightarrow 2Cl^-(aq)$ | +1.36 |
| $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- = 2Cr^{3+}(aq) + 7H_2O(I)$ | +1.33 |
| $MnO_2(s) + 4H^+(aq) + 2e^- \implies Mn^{2+}(aq) + 2H_2O(I)$ | +1.23 |
| $O_2(g) + 4H^+(aq) + 4e^- = 2H_2O(l)$ | +1.23 |
| Br ₂ (/) + 2e ⁻ === 2Br ⁻ (aq) | +1.07 |
| $NO_3^{-}(aq) + 4H^+(aq) + 3e^{-} \implies NO(g) + 2H_2O(I)$ | +0.96 |
| $2Hg^{2+}(aq) + 2e^{-} \implies Hg_{2}^{2+}(aq)$ | +0.92 |
| $Hg_2^{2+}(aq) + 2e^- = 2Hg(l)$ | +0.85 |
| $Ag^+(aq) + e^- \Longrightarrow Ag(s)$ | +0.80 |
| Fe ³⁺ (aq) + e ⁻ === Fe ²⁺ (aq) | +0.77 |
| $O_2(g) + 2H^+(aq) + 2e^- = H_2O_2(aq)$ | +0.68 |
| $MnO_{4}^{-}(aq) + 2H_{2}O(I) + 3e^{-} \implies MnO_{2}(s) + 4OH^{-}(aq)$ | +0.59 |
| $l_2(s) + 2e^- \Longrightarrow 2l^-(aq)$ | +0.53 |
| $O_2(g) + 2H_2O(l) + 4e^- = 4OH^-(aq)$ | +0.40 |
| $Cu^{2+}(aq) + 2e^{-} \Longrightarrow Cu(s)$ | +0.34 |
| $AgCl(s) + e^{-} \implies Ag(s) + Cl^{-}(aq)$ | +0.22 |

Using Standard Potentials: Cell EMF

Oxidizing and Reducing Agents

- The more positive E°_{red} the stronger the oxidizing agent on the left.
- The more negative E°_{red} the stronger the reducing agent on the right.
- A species on the higher to the left of the table of standard reduction potentials will spontaneously oxidize a species that is lower to the right in the table.
- That is, F₂ will oxidize H₂ or Li; Ni²⁺ will oxidize Al(s).
- Any species on the right will spontaneously reduce anything that is higher to the left in the series.









Relative Reactivities of Metals

Which metals can displace H_2 from acid?

The standard hydrogen half-reaction represents the reduction of $\rm H^{+}$ from acids to form molecular hydrogen, $\rm H_{2}:$

$$2 \text{ H}^+_{(aq)} + 2 \text{ e}^- \longrightarrow \text{H}_{2(g)} \qquad E^\circ = 0.00 \text{ V}$$

The metals Li through Pb lie below hydrogen in the electromotive series Table. These will give a positive E^{o}_{cell} when reducing H⁺.

For example iron:

$$Fe_{(aq)} + 2e^{-} \longrightarrow Fe^{2e_{(aq)}} + 2e^{-} - E^{o} = 0.44 \text{ V} \quad \text{[oxidation]}$$

$$2 \text{ H}^{+}_{(aq)} + 2e^{-} \longrightarrow \text{H}_{2(g)} \qquad E^{o} = 0.00 \text{ V} \quad \text{[reduction]}$$

$$Fo_{a} + 2 \text{ H}^{+} \qquad \text{H}_{a} + Eo^{2+} \qquad E^{o} = 0.44 \text{ V}$$

$$Fe_{(s)} + 2 H^{+}_{(aq)}$$
 $H_{2(g)} + Fe^{2+}_{(aq)}$ $E^{o}_{cell} = 0.44 V$

If $E_{\text{cell}}^{\text{o}}$ of metal A for the reduction of H⁺ is more positive than $E_{\text{cell}}^{\text{o}}$ of metal B, metal A is a stronger reducing agent than metal B. A is more reactive than B and is a more "active" metal.

QUESTION

A galvanic cell constructed by using the standard hydrogen electrode and a solid piece of cadmium in a solution of $CdCl_2$ produces a voltage of 0.40V. Hydrogen gas is produced in the reaction. Without consulting any tables, what would you predict for the voltage of the cadmium half reaction? What would be the reducing agent in the cell?

