Gibb's Free Energy (ΔG): the energy associated with a chemical reaction that can be used to do __work__ .

Because of the following equation, the sign of ΔG will always be the __opposite__ of cell potential, E°

(this does NOT mean they are inversely proportional!!)

$$\Delta G^o = -nFE^o_{cell}$$

The variables are: n = number of moles of electrons transferred in a **BALANCED** redox reaction

F = faraday's constant = 96,485 C/ mol e⁻ (charge on one mole of electrons)

Remember: E° is measured in volts, and V = J/C

ΔG and K are related by the following equation at standard conditions (1 M, 1 atm, 298 K)

$$\Delta G^o = -RT \ln K$$

$$\ln K = \frac{-\Delta G^o}{RT}$$

The variables are: R = universal gas constant = 8.314 J mol⁻¹ K⁻¹
T = temperature (in Kelvin)
K = equilibrium constant
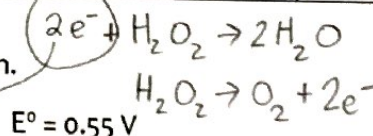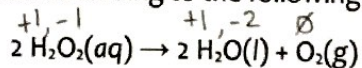
- This equation can be rewritten to give: $K = e^{-\Delta G^o/RT}$

- The units for $\Delta G^o = \dfrac{\text{joules}}{\text{moles}_{reaction}} = \dfrac{J}{mol_{rxn}}$

Summary

E^o_{cell}	ΔG^o	K	K & Q Relationship	Reaction Direction	Spontaneity in the Forward Direction
+	−	K > 1	K > Q	Forward	Spontaneous
−	+	K < 1	K < Q	Reverse	Non-spontaneous
= 0	= 0	K = 1	K = Q	No reaction	n/a

Example: At 25°C, H_2O_2 decomposes according to the following equation.

$2e^- + H_2O_2 \rightarrow 2H_2O$

$$\underset{+1,-1}{2\,H_2O_2(aq)} \rightarrow \underset{+1,-2}{2\,H_2O(l)} + \underset{\emptyset}{O_2(g)}$$

$H_2O_2 \rightarrow O_2 + 2e^-$

E° = 0.55 V

a. Determine the value of the standard free energy change, ΔG°, for the reaction at 25°C.

$$\Delta G^o = -nFE = -(2\,mol\,e^-)(96,485 \tfrac{C}{mol\,e^-})(0.55 \tfrac{J}{C})$$

1V = J/c

$$= \boxed{-1.1 \times 10^5 \ J/mol_{rxn}}$$

b. Determine the value of the equilibrium constant, K_{eq}, for the reaction at 25°C.

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{+1.1 E5 \ J/mol}{(8.315 \tfrac{J}{mol \cdot K})(298K)} = 44.393$$

$$\Rightarrow K = e^{44.393} = \boxed{1.9 \times 10^{19}}$$

> ➢ ↑ [reactants] OR ↓ [products]:
  - Make the reaction _more_ thermodynamically favorable (more spontaneous)
  - ↑ reaction driving force, thus:
    - ○ ↑ E_{cell}, ↑ voltage

- ↓ [reactants] OR ↑ [products]:
  - Make the reaction _less_ thermodynamically favorable (less spontaneous)
  - ↓ reaction driving force, thus:
    - ○ ↓ E_{cell}, ↓ voltage

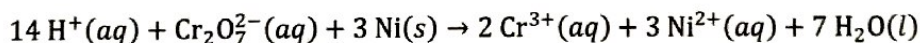As a voltaic cell discharges, reactants are consumed and products are generated.

Therefore, as the cell operates, the conditions become non-standard and the voltage _drops_ !

→ But if you **decrease** _both_ reactant AND product concentration **by the same factor**:

- Spontaneity is unaffected!
- $E_{cell} = E^{\circ}_{cell}$
- However, fewer reactants means that the electrochemical cell will operate for a shorter _time_ before running out of reactants! The reverse is true if you increase both by the same factor.

