CHAPTER 19 – Chemical Thermodynamics

Section 19.1 – Spontaneous Processes

(a) The first law of thermodynamics states that energy is ___________________________.

(b) In the equation $\Delta E = q + w$,

ΔE refers to the change in the __________________________ of a system,

q is the __________ that is absorbed (or released) by the system.

w is the __________ that is done on the system (or on the surroundings).

(c) A spontaneous process is one that proceeds ____

____

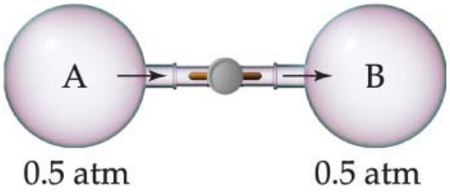
(d) A spontaneous process occurs in one direction only. The reverse of any spontaneous process is always _____________________________________.

(e) Decide if each of the following processes would be spontaneous or nonspontaneous under the given conditions.

(i) $H_2O(l) \rightarrow H_2O(s)$ at –10°C and 1 atm

____

(ii) The gas in flask B moving completely from flask B into flask A.



____

(iii) $H_2O(l) \rightarrow H_2(g) + ½\,O_2(g)$ at 25°C and 1 atm

____

(iv) $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ with 1.0 g $NaCl(s)$ and 1.0 L H_2O at 25°C and 1 atm

____

(v) $H_2O(l) \rightarrow H_2O(g)$ at 100°C and 1 atm

____

(f) The answer to (e) part (v) is somewhat ambiguous. If a pure solid is at its normal melting point or if a pure liquid is at its normal boiling point, there is no preferred direction for the process because the two phases are in a state of _________________________ in which they are interconverting at the same rate.

(g) As seen in Figure 19.3, spontaneity can depend on ________________________.
Ice melts at T > 0^oC and liquid water freezes at T < 0^oC.

(h) It is important to understand that just because a process or a reaction is thermodynamically favored, it does not necessarily mean that it will occur at an observable ______________. One example of a chemical reaction that is spontaneous at room temperature, but normally takes a long time to occur is the conversion of iron into _________________.

(i) Although the majority of spontaneous reactions are exothermic, there are some spontaneous endothermic processes that do occur. Two examples are the ______________________ of ice at room temperature and the ___________________ of solid ammonium nitrate (NH_4NO_3) in which, was mentioned on page 516 in your textbook.

(j) A nonspontaneous process can occur only if the __________________________ do work on the ___________________.

Section 19.2 – Entropy and the Second Law of Thermodynamics

(a) Entropy is associated with the extent of _______________________ in a system. Entropy can also be associated with the extent to which ____________________ is distributed among the various motions of the molecules of the system.

(b) The symbol ΔH refers to the change in _________________, and ΔS refers to the change in ________________.

NOTE: You do not need to worry about Equation 19.2 on page 790, and we will not do any calculations involving that equation.

The following information comes from the AP Chemistry Course and Exam Description.

- Entropy may be understood in qualitative terms rather than formal statistical terms. Although this is not the most rigorous approach to entropy, the use of qualitative reasoning emphasizes that the goal is for students to be able to make predictions about the direction of entropy change, ΔS^o, for many typical chemical and physical processes.

- Entropy increases when matter is dispersed. The phase change from solid to liquid, or from liquid to gas, results in a dispersal of matter in the sense that the individual particles become more free to move, and generally occupy a larger volume. Another way in which entropy increases in this context is when the number of individual particles increases when a chemical reaction proceeds whose stoichiometry results in a larger number of product species than reacting species. Also, for a gas, the entropy increases when there is an increase in volume (at constant temperature), and the gas molecules are able to move within a larger space.

- Entropy increases when energy is dispersed. From kinetic molecular theory, we know that the distribution of kinetic energy among particles of gas broadens as the temperature increases. This is an increase in the dispersal of energy, as the total kinetic energy of the system becomes spread more broadly among all of the gas molecules. Thus as temperature increases, the entropy increases.

(c) Predict the sign of ΔH and ΔS for each phase change. Consider each change from the point of view of the system.

Phase change	sign of ΔH	sign of ΔS
melting (at the normal MP)		
freezing (at the normal MP)		
evaporation (at the normal BP)		
condensation (at the normal BP)		

Section 19.3 – Molecular Interpretation of Entropy

With respect to ΔS, all you need to know is the following information.

The entropy of the system increases (i.e., positive ΔS) when any of the following changes occur.

- The volume of a gas increases (at constant temperature).
- The temperature increases.
- The number of molecules increases.
- The state of matter changes from solid to liquid, from liquid to solid, or from solid to gas.
- A solid dissolves in a solvent to form a solution.

