

# Section 17.4

## Potential, Free Energy, and Equilibrium



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# Learning Objectives



- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

## $\Delta G^\circ$ and Electric Work



- The standard free energy change of a process,  $\Delta G^\circ$  is the maximum work that can be performed by a system,  $w_{\max}$ .
- In the case of a redox reactions essentially all the work is associated with transferring the electrons from reductant-to-oxidant,  $w_{\text{elec}}$

$$\Delta G^\circ = w_{\max} = w_{\text{elec}}$$

## $E^\circ$ and $\Delta G^\circ$



- The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\begin{aligned}\Delta G^\circ &= w_{\text{elec}} = -nFE_{\text{cell}}^\circ \\ \Delta G^\circ &= -nFE_{\text{cell}}^\circ\end{aligned}$$

- $n$  is the number of moles of electrons transferred
- $F$  is **Faraday's constant**, 96,485 C/mol.
- $E_{\text{cell}}^\circ$  is the standard cell potential.

## $E^\circ$ and $K$



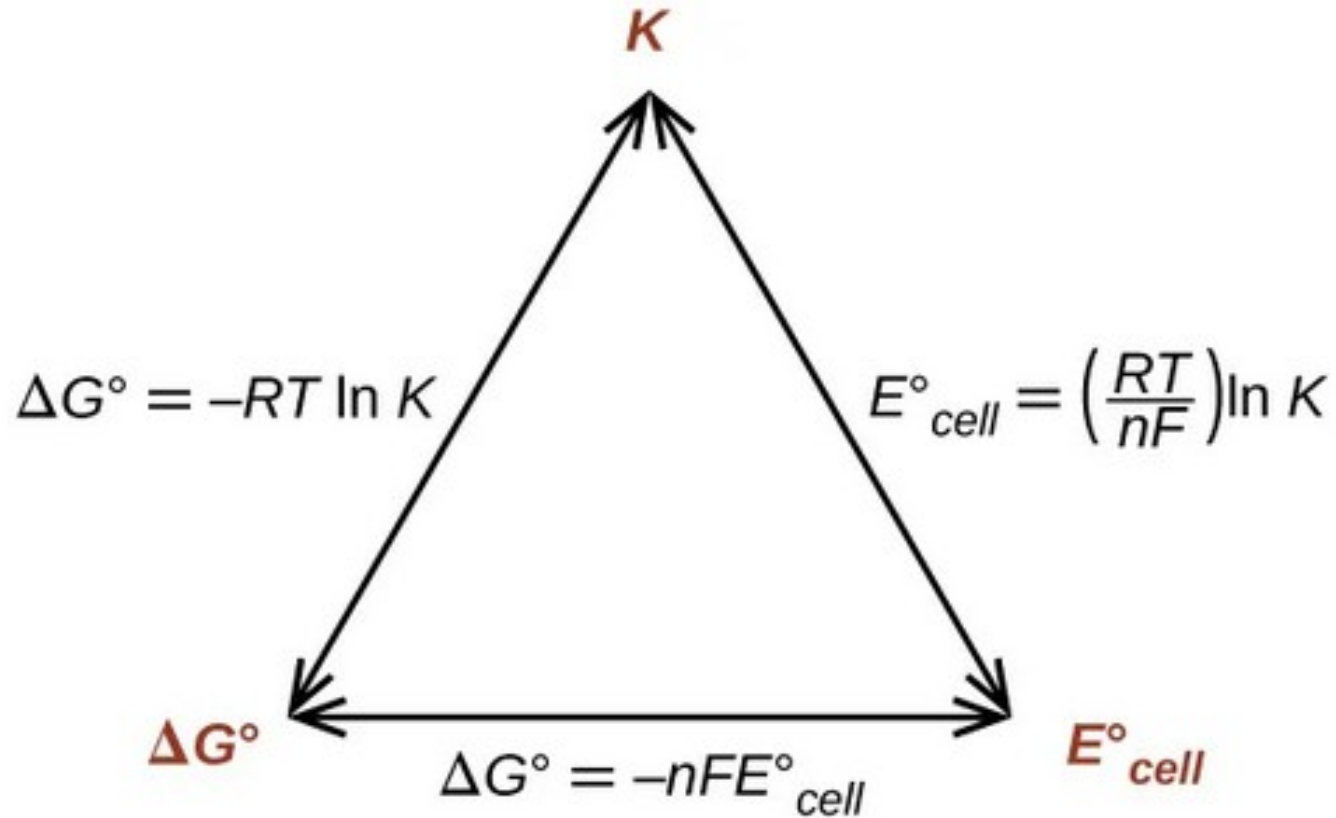
- Combining a previously derived relation between  $\Delta G^\circ$  and  $K$  and the equation relating  $\Delta G^\circ$  and  $E^\circ_{\text{cell}}$  yields the following:

$$\Delta G^\circ = -RT \ln K = -nFE^\circ_{\text{cell}}$$

$$E^\circ_{\text{cell}} = \left( \frac{RT}{nF} \right) \ln K$$

- This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product.

# Visualizing Relations



# Summary



$K$	$\Delta G^\circ$	$E^\circ_{\text{cell}}$	
$> 1$	$< 0$	$> 0$	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
$< 1$	$> 0$	$< 0$	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
$= 1$	$= 0$	$= 0$	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

# The Nernst Equation



- Most of the redox processes do not occur under standard state conditions.
- The relationship between potential and free energy change combined with the equation for nonstandard state can be used to find the cell potential at nonstandard state.

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

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q$$

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



## A Convenient Simplification



- A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and standard temperature (298 K), along with a factor converting from natural to base-10 logarithms, have been included:

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

# Concentration Cells



- A concentration cell is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode
- The potential of a concentration cell is determined only by the difference in concentration of the chosen redox species.



$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592\text{ V}}{2} \log \frac{0.10}{0.50} = +0.021\text{ V}$$