Chapter 16 Spontaneity, Entropy and Free Energy

1st law of thermodynamics:
- Energy can not be created or destroyed
- Energy of universe is constant

Spontaneous process:
- Process that occurs without outside intervention
- May be fast or slow reaction
  - Combustion is usually fast
  - Conversion of diamond to graphite is slow

Entropy (S):

A measure of the randomness or disorder of particles

Is the driving force for spontaneous rxn or process

For process to be spontaneous entropy must increase

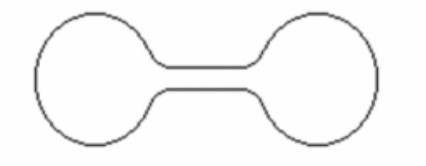
Must be positive in value

$S_{solid} < S_{liquid} < S_{gas}$

Unit of measure: J/K· mol

Describes the number of arrangements (positions or energy levels of particles) that are available to a system in a given state.

Known as positional entropy:



#molecules	probability all molecules on one side of container
1	½
2	½ x ½ = ¼ $(1/2)^2$
3	½ x ½ x ½ = 1/8 $(1/2)^3$
4	½ x ½ x ½ x ½ = 1/16 $(1/2)^4$
5	½ x ½ x ½ x ½ x ½ = 1/32 $(1/2)^5$
10	$(1/2)^{10}$ = 1/1024
n	$(1/2)^n$

2nd law of thermodynamics:

In any spontaneous process there is always an increase in the entropy of the universe.

Entropy of the universe is increasing

For a given change to be spontaneous, ΔS_{univ} must be positive

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

Entropy changes in surroundings are primarily determined by the heat flow (enthalpy).

Exothermic rxn in a system at constant temp. increase the entropy of the surroundings.

ΔS_{surr} = positive

S = +

Endothermic rxn in a system at constant temp. decrease the entropy of the surroundings.

ΔS_{surr} = negative

S = −

The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures.

Δ entropy is + for spontaneity

$$\Delta S_{surr} = - \frac{\Delta H}{T \text{ (Kelvin)}}$$

Use negative sign for the surroundings (means heat leaves system). exothermic

Positive sign for the system (means heat goes into system). endothermic

3rd law thermodynamics:

Entropy of perfect crystal is 0 at 0 K.

The more complex the molecule the higher the entropy value.

For a rxn:

$$\Delta S_{rxn} = \Sigma S_{prod.} - \Sigma S_{react.}$$

$$\Delta H = \sum H_{prod.} - \sum H_{react}$$

Dependence of Spontaneity on Temperature

ΔS	ΔH	Results
Positive	Negative	Spontaneous at ***all*** temperatures
Positive	Positive	Spontaneous at ***high*** temperatures
Negative	Negative	Spontaneous at ***low*** temperatures
Negative	Positive	Not spontaneous at ***any*** temperature