NOTE: You don't have to understand the Boltzmann equation or the concept of microstates. You do not need to worry about Equations 19.5 and 19.6 on page 795, and we will not do any calculations involving those equations.

(a) According to the information in Figure 19.10, when an ionic solid dissolves in water, the entropy of the ions in the crystal lattice (decreases increases) because the ions become more spread out and possess more energy of motion. On the other hand, the entropy of the water molecules (decreases increases) because some of the water molecules have lost freedom of motion when forming ion-dipole interactions with the solute.

(b) For each of the following changes, decide if the entropy of the system is increasing or the entropy is decreasing. Predict the sign of ΔS.

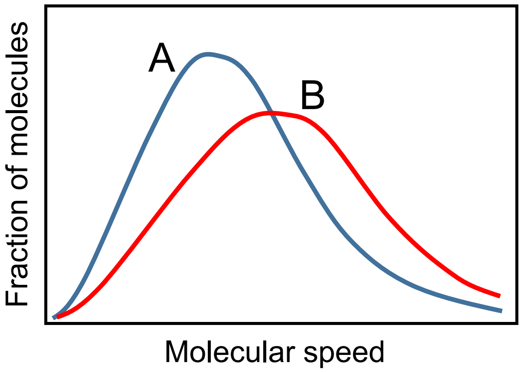
Change	sign of ΔS
$Fe(s) \rightarrow Fe(l)$	
$Br_2(g) \rightarrow Br_2(l)$	
$C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq)$	
$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$	
$N_2O_4(g) \rightarrow 2\ NO_2(g)$	

(c) According to the third law of thermodynamics, the entropy of a pure crystalline substance at absolute zero is equal to _____________.

Section 19.4 – Entropy Changes in Chemical Reactions

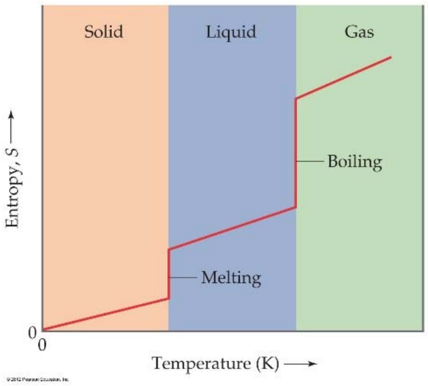
(a) We know that entropy (decreases increases) when the temperature of the system is increased.

(b) Which curve (A or B) represents a sample of gas that has higher entropy? Explain.



See a similar diagram to this one by looking at Figure 10.17 on page 403

(c) Explain why there are vertical jumps in the graph shown at right at the melting and boiling points, even though there is no change in the absolute temperature of the substance.



(d) The values for the standard molar entropy (S^o) of various substances can be found in Table 19.1 on page 801 and in Appendix C on page 1059.

(i) What units are normally used for S^o? _____________

(ii) The standard enthalpy of formation (ΔH_f^o) and the standard entropy (S^o) both involve the superscript "o". What does it mean when a symbol carries a superscript "o" ?

____

(e) Enthalpies of formation (ΔH_f^o) of elements at 298 K (are are not) equal to zero.

Standard molar entropies of elements at 298 K (are are not) equal to zero.

(f) The standard molar entropy for a gaseous substance is (smaller greater) than the value of S^o for the corresponding liquid or solid.

(g) Standard molar entropies generally (decrease increase) with increasing molar mass and with an increasing number of atoms in the formula of a substance.

(h) Write Equation 19.8, found on page 802: ____

(i) Use the values of S^o in Appendix C to calculate ΔS^o for the following reaction. Does the sign of ΔS^o for this reaction make sense? Explain.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

(j) Use the values of S° in Appendix C to calculate ΔS° for the following reaction. Does the sign of ΔS° for this reaction make sense? Explain.

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(g)$$

NOTE: You don't need to worry about Equation 19.9 on page 803, and we won't do any calculations involving this equation.

Section 19.5 – Gibbs Free Energy

(a) When $NH_4NO_3(s)$ dissolves in water, the sign of ΔH° is (negative positive) because the process is (endothermic exothermic).

The sign of ΔS° for this process is (negative positive) because the ions in the solid crystal have more freedom to move around when the solid dissolves in water.

(b) When Na(*s*) and $Cl_2(g)$ react to form NaCl(*s*), the sign of ΔH° is (negative positive) because the process is (endothermic exothermic).

The sign of ΔS° for this process is (negative positive) because the particles of solid have less freedom of movement than the particles of a gas.

