

AP Chemistry

Chapter 19 Outline

A. Chemical Thermodynamics

- a. Energy is conserved, i.e., it is neither created nor destroyed in any process.
 - i. $\Delta E = q + w$
 - ii. The quantity of energy lost by a system equals the quantity gained by its surroundings.
- b. A spontaneous process proceeds on its own without any outside assistance
 - i. Reactions that are spontaneous in one direction are nonspontaneous in the opposite direction.
 1. Experimental conditions—temperature, pressure—may determine if a process is spontaneous.
 2. Just because a process is spontaneous doesn't mean it will occur at an observable rate.
 - ii. Thermodynamics tells us the direction and extent of a rxn but nothing about the speed of the reaction.
- c. State functions are properties that define a state but don't depend on how that state was reached
 - i. q and w are not state functions: they depend on the path taken
 - ii. Temperature, internal energy, and enthalpy are state functions
- d. In a reversible process a system is changed in such a way that the system and surroundings can be restored to their original state by exactly reversing the change
 - i. A reversible change produces the maximum amount of work that can be achieved by the system on the surroundings.
 - ii. Irreversible process is one that cannot simply be reversed to restore the system and surrounding to their original states
 1. All real processes are irreversible.
 2. Any spontaneous process is irreversible.
 - a. Even if the system is returned to its original condition, the surroundings will have changed.

B. Entropy and the second law of thermodynamics

- a. Entropy, S , is associated with the amount of randomness in a system.
 - i. S is a state function
 - ii. $\Delta S = S_{\text{final}} - S_{\text{initial}}$
 - iii. if T is constant, $\Delta S = \frac{q_{\text{rev}}}{T}$ for any process (T in Kelvin) where q is the enthalpy change for an isothermal process—such as a phase change
- b. Entropy increases in any spontaneous process.
 - i. The sum of the entropy change of the system and the surroundings for any spontaneous process is always greater than zero.
 - ii. Any irreversible process results in an overall increase in entropy.
 - iii. A reversible process results in no overall change in entropy.
- c. Second Law of Thermodynamics: The total entropy of the universe increases in any spontaneous process.

C. The Molecular Interpretation of Entropy

a. Molecular motions and energy

- i. KMT: The average kinetic energy of molecules of an ideal gas is directly proportional to the absolute temperature of the gas.
- ii. Hotter systems have a broader distribution of molecular speeds.
- iii. Three kinds of [molecular motion](#):
 1. Translational: moving in a direction (changing coordinates)
 2. Vibrational: squishing and separating, as if on a spring
 3. Rotational: tumbling or spinning

b. Boltzmann's equation and microstates

- i. Microstate = "snapshot" or single possible arrangement of the positions and energies of the individual particle in a sample of matter
 1. Entropy increases with the number of microstates of the system.
 2. Increased freedom of motion: Gases have more entropy than liquids or solutions, which have more entropy than solids.
 3. Increased dispersion (spreading out) of energy
 4. Increased randomness
 - a. Note: dissolving of salts with highly charged ions can result in a net decrease of entropy! (waters of hydration can be thought of as being more confined)
- ii. Each thermodynamic state has a characteristic number of microstates, W , associated with it
 1. In general, the number of microstates available to a system increases with an increase in volume, an increase in temperature, or an increase in the number of particles.
- iii. $S = k \ln W$ (For this course, this isn't an equation you're expected to do calculations with on a test)

c. Third Law of Thermodynamics

- i. The entropy of a pure crystalline substance at absolute zero is zero.
- ii. A perfect crystal, with no thermal motion, can have only one microstate!

D. Entropy Changes in Chemical Reactions

a. Standard molar entropies are usually reported as J/mol K for the pure substance at 1 atm pressure.

- i. The standard molar entropies of elements are NOT zero!
- ii. The standard molar entropies of gases are greater than those of liquids and solids.
- iii. Standard molar entropies increase with increasing molar mass.
- iv. Standard molar entropies generally increase with an increasing number of atoms in the formula (more degrees of freedom for motion).
 1. $\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$
You need to be able to do these calculations!

- b. Entropy changes in the surroundings
- Remember: the surroundings serve essentially as a large, constant temperature heat source (or heat sink)
 - The entropy change of the surroundings depends on how much heat is absorbed or released by the system
 - If the system undergoes an exothermic process, the surroundings will experience an increase in entropy, and vice-versa
 - $\Delta S_{surr} = \frac{-q_{sys}}{T}$ where q is the enthalpy change for an isothermal process at constant pressure

E. Gibb's Free Energy

- $\Delta G = \Delta H - T\Delta S$ Be able to do these calculations!
Watch units for ΔH (often given in kJ/mol), ΔS (often given in J/K), T in Kelvin
- Use ΔH , ΔS to predict whether a given reaction occurring at constant temperature and pressure will be spontaneous
 - If ΔG is negative, the reaction is spontaneous in the forward direction.
 - If ΔG is zero, the reaction is at equilibrium.
 - If ΔG is positive, the reaction is nonspontaneous (but the reverse reaction will be spontaneous).
- ΔG is sometimes called the "driving force" of the reaction
 - Free energy is a state function
 - Free energy values have been tabulated at standard conditions
 - Unlike enthalpy and entropy, there is no physical property of matter that relates to Gibbs free energy
 - $\Delta G^\circ = \Sigma nG^\circ(\text{products}) - \Sigma nG^\circ(\text{reactants})$
You need to be able to do these calculations
- Free energy and temperature
 - The sign of ΔG depends on the signs and magnitudes of ΔH and $T\Delta S$. You must know or be able to figure out these relationships!

Sign of ΔH	Sign of ΔS	Sign of ΔG	Comments
-	+	-	Rxn is spontaneous at all temperatures
+	-	+	Rxn is nonspontaneous at all temperatures
-	-	indeterminate	Spontaneous at low T (enthalpy driven at low T)
+	+	indeterminate	Spontaneous at high T (entropy driven at high T)

- For the indeterminate cases, the enthalpy term dominates at low temperatures; the entropy term dominates at high temperatures.

- iii. One type of common problem: above/below what temperature will a certain rxn be spontaneous? Set $\Delta G = 0$, solve for T

F. Free energy and the equilibrium constant

- a. For rxns at nonstandard conditions (most reactions occur at nonstandard conditions!)
- i. $\Delta G = \Delta G^\circ + RT \ln Q$
 1. R is the universal gas constant (J/mol K)
 2. Q is the reaction quotient (ratio of products/reactants right now)
- b. $\Delta G^\circ = -RT \ln K$ Know and be able to use this equation
- c. $K = e^{-\Delta G^\circ / RT}$ Know and be able to use this equation, too
- i. Pay attention to units: J, kJ, Kelvin temperature
 - ii. Use the R value 8.314 J/mol K
- d. Relating Gibbs free energy and the equilibrium constant
- i. If ΔG° is negative, $K > 1$

If the reaction occurs spontaneously, products will be favored
 - ii. If ΔG° is positive, $K < 1$

If the reaction is nonspontaneous as written, reactants will be favored
 - iii. If $\Delta G^\circ = 0$, $K = 1$