

# Thermodynamics: The Big Picture

1. A reaction's change in free energy indicates its favorability; thus, a favorable reaction has  $\Delta G < 0$ .
2. For a redox reaction, the potential also indicates its favorability; thus, a favorable redox reaction has  $E > 0$ .
3. A reaction that is thermodynamically favorable may not occur for kinetic reasons; thus, failing to see a reaction does not imply that  $\Delta G < 0$ .
4. Together, the sign of a reaction's  $\Delta H$  and  $\Delta S$  indicate how its favorability changes with  $T$ ; thus, at least one of the following is required if a reaction is favorable:  $\Delta H < 0$  and/or  $\Delta S > 0$ .
5. A reaction's favorability depends on the concentrations of reactants and products, as described by  $\Delta G = \Delta G^\circ + RT \ln Q$ ; thus, a reaction's  $\Delta G$  changes as the reaction progresses.
6. A favorable reaction proceeds until it reaches equilibrium where  $\Delta G = 0$ ; thus,  $\Delta G^\circ = -RT \ln K$ .
7. A reaction's  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are state functions whose values depend only on where the reaction begins and where it ends; thus, we can calculate their values using any set of reactions of our choosing.
  - $\Delta H^\circ = \left[ \sum_i n_i \Delta H_{f,i}^\circ \right]_{products} - \left[ \sum_j n_j \Delta H_{f,j}^\circ \right]_{reactants}$
  - $\Delta S^\circ = \left[ \sum_i n_i \Delta S_{f,i}^\circ \right]_{products} - \left[ \sum_j n_j \Delta S_{f,j}^\circ \right]_{reactants}$
  - $\Delta G^\circ = \left[ \sum_i n_i \Delta G_{f,i}^\circ \right]_{products} - \left[ \sum_j n_j \Delta G_{f,j}^\circ \right]_{reactants}$
8. Heat, free energy, enthalpy, and entropy are conserved and are stoichiometric; thus
  - $q_{rxn} = -q_{soln}$
  - $q = mS\Delta T$
  - $\Delta H = \frac{q_{rxn}}{n_{LR}} \times \frac{\nu_{LR}}{\text{mol}_{rxn}}$
9. The potential of a redox reaction is independent of stoichiometry; thus  $\Delta G = -nFE$ , where  $n$ , the number of electrons transferred from the reducing agent to the oxidizing agent, accounts for stoichiometry when converting potential to free energy.