- 1. -0.40 V; the reducing agent would be H⁺
- 2. -0.40 V; the reducing agent would be Cd
- 3. 0.40 V; the reducing agent would be H+
- 4. 0.40 V; the reducing agent would be Cd

| Relative Reactivities of Metals | | | | | |
|---|---|--|--|--|--|
| Metals that cannot displace H_2 from acid. | | | | | |
| The coinage metals [Group 1B(11)]–C strong enough reducing agents to reduc | u, Ag, and Au–are not ce H ⁺ from acids: | | | | |
| $\begin{array}{c} Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^{-} \\ 2 H^{+}_{(aq)} + 2 e^{-} \longrightarrow H_{2 (g)} \end{array}$ | $-E^{\circ} = -0.80 \text{ V}$ $E^{\circ} = -0.00 \text{ V}$ | | | | |
| $2 \operatorname{Ag}_{(s)} + 2 \operatorname{H}^{+}_{(aq)} \rightarrow 2 \operatorname{Ag}^{+}_{(aq)} + \operatorname{H}_{2 (g)}$ | $E^{\rm o}_{\rm cell} = -0.80 {\rm V}$ | | | | |

If the E^{o}_{cell} is negative, the reaction is not spontaneous.

The higher the metal in the table, the more negative is its E°_{cell} . The lower its reducing strength, and the less active it is. Thus, gold is less active than silver, which is less active than copper.









| Comparison of Voltaic and Electrolytic Cells | | | | | | |
|--|-----|----------------|-----------|-----------|------|--|
| | | _ | Electrode | | | |
| Cell Type | ∆G | $E_{\rm cell}$ | Name | Process | Sign | |
| Voltaic | < 0 | >0 | Anode | Oxidation | - | |
| Voltaic | < 0 | >0 | Cathode | Reduction | + | |
| Electrolytic | >0 | < 0 | Anode | Oxidation | + | |
| Electrolytic | >0 | < 0 | Cathode | Reduction | - | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Spontaneity of Redox Reactions

EMF and Free-Energy Change

• We can show that

 $\Delta G = -nFE$

- ΔG is the change in free-energy, *n* is the number of moles of electrons transferred, *F* is Faraday's constant, and *E* is the emf of the cell.
- We define
- 1F = 96,500 C/mol = 96,500 J/Vmol
- C = Coulomb, the charge of 6.242×10^{18} electrons
- V = Volt (the electric potential)
- Since *n* and *F* are positive, if $\Delta G > 0$ then E < 0.

Effect of Concentration on Cell EMF

- A voltaic cell is functional until E = 0 at which point equilibrium has been reached.
- The point at which *E* = 0 is determined by the concentrations of the species involved in the redox reaction.

The Nernst Equation

• The Nernst equation relates emf to concentration using

 $\Delta G = \Delta G^{\circ} + RT \ln Q$

and noting that

$$-nFE = -nFE^{\circ} + RT \ln Q$$

Effect of Concentration on Cell EMF

The Nernst Equation

• This rearranges to give the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

• The Nernst equation can be simplified by collecting all the constants together using a temperature of 298 K:

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

- (Note that change from natural logarithm to base-10 log.)
- Remember that *n* is number of moles of electrons.

Calculating K and ΔG^{o} from E^{o}_{cell}

Problem: Lead can displace silver from solution:

$$Pb_{(s)} + 2 Ag^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + 2 Ag_{(s)}$$

Silver is a valuable by-product in the industrial extraction of lead from its ore. Calculate *K* and ΔG° at 25°C for this reaction.

First calculate E^{o}_{cell} and then substitute the value to find K and ΔG^{o} .

















QUESTION Cells in which both compartments of the galvanic cell contain

Certs in which both comparison the garvanic cert contain the same ion are called <u>concentration cells</u>. If such a cell were constructed with the $[Ag^*]$ in one cell at 0.050 M and the other at .0050 M, what would be the predicted voltage at 25°C?

 E° for Ag⁺ + $e^- \rightarrow$ Ag (s) = 0.80 V

1. 0.0591 V

2. 0.94 V

3. 0.66 V

4. I'm not sure.





