Electrochem Equilibrium

Equilibrium: Recall that many chemical reactions are reversible. We show this with a double-ended arrow: ⇌

➔ Surprise! The exchange of e⁻ in a redox reaction is reversible, and therefore relevant to equilibrium.

At Equilibrium:

- Forward and backward reactions continue at the same rate.
- There is NO NET movement between reactants and products, which means there is NO measurable voltage in an electrochemical cell at equilibrium!
- **Voltaic/Galvanic cell at equilibrium = dead battery!**

The Equilibrium Constant, K: ratio of products to reactants at equilibrium (at given temperature).

If you have the following equilibrium reaction, $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{[Products]^{coefficient}}{[Reactants]^{coefficient}}$$

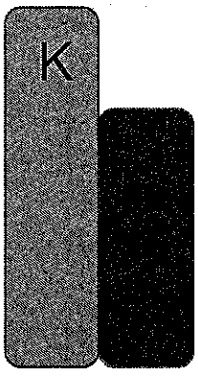
Since pure solids and liquids are not included in the K expression, only aqueous (or rarely, gaseous) reactants and products are included in the equilibrium constant expression, K, for electrochemical cells.

The Reaction Quotient, Q

In a standard galvanic/voltaic cell:

- K >> 1 and Q = 1 (since [reactants] = [products] = 1.0 M)
- Thus, K > Q and the reaction spontaneously makes products
  - Since this is a redox reaction, as products are made, electrons are transferred = current flows!
- Once the reaction has run long enough that K = Q, equilibrium is reached and no current flows (i.e. dead battery)

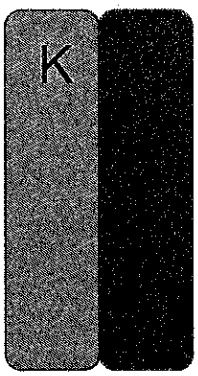
Voltaic Cell, Standard Conditions (1.0 M)



K >> Q
Products Form/Current Flows
V = E^{o}_{cell}

voltage **decreases** as system approaches equilibrium

Cell at Equilibrium

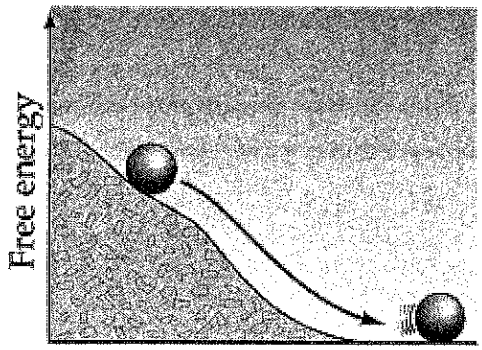
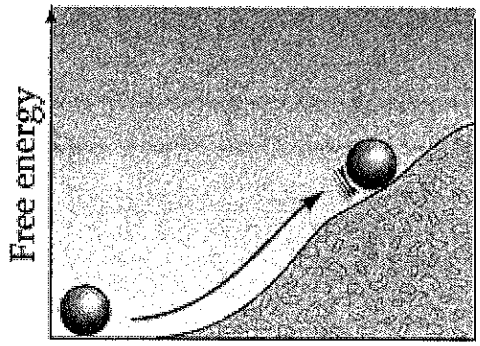


K = Q
No Products Form = No Current
Dead Battery (0 V)

Gibb's Free Energy (ΔG)

ΔG = change in free energy = ability to do Work

→ Next unit, we will talk more about the meaning of "free energy", but for this unit you need to be able to use the numerical value of ΔG to predict the spontaneity of a reaction.

Exergonic Reaction (−ΔG)	Endergonic Reaction (+ΔG)
Spontaneous (Thermodynamically Favorable)	Not Spontaneous (Thermodynamically Unfavorable)
$+E^{o}_{cell}$ = voltage created (battery)	$-E^{o}_{cell}$ = external power source needed
	

The relationship between Gibb's free energy and cell potential can be quantified through the following equation:

"−nunfe"

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

} on formula chart!

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^{o} is measured in volts, and 1 V = 1 J/C $\quad 1\,V = 1\,\frac{J}{C}$

Note about Units:

ΔG is *usually* measured in kJ/mol or J/mol. Mastering Chem only uses units of kJ or J.

AP units

Mastering Chem.

Let's Practice!

1. Identify n (the number of moles of electrons transferred) in each of the following reactions (hint: think about the half-reactions).

   a. $2\,Ce(s) + 3\,Ni^{2+}(aq) \rightleftharpoons 2\,Ce^{3+}(aq) + 3\,Ni(s)$ $\quad n =$ 6 mol e^-/mol_{rxn}

   b. $Sn(s) + 2\,Ag^{+}(aq) \rightleftharpoons Sn^{2+}(aq) + 2\,Ag(s)$ $\quad n =$ 2 mol e^-/mol_{rxn}

2. Calculate ΔG° (in kJ/mol) for this reaction: $Fe(s) + Cu^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cu(s)$, where $E^{o}_{cell} = 0.79$ V. Is this reaction thermodynamically favorable? Explain.

$$\Delta G^{o} = -n\,F\,E^{o}_{cell} = -\left(2\,\frac{mol\,e^-}{mol_{rxn}}\right)\left(96{,}485\,\frac{C}{mol\,e^-}\right)\left(0.79\,\frac{J}{C}\right) = -152{,}466$$ (2 s.f.)

$$= -150{,}000\,\frac{J}{mol_{rxn}} \times \frac{1\,kJ}{1000\,J} = -150\,kJ/mol_{rxn}$$

−ΔG ⇒ yes, thermodynamically favorable!

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

"-RatLink"

$$\Delta G^o = -RT \ln K$$ } on formula chart!

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: $K = e^{-\Delta G^o/RT}$ Not on F.C.! If you can't derive, memorize!
- The units for $\Delta G^o = \frac{\text{joules}}{\text{moles}_{\text{reaction}}} = \frac{\text{J}}{\text{mol}_{\text{rxn}}}$ **but Mastering Chem uses J**

Summary

E^o_{cell}	ΔG^o	K	**Thermodynamically favorable?**
+	−	K > 1	Favorable
−	+	K < 1	Not favorable
= 0	= 0	~~K=1~~ K=Q	n/a

Let's Practice!

1. The standard cell potential, E^o_{cell}, is +0.67 V for the balanced oxidation-reduction reaction shown below:

$$S_4O_6^{2-}(aq) + 2\ Cr^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + 2\ S_2O_3^{2-}(aq)$$

a. Calculate the free energy change for the cell (in kJ/mol_{rxn}).

$$\Delta G^\circ = -nFE^\circ_{cell} = -\left(2\ \frac{mol\ e^-}{mol_{rxn}}\right)\left(96{,}485\ \frac{C}{mol\ e^-}\right)\left(0.67\ \frac{J}{C}\right) = -130{,}000\ J/mol_{rxn}$$

$$\times\ \frac{1\ kJ}{1000\ J}$$

$$= -130\ kJ/mol_{rxn}$$

b. Calculate the equilibrium constant for this reaction (at 25°C).

$$\Delta G^\circ = -RT \ln K \Rightarrow \ln K = \frac{-\Delta G^\circ}{RT} = \frac{+130{,}000\ J/mol_{rxn}}{\left(8.314\ \frac{J}{mol \cdot K}\right)(298\ K)} = 52.47$$

$$K = e^{52.47} = 6.1 \times 10^{22}$$

K>>1, VERY favorable! ^^