CHM 112 Chapter 16 Thermodynamics Study Guide

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** ΔS^0_{rxn} **and** ΔG^0_{rxn}**}**

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

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

$\Delta G = \Delta G° + RT\,ln(Q)$

$\Delta G° = -RT\,ln(K)$

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 – ΔS system.
A) water freezing negative
B) ice melting positive

C) water evaporating positive
D) salt dissolving in water positive

E) dry ice subliming positive

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

CO_2 C_3H_8 SO

$SO < CO_2 < C_3H8$

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 ΔS surroundings.**
- d) **$\Delta S^0_{rxn} = \Sigma$ #moles S^0(products) – Σ #moles S^0 (reactants)**
- e) **$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$**
- f) **$\Delta S_{surr} = -\frac{\Delta H}{T}$**

3) Calculate $\Delta S°_{rxn}$ for the following reaction.

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

= +113.7 J/K

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

$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(g)$ $\Delta H = -1267$ kJ

= 3180 J/K

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) $\Delta G^0_{rxn} = \Sigma$ #moles ΔG^0_f (products) – Σ #moles ΔG^0_f (reactants) Get the ΔG^0_f values from the text.
- c) **Entropy, Enthalpy and free energy are all state functions**
  - a. **Know how to calculate ΔG^0, ΔS^0 and ΔH^0 for reactions at 298 K (Off the charts!)**
  - b. **$\Delta H^0_{rxn} = \Sigma\ n_p\ \Delta H^0_f$ (products) – $\Sigma\ n_r\ \Delta H^0_f$ (reactants) {same for ΔS^0_{rxn} and ΔG^0_{rxn}}**
  - c. **At 298 K, you can calculate ΔG directly off the charts.**
- d) **Since G is a state function**
  - a. **Reversing a reaction changes sign of ΔG**
  - b. **When adding reactions, must add the ΔG's**
  - c. **If a reaction is multiplied by a number, then ΔG is also multiplied by the same number**
- e) **We can use Hess's Law to calculate ΔG for a reaction.**
- f) **Off of 25 °C, you cannot calculate ΔG directly from the charts. You must calculate ΔH and ΔS and plug in T to get ΔG.** **$\Delta G = \Delta H - T\Delta S$**
- g) **Under non-standard conditions, $\Delta G = \Delta G^0 + RT \ln Q$ (where Q is the reaction quotient)**

h) Free energy and equilibrium constant are related as $\Delta G^\circ = -RT\ln K_{eq}$

a. If $\Delta G^\circ < 0$, $K_{eq} > 1$ If $\Delta G^\circ > 0$, $K_{eq} < 1$ If $\Delta G^\circ = 0$, $K_{eq} = 1$

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

T>470 K

6. Estimate ΔG°_{rxn} for the following reaction at 500.0 K. (Calculate ΔH° and ΔS°)

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

$\Delta G^\circ = -155$ kJ

7. Calculate the ΔG°_{rxn} at 25°C.
$2\,H_2S(g) + 3\,O_2(g) \rightarrow 2\,SO_2(g) + 2\,H_2O(g)$

$\Delta G^\circ = -990.6$ kJ

8. (A) For the reaction: $2NO(g) + O_2(g) \rightleftarrows 2\,NO_2(g)$: What is ΔG°_{rxn} and K at 25°C?

$\Delta G^\circ = -72.6$ kJ K = 5.3×10^{12}

(B) What is the value of ΔG if $P_{NO(g)} = 10.0$ atm, $P_{O_2(g)} = 10.0$ atm, $P_{NO_2(g)} = 0.0.100$ atm? Will the reaction be more or less spontaneous under these conditions?

$\Delta G = -101$ kJ

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.