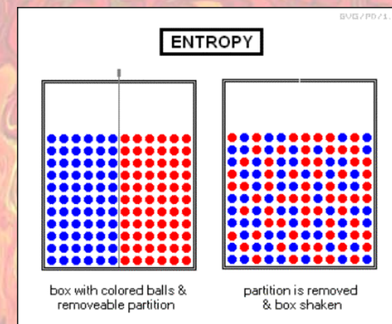
Thermodynamic Laws

- The 1st Law of Thermodynamics:
  - Energy can be converted from one form to another, but cannot be created or destroyed (energy of the universe is constant)
- The 2nd Law of Thermodynamics:
  - The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process (the entropy of the universe is increasing)
- The 3rd Law of Thermodynamics:
  - The entropy of a perfect crystalline substance is zero at absolute zero

Reference: Chemistry 7th ed., Chang, Chemistry 7th ed., Zumdahl

Entropy

- **Entropy (S or ΔS):** a measure of the degree of disorder



Entropy

- Nature is always moving toward higher entropy (more disorder…look at your bedroom for an example of this)
- **High S** ⟷ **Low S**

Gas — Liquid/Aq. — Solid

How would a crystalline solid vs. noncrystalline solid compare?

Entropy

- $\Delta S = \Sigma S_{products} - \Sigma S_{reactants}$
- A positive change in entropy (increase) promotes spontaneous reactions
- Units for S are typically $\frac{J}{mol \bullet K}$ (be careful with units!)

Entropy Example

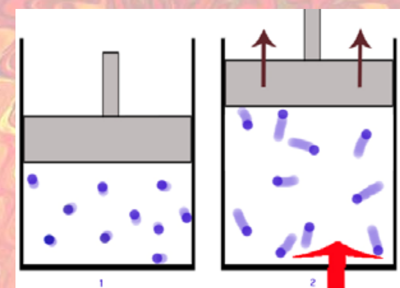
Calculate ΔS for the following reaction:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

Substance	**S (J/mol•K)**
CH_4	186.3
O_2	205.0
CO_2	213.6
H_2O	69.91

Gibbs Free Energy

- **Free energy**: capacity of a system to do work



- Useful in predicting if a reaction is ***spontaneous***

What is spontaneity?

- **spontaneous reaction**: a chemical reaction that occurs without any outside energy
- *Example:*
  - At room temperature:
    - Spontaneous: ice → liquid water
    - Not spontaneous: liquid water → ice

Why do we care about spontaneity?

- It is almost impossible to know details about every chemical reaction and determine if a reaction will occur on its own
- *Examples:*
  - Does NaOH decompose spontaneously? Can you store it in the chemical store room with other chemicals or does it need a special environment?
  - Why is hydrogen peroxide (H_2O_2) stored in a brown opaque bottle? Could it be that when exposed to light H_2O_2 spontaneously decomposes?

Spontaneity can be predicted using the Gibbs Free Energy equation

Gibbs' Free Energy Equation

$\Delta G = \Delta H - T\Delta S$

Δ G = Gibbs Free Energy
Δ H = heat or enthalpy
T = temperature (in KELVIN: K = °C + 273.15)
Δ S = entropy

$\Delta G > 0$ ➔ reaction is NOT spontaneous
$\Delta G < 0$ ➔ reaction is spontaneous

- *Note: Units for ΔH are usually kJ and units for ΔS are usually J – be sure to convert!*
- (named after Josiah Gibbs, a pioneer in thermodynamics in the late 1800's)

Gibbs Free Energy Cont.

How enthalpy and entropy are related to spontaneity

$\Delta G = \Delta H - (T\Delta S)$

ΔH	ΔS	Spontaneity
- (exo)	+ (disordering)	Always (at all temps.) spontaneous (ex. Zn in HCl)
- (exo)	- (ordering)	Only at low temps. (ex. Freezing water)
+(endo)	+ (disordering)	Only at high temps. (ex. Decomp of Baking Soda)
+ (endo)	- (ordering)	Never spontaneous (ex. Photosynthesis)

Reminder: If heat/energy is a product ΔH is negative

Gibbs Free Energy Example

Calculate the free energy change for the formation of NO*(g)* from N_2*(g)* and O_2*(g)* at 298K given ΔH=180.7 kJ and ΔS=24.7 J/K. Is the reaction spontaneous under these circumstances?

$N_2\,(g) + O_2\,(g) \rightarrow 2NO\,(g)$