Name ____________________________ **Chem 163 Section**: ______ **Team Number:** ______

ALE 19. Entropy

(Reference: 20.1 Silb*erberg 5th edition*)

When a system changes, does it become more disordered?

The Model: Number of Particles and Disorder

In *Chem 161*, we learned about enthalpy (*H*, "heat content") and changes in enthalpy (ΔH) for a chemical reaction. While *most* spontaneous reactions involve heat being liberated from the chemical system and released to the surroundings of the system (*i.e.*, $\Delta H < 0$), not *all* spontaneous reactions are exothermic. To fully understand what causes a process to be spontaneous, we must know more than just the direction of the flow of energy between the system and its surroundings. We must also know whether the system becomes less or more disordered as a result of the process.

Entropy is the thermodynamic quantity that represents how much disorder there is within a system. Entropy is represented by *S* and the entropy for a *given* number of particles has units of J/K. The **molar entropy** for a *variable* amount of a substance has units of J mol^{-1} K^{-1}.

Key Questions

1 a. Have you ever had the pleasure of babysitting? Imagine the amount of chaos there is when you are babysitting one child. Compare that to the amount of chaos there is when (in the same house as before) you are now babysitting two children. Now think about three (or even more) children. As the number of children in the house increases, the disorder within the house…. decreases/remains constant/increases. (Circle your choice.) And NO! While you may be tempted to put the kiddies in straight jackets or cages or even sedating the rug rats with drugs, their parents would not appreciate that.)

b. Now extend this analogy to a chemical system. As the number of particles in a system increases, the entropy of the system decreases/remains constant/increases. (Circle your choice.)

2. In the stratosphere (the region extending from roughly 10 to 30 miles above the Earth's surface), molecular oxygen combines with atomic oxygen to form ozone according to eqn **1**.

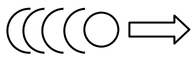
$$O_2(g) + O(g) \rightarrow O_3(g) \qquad (1)$$

Based *qualitatively* (*i.e.*, without performing any calculation) on how the entropy of the system changes when the reaction takes place, determine whether this reaction is thermodynamically favorable or not. *Briefly explain your answer*. (Does the disorder of the system decrease or increase? In your experience, do spontaneous processes occur when the disorder of the system changes in that way?)

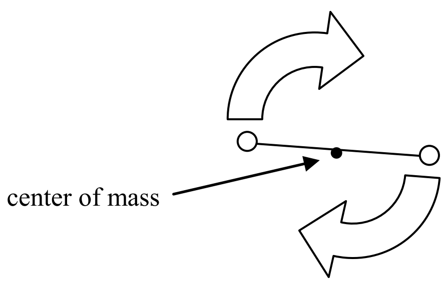
The Model: Molecular Motion and Disorder

The entropy of a chemical system is proportional to the total number of ways that the particles have of moving. The three types of movement are: translational motion, rotational motion and vibrational motion. ,

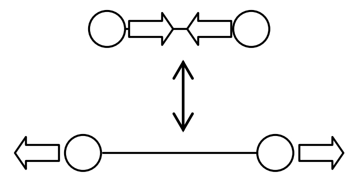
Translational motion



Rotational motion



Vibrational motion



The more ways that the particles within a chemical system can move, the more entropy the system will have. It is also possible that excited electronic states of a system are populated, and this further contributes to the system's entropy.

Key Questions

3. Since the noble gases are monatomic species, translational motion is the major type of motion that contributes to their entropies. The entropy of 1 mol of each noble gas at 25 °C and 1 atm is shown to the right. If they all have the same number of *atoms*, why do the noble gases have different entropies?

Gas	$\boldsymbol{S}°$(J/mol·K)
He	126
Ne	146
Ar	155
Kr	164

4. Many students may unfortunately have responded to Question 3 by referring to the gases' molar masses. Consider the entropies of sodium bromide and sodium nitrate. Why does sodium nitrate have a greater molar entropy than sodium bromide? (*Hint*: Nitrate is a polyatomic anion.)

