

## Thermodynamics: The Second & Third Laws

7<sup>th</sup> Edition: Focus 4F-J

Problems 4F: 1, 3, 5, 7, 9, 13, 17; 4G: 1, 3, 5; 4H: 1, 3, 5, 7, 11; 4I: 1, 3, 5, 7, 9;  
4J: 1, 3, 5, 7, 9, 11, 13, 15, 17; and 4.21, 4.37, 4.43, 4.45, 4.51, 4.59, 4.61

Focus 5G.3, 5G.4, 5J.3 and go through Examples 5J.4 and 5J.5  
(The rest of Focus 5 was covered in Chemical Equilibrium.)

Problems 5G: 13, 15, 17, 19, 21; 5J: 11, 13, 15; and 5.55, 5.61

After going through the readings & problems and attending the lectures & discussion groups, you should be able to:

- State and explain the Boltzmann equation for entropy.
- Know how to calculate the number of microstates ( $W$ ) to calculate entropy ( $S = k_B \ln W$ ).
- Calculate the work of expansion when the pressure is not constant,  $w = -nRT \ln \frac{V_2}{V_1}$ .
- Apply the 1st and 2nd laws of thermodynamics to calculate the change in energy and entropy of a system.
- State and explain the second ( $\Delta S = \frac{q_{REV}}{T}$ ) and third law of thermodynamics ( $\lim_{T \rightarrow 0K} S = 0$ ).
- Explain how temperature, volume, and state of matter affect the entropy of a substance.
- Predict which of two systems has the greater entropy, given their compositions and conditions.
- Calculate changes in entropy due to changes in volume ( $\Delta S = n R \ln \frac{V_2}{V_1}$ ).
- Calculate changes in entropy due to changes in temperature ( $\Delta S = n C \ln \frac{T_2}{T_1}$ ).
- Calculate the standard reaction entropy from standard molar entropies.
- Show how  $\Delta S$  is related to  $\Delta H$  for a change at constant temperature and pressure and explain the relationship.
- Show that  $\Delta S_{TOTAL} > 0$  for a spontaneous process.
- Show how the Gibbs free energy change accompanying a process is related to the direction of spontaneous reaction.
- Calculate a standard reaction free energy from the standard enthalpy of reaction and standard molar entropies ( $\Delta G^\circ_{RXN} = \Delta H^\circ_{RXN} - T\Delta S^\circ_{RXN}$ ).
- Calculate the standard reaction free energy from standard free energies of formation ( $\Delta G^\circ_{RXN} = \sum \Delta G^\circ_f(\text{PRODUCTS}) - \sum \Delta G^\circ_f(\text{REACTANTS})$ ).

- Predict the temperature at which a process with a known  $\Delta H^\circ$  and  $\Delta S^\circ$  becomes spontaneous.
- Understand the relationship between free energy,  $\Delta G$ , and maximum work under conditions of constant temperature and pressure for systems not at equilibrium. ( $w_{(max)} = \Delta G = \Delta G^\circ + RT \ln Q$ )
- Understand that systems at equilibrium do no work as  $\Delta G = 0$  at equilibrium.
- Understand that we study systems at equilibrium to observe and determine useful relationships. E.g., The standard Gibbs free energy of a reaction (difference in Gibbs free energy between reactants and products for a reaction under standard conditions) is related to the relative amounts of reactants and products at equilibrium (equilibrium constant). Observing/determining concentrations of reactants and products at equilibrium is straight-forward. Observing/measuring free energy differences is difficult.
- Understand statements such as, “the larger the equilibrium constant, the more stable the product”.
- Calculate standard reaction free energy from  $\Delta G^\circ$  and the composition of the reaction mixture (K).
- Calculate an equilibrium constant from  $\Delta G^\circ$  using  $\Delta G^\circ = -RT \ln K$ .
- Know how to derive and use the van't Hoff equation ( $\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ ) to show the temperature dependence of K, and calculate K at different temperatures.
- Use the above concepts and equations in organic reactions, and environmental and biological examples (coupling of favorable reactions to drive unfavorable reactions; ATP hydrolysis, etc.).