(c) Write Equation 19.12, found on page 804: ____

(d) The sign of ΔG for a chemical or physical process gives us valuable information about whether or not a process is spontaneous (thermodynamically favored) under a certain temperature and pressure.

If ΔG < 0, the reaction is ____________________________ in the forward direction.

If ΔG = 0, the reaction is at __________________________.

If ΔG > 0, the reaction is ____________________________ in the forward direction. Work must be done in order to make it occur. The reverse reaction is ____________________________.

(e) In any spontaneous process carried out at constant temperature and pressure, the free energy always __________________.

(f) When $Q < K$, the reaction proceeds spontaneously toward the (left right)

until equilibrium is achieved.

When $Q > K$, the reaction proceeds spontaneously toward the (left right)

until equilibrium is achieved.

When $Q = K$, the reaction has achieved equilibrium.

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g) \qquad \Delta H^o = -196.6\ kJ \quad \Delta S^o = -189.6\ J/K$$

(g) Use the Gibbs free energy equation to calculate the value of ΔG^o for the reaction shown above. Pay attention to units, because the units of ΔH^o and ΔS^o are not the same.

This reaction (is isn't) thermodynamically favored at 298 K because the sign

of ΔG^o is (negative positive).

(h) Which of the following statements is most likely to be true regarding the reaction shown in part (g)?

_______ The reaction is driven by ΔH^o.

_______ The reaction is driven by ΔS^o.

_______ The reaction is driven by both ΔH^o and ΔS^o.

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H^o = +26\ kJ \qquad \Delta S^o = +108.7\ J/K$$

(i) Use the Gibbs free energy equation to calculate the value of ΔG^o for the reaction shown above. Pay attention to units, because the units of ΔH^o and ΔS^o are not the same.

This reaction (is isn't) thermodynamically favored at 298 K because the sign of

ΔG^o is (negative positive).

(j) Which of the following statements is true regarding the reaction shown in part (i)?

_______ The reaction is driven by ΔH^o.

_______ The reaction is driven by ΔS^o.

_______ The reaction is driven by both ΔH^o and ΔS^o.

(k) Write Equation 19.14, found on page 806: ____

(l) Use the data table in Appendix C (page 1059) to find the values of ΔG_f^o for $SO_2(g)$ and $SO_3(g)$. By definition, ΔG_f^o for $O_2(g)$ = 0 kJ/mol. Use this information and Equation 19.14 to calculate the value of ΔGº for this reaction: $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$

The following information comes from the AP Chemistry Course and Exam Description.

- The phrase “thermodynamically favored” means that products are favored at equilibrium (K > 1).
- Historically, the term “spontaneous” has been used to describe processes for which $\Delta G^o < 0$. The phrase “thermodynamically favored” is used here to avoid misunderstanding and confusion that can occur because of the common connotation of the term “spontaneous,” which students may believe means “immediately” or “without cause.”
- In those cases where $\Delta H^o < 0$ and $\Delta S^o > 0$, there is no need to calculate ΔGº in order to determine that the process is thermodynamically favored.
- The fact that a process is thermodynamically favored does not mean that it will proceed at a measurable rate.
- Any process in which both $\Delta H^o > 0$ and $\Delta S^o < 0$ is not thermodynamically favored and the process must favor reactants at equilibrium (K < 1)
- When $\Delta G^o > 0$, the process is not thermodynamically favored.
- When $\Delta G^o < 0$, the process is thermodynamically favored.

Section 19.6 – Free Energy and Temperature

(a) If ΔHº is negative and ΔSº is positive for a certain process, then the sign of ΔGº for this process must be (negative positive) and this process must be thermodynamically favored at all temperatures.

(b) On the other hand, if ΔHº is positive and ΔSº is negative for a certain process, then the sign of ΔGº for this process must be (negative positive) and this process would NOT be thermodynamically favored at any temperature. In fact, the reverse process would be favored.

(c) If ΔHº is negative and ΔSº is negative for a certain process, this process would be

thermodynamically favored at ________ temperatures and would not be favored at

__________ temperatures.

(d) If ΔHº is positive and ΔSº is positive for a certain process, this process would be

thermodynamically favored at ________ temperatures and would not be favored at

__________ temperatures.

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g) \qquad \Delta H^o = -196.6\text{ kJ} \quad \Delta S^o = -189.6\text{ J/K}$$

(e) Use the Gibbs free energy equation to calculate the following. Assume that the values of ΔH and ΔS do not change with temperature.

ΔG for this reaction at 750 K ____

ΔG for this reaction at 1250 K ____

(f) Since ΔG = zero when a reaction is at equilibrium, calculate the temperature at which the reaction in part (e) would achieve equilibrium.

