Chapter 17 Part 4

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E_{cell} and Spontaneity

- Galvanic cells (also called voltaic cells) are electrochemical cells in which spontaneous redox reactions produce electrical energy
- A redox reaction is spontaneous when it's cell potential (E_{cell}) is a positive value

Predicting Spontaneity using E°_{cell}

Will a spontaneous reaction occur in the forward direction for the following reaction? $E^{\circ}_{Al^{3+}/Al} = -1.676$ v. $E^{\circ}_{Cu^{2+}/Cu} = 0.340$ v.

$$2\ Al(s) + 3\ Cu^{2+}(aq) \rightarrow 3\ Cu(s) + 2\ Al^{3+}(aq)$$

Predicting Spontaneity using E°_{cell}

Identify the spontaneous cell.

$$Cu^+(aq) + e^- \rightarrow Cu(s) \qquad 0.52\ v$$
$$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s) \qquad -0.44\ v$$
$$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s) \qquad -1.66\ v$$

A. $Cu(s)|Cu^+(1\ M)\,\|\,Fe^{2+}(1\ M)|Fe(s)$
B. $Cu(s)|Cu^+(1\ M)\,\|\,Al^{3+}(1\ M)|Al(s)$
C. $Fe(s)|Fe^{2+}(1\ M)\,\|\,Al^{3+}(1\ M)|Al(s)$
D. $Fe(s)|Fe^{2+}(1\ M)\,\|\,Cu^+(1\ M)|Cu(s)$

Spontaneity Review

Property	Condition when forward reaction is spontaneous	Condition when forward reaction is nonspontaneous (reverse reaction is spontaneous)
ΔS_{univ}	Positive	Negative
E_{cell}	Positive	Negative
ΔG	Negative	Positive

Relating E°_{cell} and ΔG°

$$\Delta G^\circ = -nFE^\circ_{cell}$$

- F is Faraday's constant (96,485 C/mol e^-)
- n is the number of electrons transferred from the anode to the cathode in the balanced redox reaction
- ΔG° is in the units J/mol

Determining n

What is the value of n in each of the following reactions?

A. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

B. $Na(s) + Ag^{+}(aq) \rightarrow Na^{+}(aq) + Ag(s)$

C. $Cu(s) + 2\ Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$

D. $2\ Al(s) + 3\ Cu^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cu(s)$

E. $I_2(s) + 2\ Br^{-}(aq) \rightarrow 2\ I^{-}(aq) + Br_2(l)$

Determining a ΔG° from E°_{cell}

Use E° data to determine the ΔG° for the reaction. $E^\circ_{Zn^{2+}/Zn} = -0.763$ v. $E^\circ_{Cl_2/Cl^-} = 1.358$ v.

$$Zn(s) + Cl_2(g) \rightarrow ZnCl_2(aq)$$

Relating E°_{cell} and K_{eq}

$$\Delta G^{\circ} = -RT\ln K_{eq} = -nFE^{\circ}_{cell}$$

$$E^{\circ}_{cell} = \frac{RT}{nF}\ln K_{eq}$$

At room temperature ($T = 298.15$ K),

$$E^{\circ}_{cell} = \frac{0.02569}{n}\ln K_{eq}$$

Relating K_{eq} to E°_{cell}

What is the value of the equilibrium constant K_{eq} for the reaction between copper metal and iron(III) ions in aqueous solution at 25 °C? $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.771$ v. $E^{\circ}_{Cu^{2+}/Cu} = 0.340$ v.

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

The Nernst Equation (Relating E_{cell} to E°_{cell})

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

At room temperature ($T = 298.15$ K),

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{n} \log Q$$

- Q is the reaction quotient, and concentrations (in molarity) and partial pressures (in atmospheres) may both be placed into Q simultaneously.

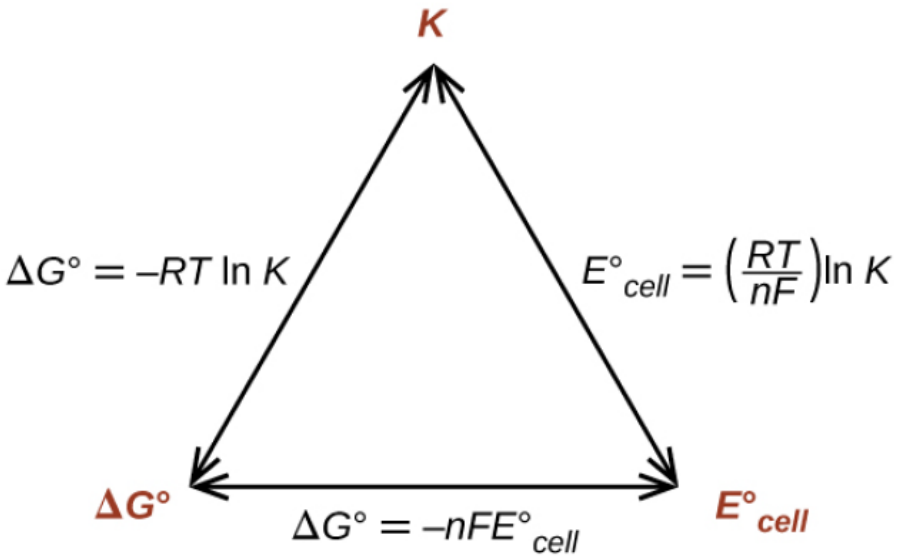
Predicting Spontaneity in Nonstandard Conditions

Will the cell reaction proceed spontaneously as written for the following cell? $E^{\circ}_{Sn^{2+}/Sn} = -0.137$ v. $E^{\circ}_{Pb^{2+}/Pb} = -0.125$ v.

$$Sn(s)|Sn^{2+}(0.50\ M)||Pb^{2+}(0.0010\ M)|Pb(s)$$

Relating E°_{cell}, ΔG°, and K_{eq}

- If given any one of E°_{cell}, ΔG°, or K_{eq}, the others can be found by using the triangle shown here.



Relating E°_{cell}, ΔG°, K_{eq}, and E_{cell}

What are the values of E°_{cell}, ΔG°, K_{eq}, and E_{cell} for the voltaic cell below at room temperature? $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.771\text{v}$. $E^{\circ}_{Ag^{+}/Ag} = 0.800$ v.

$$Pt|Fe^{2+}(0.10\ M)|Fe^{3+}(0.20\ M)||Ag^{+}(1.0\ M)|Ag(s)$$

Relating E°_{cell}, ΔG°, K_{eq}, and E_{cell}

When E°_{cell} is positive, what is true for ΔG° and K_{eq}?

A. ΔG° is negative and K_{eq} is greater than 1.
B. ΔG° is negative and K_{eq} is less than 1.
C. ΔG° is positive and K_{eq} is greater than 1.
D. ΔG° is positive and K_{eq} is less than 1.