Applications of Thermodynamics
9.1 Introduction to Entropy
9.2 Absolute Entropy and Entropy Change
Worksheet Key

1) Do the following processes produce an increase or a decrease in entropy?

a. $H_2O(l) \rightarrow H_2O(g)$ **Increase** – liquid to gas

b. $N(g) + O(g) \rightarrow NO(g)$ **Decrease** – fewer moles

c. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ **Decrease** – fewer moles

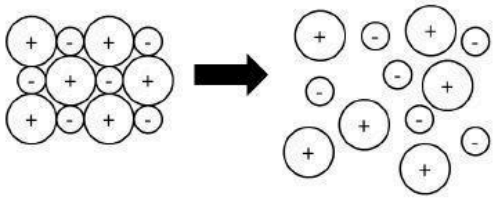
d. $C_8H_{18(g)} + 25\ O_{2(g)} \rightarrow 16\ CO_{2(g)} + 18\ H_2O_{(g)}$ **Increase** – more moles

e. $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ **Decrease** – fewer moles and gas to solid

f. $MgCl_2(s) + H_2O(l) \rightarrow MgO(s) + 2\ HCl(g)$ **Increase** – more moles and two moles of gas on the products side.

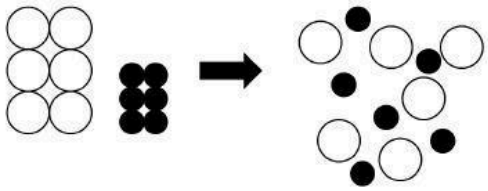
2) Is the sign for the entropy change associated with the following reactions or physical processes positive or negative?

a.



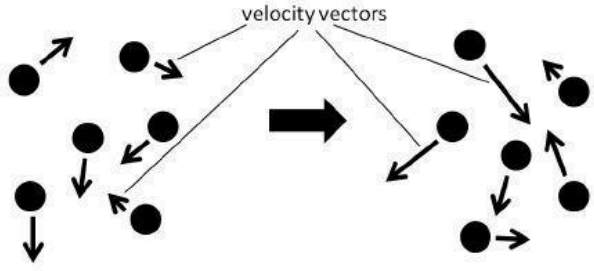
Positive

b.



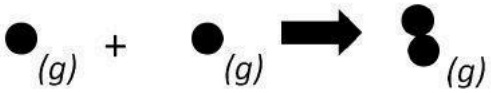
Positive

c.



Positive – The temperature of the system increased, as the velocity vectors indicate that the average velocity of the particles increased. The range in the amount of kinetic energy contained by the gaseous particles within a system broadens as the temperature increases (see Boltzmann distribution). Entropy increases when energy is dispersed.

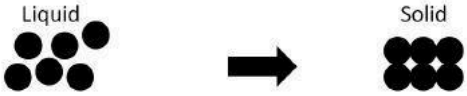
d.



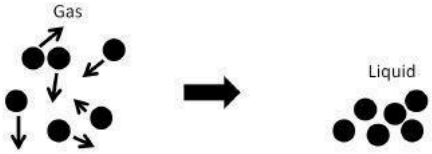
Negative

3) Which of the representations below depicts the most negative change in entropy? Justify your answer.

I.



II.



Representation (II) depicts the most negative change in entropy. Gases have very high entropy values, as gas particles have the greatest freedom to move and ideally they have no attractions for one another. This results in an extremely large number of possible arrangements. When a gas condenses, forces of attraction between particles are formed and randomness decreases. The change in entropy associated with the solidification of a liquid is less negative. See the slide titled "$\Delta S > 0$ when adding heat."

4) Find the entropy change, ΔS°, for the following reactions using the S° values in the appendix of your textbook.