Practice:

1. In the reaction below, a piece of solid nickel is added to a solution of potassium dichromate.

$$14\,H^+(aq) + Cr_2O_7^{2-}(aq) + 3\,Ni(s) \rightarrow 2\,Cr^{3+}(aq) + 3\,Ni^{2+}(aq) + 7\,H_2O(l)$$

$$3\,Ni_{(s)} \rightarrow 3\,Ni^{2+}_{(aq)} + 6e^-$$

How many moles of electrons are transferred when 1 mole of potassium dichromate is mixed with 3 mol of nickel?

a. 2 moles of electrons   c. 5 moles of electrons

b. 3 moles of electrons   (d.) 6 moles of electrons

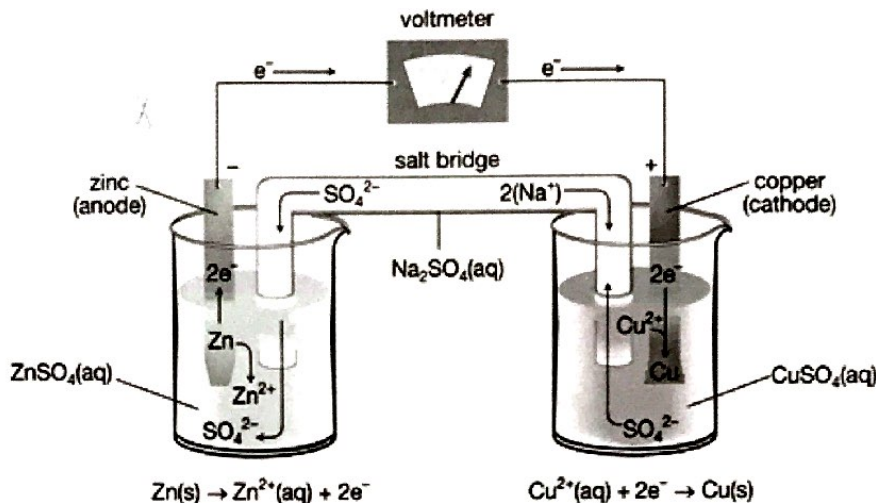2. Calculate the standard free energy of the following reaction at 25°C.
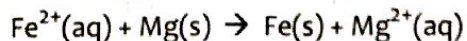
$$Fe^{2+}(aq) + Mg(s) \rightarrow Fe(s) + Mg^{2+}(aq) \qquad E^{\circ}_{cell} = 1.92\ V$$

a. -1.6×10^5 kJ/mol$_{rxn}$ c. -3.7×10^5 kJ/mol$_{rxn}$

b. -160 kJ/mol$_{rxn}$ (d.) -370 kJ/mol$_{rxn}$

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

$$= -(2\ mol\ e^-)\left(96,485\,\tfrac{C}{mol\ e^-}\right)\left(1.92\,\tfrac{J}{C}\right)$$

$$= -2 \times 100,000 \times 2 = -4E5\ \tfrac{J}{mol_{rxn}} = -400\ \tfrac{kJ}{mol_{rxn}}$$

3. A voltaic cell is constructed based on the following reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

a. Complete the chart below.

Conditions	Effect on Rxn Driving Force	Ecell vs. E°cell	Effect on voltage	Effect on time cell can run
Addition of Cu(s)	none	Same	none	none
[ZnSO₄] = 1.0 M, [CuSO₄] = 0.3 M	↓	$E_{cell} < E^0_{cell}$	↓	↓
Removal of salt bridge	↓ to Ø	n/a	↓ to Ø	very ↓
[ZnSO₄] = 0.5 M, [CuSO₄] = 1.0 M	↑	$E_{cell} > E^°_{cell}$	↑	none
Removal of all Zn(s)	↓ to Ø	n/a	↓ to Ø	very ↓
[ZnSO₄] = 2.0 M, [CuSO₄] = 2.0 M	none	Same	none	↑
The cell has been running for 2 hours.	↓	$E_{cell} < E^°_{cell}$	↓	↓
[ZnSO₄] = 1.0 M, [CuSO₄] = 1.7 M	↑	$E_{cell} > E^°_{cell}$	↑	↑

b. A student accidentally adds additional ZnSO₄ to the Zn(s)/Zn²⁺(aq) half-cell. What happens to the magnitude of the cell voltage (relative to the standard cell)? Justify your answer.

Adding extra $ZnSO_4$ will ↑ $[Zn^{2+}]$, a product, decreasing the driving force of the rxn + thus decreasing the cell voltage.

c. Is the value of the equilibrium constant for the cell reaction greater than 1, less than 1, or equal to 1? Explain.

$K > 1$, b/c this is a voltaic cell, which means it is thermodynamically favorable + therefore product-favored. (or b/c $-\Delta G \Rightarrow K > 1$ b/c $\Delta G = -RT \ln K$)

d. What must be true about the standard free energy change of this reaction, $\Delta G°$? Justify.

$-\Delta G°$, b/c $K > 1$ and $\Delta G° = -RT \ln K$