Entropy: Let the chaos begin!

Entropy can be considered the extent of randomness or disorder in a chemical or physical system.

- The second law of thermodynamics states that entropy of the universe will increase over time.
  - + ΔS implies increasing entropy and – ΔS implies decreasing entropy
  - Nature tends towards + (increasing) entropy!
- The more positions available (the more space, or more places something can move) the greater the entropy.

The entropy change for a system (Δ) is calculated from the absolute entropies of the products and reactants.

$$\Delta S^{\circ}_{system} = \sum[S^{\circ}(\text{products})] - \sum[S^{\circ}(\text{reactants})]$$] on F.C. ☺

Units of Entropy: $\frac{J}{mol \cdot K} = J \cdot mol^{-1} \cdot K^{-1}$

Entropy of an element in its most stable form is NOT zero!

- The third law of thermodynamics states that the entropy of a perfect, pure crystal at zero K is given a value of zero.
- Thus, all absolute entropies for substances in the real world (above 0 K, not a pure substance, not perfect crystals) are + → even elements!

Two biggest factors for evaluating ΔS_{rxn}

1) Change in State of matter (gas >> aqueous > liquid > solid)
2) Change in # of particles (↑ particles = ↑ places for particles to be = ↑ entropy)

Entropy Relationships

increased entropy! (more possible positions = more disorder)

high entropy

↑ ΔS

low entropy

gas

↑

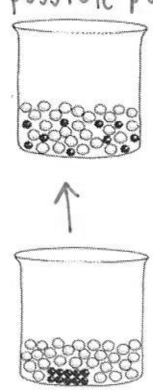
aqueous

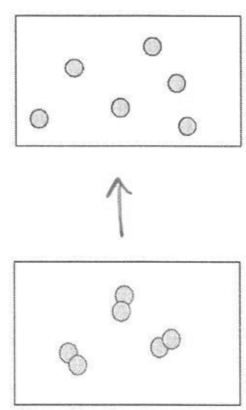
↑

liquid

↑

solid





decreased entropy

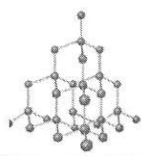
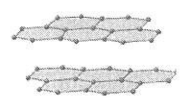
In order of lowest to highest entropy:

Solids < Liquids < Aqueous solutions << Gases < More moles of Gas

Rules for comparing entropy of individual molecules or materials:

- → Entropy ↑ with higher temperature: more motion, more possible arrangements
- → Entropy ↑ if substance dissolves in a solvent: more possible arrangements
- → Entropy of a gas:
  - ↓ with ↑ pressure
  - ↑ with ↑ volume
- → Entropy is ↑ for weakly bonded compounds than for very strong covalent bonds: atoms have more wiggle room, more positional entropy
- → Entropy ↑ as the complexity (# of atoms, # of heavier atoms, # of e^-, etc) of a molecule ↑

Examples:

Less Entropy	More Entropy	Why?
diamond 	graphite 	Graphite has fewer bonds, more possible arrangements
butane gas (2 atm)	butane gas (1 atm)	Decreasing gas pressure increases volume, allowing more possible positions
$F_2(g)$	$Cl_2(g)$	$Cl_2(g)$ has more electrons/molar mass than $F_2(g)$, thus more possible arrangements of particles

Practice:

1) For the following reactions, is the entropy of the reaction *increasing* or *decreasing*?

a. $2\ NO_2(g) \rightarrow N_2O_4(g)$ Entropy is decreasing Why? decreasing # of particles

b. $H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$ Entropy is about the same Why? no change in state or # of particles

c. $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$ Entropy is increasing Why?

solid + aqueous (reactants) changed to aqueous, liquid, + gas (products)

2) Place the following in order of increasing entropy:

a) methane (CH_4), propane (C_3H_8), ethane (C_2H_6) CH_4, C_2H_6, C_3H_8 (↑ # atoms = ↑ S)

b) NaCl(s), LiCl(s), RbCl(s), KCl(s) LiCl, NaCl, KCl, RbCl (↑ MM/# e^- = ↑ S)

c) O_2 (1 atm), O_2 (3 atm), O_2 (0.25 atm) 3 atm, 1 atm, 0.25 atm (↓ P = ↑ V = ↑ S)