	ΔH_f^o	S^o
$Br_2(l)$	0 kJ mol^{-1}	152.3 J mol^{-1} K^{-1}
$Br_2(g)$	30.71 kJ mol^{-1}	245.3 J mol^{-1} K^{-1}

(g) Calculate ΔHº and ΔSº for the following process: $Br_2(l) \rightarrow Br_2(g)$

(h) At equilibrium, ΔG = zero. When a pure substance is at its normal boiling point, equilibrium is achieved. Estimate the normal boiling point of Br_2.

Verify your answer to part (h) by looking at Figure 11.5 on page 429.

(i) Predict if the evaporation of Br_2 should be thermodynamically favored at 200 K. Confirm your prediction by calculating the value of ΔG for the process $Br_2(l) \rightarrow Br_2(g)$ at 200 K. Assume that the values of ΔH and ΔS do not change with temperature.

Section 19.7 – Free Energy and the Equilibrium Constant

	ΔH_f^o	S^o
$N_2(g)$	0 kJ mol^{-1}	191.5 J mol^{-1} K^{-1}
$H_2(g)$	0 kJ mol^{-1}	130.6 J mol^{-1} K^{-1}
$NH_3(g)$	–46.2 kJ mol^{-1}	192.5 J mol^{-1} K^{-1}

(a) Consider the following reaction: $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

(i) What is the value of ΔH° for this reaction? ________________________

(ii) What is the value of ΔS° for this reaction? ________________________

(iii) What is the value of ΔG° for this reaction? ________________________

(b) Write Equation 19.20, found on page 813: ________________________

(c) Use Equation 19.20 to calculate the value of *K* for the reaction $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ under standard conditions (298 K). The gas constant R = 8.314 J/mol-K. Pay attention to units, since ΔG° has units of kJ/mol_{rxn} and the value of R has units of J/mol-K

(d) If a reaction has a very small value of *K*, the reaction is said to be (reactant product)

favored and should have a ΔG° value that is (negative positive).

On the other hand, if a reaction has a very large value of *K*, the reaction is said to be

(reactant product) favored and should have a ΔG° value that is (negative positive).

(e) Suppose that a certain chemical reaction has a large value of *K* and a negative value of ΔGº. Does this imply that the reaction rate is fast or slow? Explain.

$$Cu_2S(s) \rightarrow 2\ Cu(s) + S(s) \qquad \Delta G^o = +86.2\ kJ$$

(f) Copper (can cannot) be obtained directly from Cu_2S through the reaction shown

above because this reaction (is isn't) thermodynamically favored to occur.

(g) If the reaction shown in part (f) is coupled to a favorable reaction such as the following

$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta G^o = -300.4\ kJ$$

then the overall reaction (obtained by adding these two reactions together) is thermodynamically favorable. Add these two reactions together and write the overall reaction. Calculate the overall value of ΔGº.to show that the overall reaction is thermodynamically favorable.

The following information comes from the AP Chemistry Course and Exam Description.

- Electricity may be used to cause a process to occur that is not thermodynamically favored. Useful examples are charging a battery and the process of electrolysis.

- Light may also be a source of energy for driving a process that in isolation is not thermodynamically favored. Useful examples include the following.
  - the photoionization of an atom
  - the conversion of carbon dioxide into glucose through photosynthesis

- A thermodynamically unfavorable reaction may be made favorable by coupling it to a favorable reaction, such as the conversion of ATP to ADP in biological systems. In this context, coupling means that the process involves a series of reactions with common intermediates, such that the reactions add up to produce an overall, reaction with a negative ΔGº.

	ΔH_f^o	S^o
$NaCl(s)$	–410.9 kJ mol^{-1}	72.3 J mol^{-1} K^{-1}
$Na^+(aq)$	–240.1 kJ mol^{-1}	59.0 J mol^{-1} K^{-1}
$Cl^-(aq)$	–167.2 kJ mol^{-1}	56.5 J mol^{-1} K^{-1}
$AgCl(s)$	–127.0 kJ mol^{-1}	96.1 J mol^{-1} K^{-1}
$Ag^+(aq)$	+105.9 kJ mol^{-1}	73.9 J mol^{-1} K^{-1}

(h) Use the thermodynamic data above to fill in the table below.

Process	ΔH°	ΔS°
$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$		
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$		

(i) Use the calculations from part (h) to fill in the table below.

Process	ΔG°	K_{sp}
$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$		
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$		

(j) Comparing the values of K_{sp} for NaCl and AgCl, we can see that the solubility of NaCl is much

(smaller greater) than the solubility of AgCl at 298 K.