a. $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [2(S^\circ\ H_{2(g)}) + (S^\circ\ O_{2(g)})] - [2(S^\circ\ H_2O_{(l)})]$$
$$\Delta S^\circ_{rxn} = [2(131\ J/K) + (205\ J/K)] - [2(69.9\ J/K)]$$
$$\Delta S^\circ_{rxn} = +327\ J/molK$$

b. $8\ Fe(s) + 6\ O_2(g) \rightarrow 4\ Fe_2O_3(s)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [4(S^\circ\ Fe_2O_{3(s)})] - [8(S^\circ\ Fe_{(s)}) + 6(S^\circ\ O_{2(g)})]$$
$$\Delta S^\circ_{rxn} = [4(89.96\ J/K)] - [8(27.15\ J/K) + 6(205.0\ J/K)]$$
$$\Delta S^\circ_{rxn} = -1087.4\ J/molK$$

c. $2\ CH_3OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(g)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [2(S^\circ\ CO_{2(g)}) + 4(S^\circ\ H_2O_{(g)}] - [2(S^\circ\ CH_3OH_{(s)}) + 3(S^\circ\ O_{2(g)})]$$
$$\Delta S^\circ_{rxn} = [2(214\ J/K) + 4(189\ J/K)] - [2(240\ J/K) + 3(205.0\ J/K)] = 89\ J/molK$$

d. $2\ NiS(s) + 3\ O_2(g) \rightarrow 2\ SO_2(g) + 2\ NiO(s)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [2(S^\circ\ SO_{2(g)}) + 2(S^\circ\ NiO_{(s)}] - [2(S^\circ\ NiS_{(s)}) + 3(S^\circ\ O_{2(g)})]$$
$$\Delta S^\circ_{rxn} = [2(248\ J/K) + 2(38\ J/K)] - [2(53\ J/K) + 3(205\ J/K)]$$
$$\Delta S^\circ_{rxn} = -149\ J/molK$$

e. $Al_2O_3(s) + 3\ H_2(g) \rightarrow 2\ Al(s) + 3\ H_2O(g)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [2(S^\circ\ Al_{(s)}) + 3(S^\circ\ H_2O_{(g)}] - [3(S^\circ\ H_{2(g)}) + (S^\circ\ Al_2O_{3(g)})]$$
$$\Delta S^\circ_{rxn} = [2(28\ J/K) + 3(189\ J/K)] - [3(131\ J/K) + (51\ J/K)]$$
$$\Delta S^\circ_{rxn} = 179\ J/molK$$

f. $2\ CH_3OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(l)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [2(S^\circ\ CO_{2(g)}) + 4(S^\circ\ H_2O_{(l)}] - [2(S^\circ\ CH_3OH_{(s)}) + 3(S^\circ\ O_{2(g)})]$$
$$\Delta S^\circ_{rxn} = [2(214\ J/K) + 4(69.9\ J/K)] - [2(240\ J/K) + 3(205\ J/K)]$$
$$\Delta S^\circ_{rxn} = -387\ J/molK$$

g. $2\ CO(g) + 2\ NO(g) \rightarrow 2\ CO_2(g) + N_2(g)$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = [2(S^\circ\ CO_{2(g)}) + (S^\circ\ N_{2(g)})] - [2(S^\circ\ CO_{(g)}) + 2(S^\circ\ NO_{(g)})]$$
$$\Delta S^\circ_{rxn} = [2(213.6\ J/molK) + (191.5\ J/molK)] - [2(197.6\ J/molK) + 2(210.7\ J/molK)]$$
$$\Delta S^\circ_{rxn} = 618.7\ J/molK - 816.6\ J/molK$$
$$\Delta S^\circ_{rxn} = -197.9\ J/molK$$

5) Explain why the reaction in question (4.d.) has a negative ΔS° value whereas the reaction in (4.c.) has a positive ΔS° value.

The products in reaction (4d) are much more ordered than the reactants. The reactants are composed of five moles of gas, and the products are composed of two moles of gas and four moles of liquid. Less disorder on the products side yields a negative ΔS° value. The products in reaction (4c) are less ordered than the reactants. The reactants are composed of five moles of gas, and the products are composed of six moles of gas. More

disorder on the products side yields a positive ΔS^{o} value.

6) The following questions pertain to the dissolving of solid NaCl in water.
   a. Is the ΔS value for the dissolving of NaCl positive, negative, or zero?

ΔS is positive for the dissolving of NaCl*(s)*.

   b. Does the entropy increase or decrease during the dissolving process? Justify your answer by describing the changes in entropy that occur during the dissolving process.

The entropy increases. Solid NaCl is a highly organized network of sodium and chloride ions. When it dissolves in water, that highly organized network breaks up into individual Na^{+} and Cl^{-} ions that are free to move around within the solution. The entropy increases as we start with a highly organized solid and end up with a very random and constantly changing arrangement of ions in a solution.