Salt	**Molar mass** (g/mol)	$\boldsymbol{S}°$ (J mol^{-1} K^{-1})
NaBr(*s*)	102.9	86.8
$NaNO_3$(*s*)	85.0	116.5

5. The following table gives the standard molar entropies of the three phases for various substances at 25°C.

Substance	$S°$ (J mol^{-1} K^{-1}) Solid	Liquid	Gas
Ga	40.8	59.3	169.0
NaCl	72.1	95.1	229.8
ICl	97.9	136.2	247.6
KCN	127.8	134.3	253.2

Substance	$S°$ (J mol^{-1} K^{-1}) Solid	Liquid	Gas
SrF_2	258.2	294.3	416.4
SO_3	52.3	95.6	256.7
SiI_4	258.2	294.3	416.4
N_2O_4	150.4	209.2	304.4

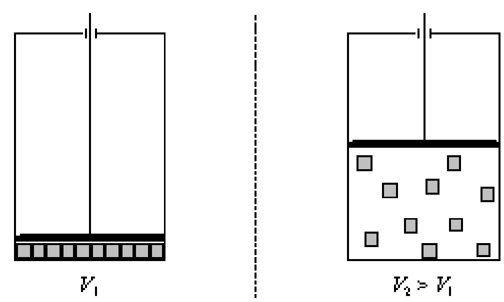
a. Recall how the Kinetic-Molecular Theory distinguishes a solid from a liquid from a gas. What types of motion do the "molecules" have within a solid? Within a liquid? Within a gas?

	Translational	**Rotational**	**Vibrational**
Solid	❑	❑	❑
Liquid	❑	❑	❑
Gas	❑	❑	❑

b. For those substances tabulated above, the entropy increases by (an average of) 34% when a solid is melted at 25 °C. But when a liquid is evaporated at 25 °C, the entropy increases by (an average of) 99%. Why is there such a tremendous difference in entropy between a liquid and its corresponding gas at the same temperature?

6. Now let's consider the expansion of a (gaseous) system into a larger volume without a change in the number of particles. For our system, we consider a cylinder with a piston that contains 10 molecules (represented by □'s.

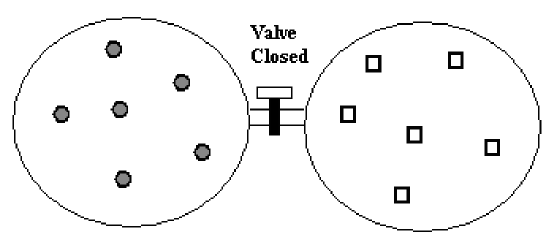
In addition to being proportional to the number of ways that particles can move, entropy is proportional to the number of ways the particles of a system can be distributed in space with respect to each other.



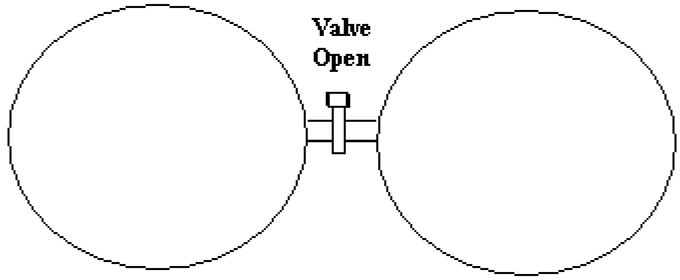
a. Which has more entropy: the gas system at <u>Volume 1</u> or <u>Volume 2</u>? (Circle your answer.)

b. Which would be "harder" for you (*i.e.*, which would be more chaotic?): babysitting 10 children in a <u>900-square-foot home</u> or the same 10 children in a <u>3000-square-foot home</u>?

7. Now let's consider the formation of an **ideal solution** (*i.e.*, a mixture in which the strength of intermolecular forces is the same after the mixing process as they were before the process). Imagine two glass bulbs are connected with the valve closed and six molecules in each bulb. Then the valve is opened.



7a. Complete the drawing of the system once the stopcock is opened and the system reaches a material equilibrium.



b. In which state does the system have more disorder, before or after the gases mixed? *Explain your answer*. (*Hint*: Look back to Question 6.)

8. Consider the following reactions of combinations of diatomic elements to form diatomic compounds at 25 °C and 1 atm.

Reaction	**$\Delta S°$ (J mol^{-1} K^{-1})**
$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$	14.1
$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$	24.9
$I_2(g) + Cl_2(g) \rightarrow 2\ ICl(g)$	11.5

In all cases (and many other examples not shown) there is no change in the number of moles of gaseous particles, and the reactions are taking place without a change in volume. So why is there consistently an *increase* in the entropy of the system?

9. Of translational, rotational, and vibrational motion, translational states are the easiest to excite by the addition of thermal energy. At low temperatures, molecules barely rotate or vibrate. According to the Kinetic-Molecular Theory of gases, the root-mean-square (rms) speed ("translational velocity") of a gas molecule of a compound with molar mass ***M*** at absolute temperature ***T*** is given by eq **2**.

$$v_{rms} = \sqrt{\frac{3RT}{M}} \qquad \textbf{(2)}$$

a. As the temperature of a gaseous system is reduced, what happens to the system's
(i.) rms speed?

(ii.) entropy?

b. If a gaseous system is reduced to absolute zero, what does the entropy of the system reduce to? *Explain*.