**Remember from Chapter 5:** 

Thermodynamics deals with energy relationships in chemical reactions

Know the definitions of system, surroundings, exothermic process, endothermic process

 $\Delta H^{0}_{rxn} = \Sigma n_{p} \Delta H^{0}_{f} (products) - \Sigma n_{r} \Delta H^{0}_{f} (reactants) \{ same for \Delta S^{0}_{rxn} and \Delta G^{0}_{rxn} \}$ 

 $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ 

 $\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$  (Use off of 25°C)

 $\Delta \mathbf{G} = \Delta \mathbf{G}^{\circ} + \mathbf{RT} ln(\mathbf{Q})$ 

```
\Delta \mathbf{G}^{\circ} = -\mathbf{R} \mathbf{T} ln(\mathbf{K})
```

## 16.1 and 2 By the end of this section, you will be able to:

- a) Distinguish between spontaneous and nonspontaneous processes
- b) Describe what happens in a spontaneous process
- c) Define entropy
- d) Explain the relationship between entropy and the number of microstates
- e) Predict the sign of the entropy change for chemical and physical processes
- f) A spontaneous process takes place without any outside intervention

A process that is spontaneous in one direction is non –spontaneous in the opposite direction Enthalpy and entropy are the two factors that determine thermodynamics favorability A system always tries to reach a state where its potential energy is the lowest. You should be able to identify whether a process is spontaneous or not

- g) Entropy is the measure of the randomness or disorder in a system Entropy generally increases when... and you should be able to predict the entropy change for a reaction without doing any calculations...
  - i. Gases are formed from solids or liquids
  - ii. Liquids /solutions formed from solids
  - iii. Number of gas molecules in a reaction increases
  - iv. Increase in temperature

## h) All spontaneous processes are associated with an increase in the randomness of the system

1) Label each as having a + or – $\Delta$ S syst	em.
--	-----

A) water freezing

B) ice melting

C) water evaporating

D) salt dissolving in water

E) dry ice subliming

```
2) Place the following in order of increasing molar entropy at 298 K.
```

CO<sub>2</sub> C<sub>3</sub>H<sub>8</sub> SO

16.3 By the end of this section, you will be able to:

- a) State and explain the second and third laws of thermodynamics
- b) Calculate entropy changes for phase transitions and chemical reactions under standard conditions
- c) Be able to calculate  $\Delta S$  surroundings.
- d)  $\Delta S_{rxn}^{0} = \Sigma \text{ #moles } S^{0}(\text{products}) \Sigma \text{ #moles } S^{0}(\text{reactants})$
- e)  $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- f)  $\Delta S_{surr} = -\frac{\Delta H}{T}$

3) Calculate  $\Delta S^{\circ}rxn$  for the following reaction.

 $N_2H_4(I) + H_2(g) \rightarrow 2 NH_3(g)$ 

4) Consider the following reaction at constant P. Use the information here to determine the value of  $\Delta S_{surr}$  at 398 K. Predict whether or not this reaction will be spontaneous at this temperature.

4 NH<sub>3</sub>(g) + 3 O<sub>2</sub>(g) → 2 N<sub>2</sub>(g) + 6 H<sub>2</sub>O(g)  $\Delta$ H = -1267 kJ

16.4 By the end of this section, you will be able to:

- a) Define Gibbs free energy, and describe its relation to spontaneity
- b) Calculate free energy change for a process using free energies of formation for its reactants and products (at 25 °C)  $\Delta G^{0}_{rxn} = \Sigma \text{ #moles } \Delta G^{0}_{f} \text{ (products)} - \Sigma \text{ #moles } \Delta G^{0}_{f} \text{ (reactants)}$  Get the  $\Delta G^{0}_{f}$  values from the text.
- c) Entropy, Enthalpy and free energy are all state functions
  - a. Know how to calculate  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  for reactions at 298 K (Off the charts!)
  - **b.**  $\Delta H^{0}_{rxn} = \sum n_{p} \Delta H^{0}_{f}$  (products)  $-\sum n_{r} \Delta H^{0}_{f}$  (reactants) {same for  $\Delta S^{0}_{rxn}$  and  $\Delta G^{0}_{rxn}$ }
  - c. At 298 K, you can calculate  $\Delta G$  directly off the charts.
- d) Since G is a state function
  - a. Reversing a reaction changes sign of  $\Delta G$
  - b. When adding reactions, must add the  $\Delta G's$
  - c. If a reaction is multiplied by a number, then  $\Delta G$  is also multiplied by the same number
- e) We can use Hess's Law to calculate  $\Delta G$  for a reaction.
- f) Off of 25 °C, you cannot calculate  $\Delta G$  directly from the charts. You must calculate  $\Delta H$  and  $\Delta S$  and plug in T to get  $\Delta G$ .  $\Delta G = \Delta H - T\Delta S$
- g) Under non-standard conditions,  $\Delta G = \Delta G^0 + RT \ln Q$  (where Q is the reaction quotient)
- $\begin{array}{ll} \text{h)} & \text{Free energy and equilibrium constant are related as } \Delta G^\circ = \ \text{RT In} K_{eq} \\ & \text{a.} & \text{If } \Delta G^\circ < 0, \ K_{eq} > 1 & \text{If } \Delta G^\circ > 0, \ K_{eq} < 1 & \text{If } \Delta G^\circ = 0, \ K_{eq} = 1 \end{array}$
- 5) Above what temperature does the following reaction become nonspontaneous?

 $3 H_2 + N_2 \rightarrow 2NH_3$ .  $\Delta H = -93 kJ; \Delta S = -198 J/K$ 

6. Estimate  $\Delta G^{\circ}_{rxn}$  for the following reaction at 500.0 K. (Calculate  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ )

 $CH_2O(g) + 2 H_2(g) \rightarrow CH_4(g) + H_2O(g)$ 

7. Calculate the  $\Delta G^{\circ}_{rxn}$  at 25°C. 2 H<sub>2</sub>S(g) + 3 O<sub>2</sub>(g)  $\rightarrow$  2 SO<sub>2</sub>(g) + 2 H<sub>2</sub>O(g) 8. (A) For the reaction:  $2NO(g) + O_2(g) \rightleftharpoons 2 NO_2(g)$ : What is  $\Delta G^{\circ}rxn$  and K at  $25^{\circ}C_2$ ?

(B) What is the value of  $\Delta G$  if P NO(g) = 10.0 atm, P O<sub>2</sub>(g) = 10.0 atm, P NO<sub>2</sub>(g) = 0.0.100 atm?

10. Label each as True or False

A) There is a "heat tax" for every energy transaction.

B) A spontaneous reaction is always a fast reaction.

C) The entropy of a system always decreases for a spontaneous process.

D) Perpetual motion machines are a possibility in the near future.