Chapter 19 - Thermodynamics

The 1st and 2nd Laws of Thermodynamics

1st Law: The Conservation of Energy **(Chapter 6)**
(Energy is neither created nor destroyed)

2nd Law: Entropy is Not Conserved **(This Chapter)**
(A process is spontaneous when the entropy of the system plus the surroundings increase)

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

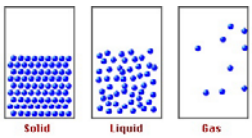
The Distinction Between Thermodynamics and Kinetics

Graphite is favored thermodynamically to form from Diamond, but the process has extremely slow kinetics.

The burning of paper is a spontaneous, *product-favored* reaction, and one that is kinetically acessible once reaction has begun.

Thermodynamics can predict if a process will occur, Kinetics describes how rapidly it will occur

Entropy, S



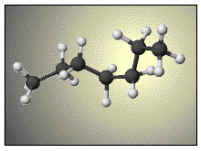
	S^o (J/K•mol)
H_2O(liq)	69.95
H_2O(gas)	188.8

S (gases) > S (liquids) > S (solids)

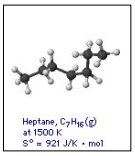
Entropy, S

Entropy of a substance increases with temperature.

Molecular motions of heptane, C_7H_{16}



Molecular motions of heptane at different temps.

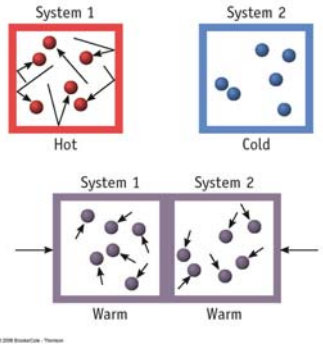


The Spreading (Dissipation) of Thermal Energy is Spontaneous

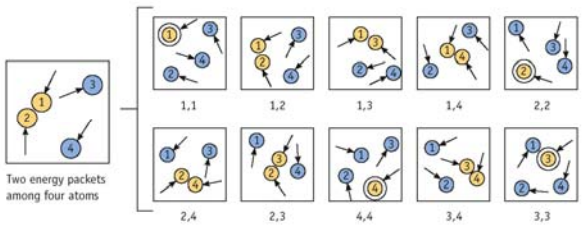
Thermodynamics *Systems* are used to keep track of matter and energy

System - A piece of the universe

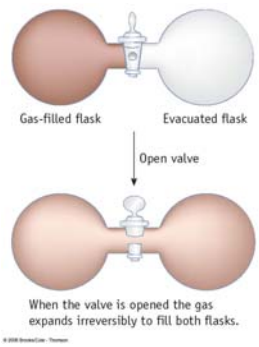
Surroundings - everything except the system



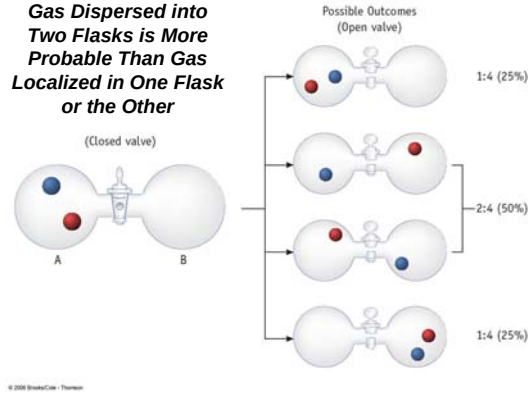
Spreading the Thermal Energy Among Two Particles is More Probable Than Placing All the Energy in One Particle



The Spreading of Molecules in Space Also Generates More Probable States



Gas Dispersed into Two Flasks is More Probable Than Gas Localized in One Flask or the Other



The Possible Combinations are Given by the Binomial Distribution

$(p + q)^n = 1$

p is the probability of a gas molecule in the left flask

q is the probability of a gas molecule in the right flask

n is the total number of gas molecules in the two flasks

Consider the distribution as n increases:

$n = 1$	$p + q$
$n = 2$	$p^2 + 2pq + q^2$
$n = 4$	$p^4 + 4p^3q + 6p^2q^2 + 6p^2q^2 + 4pq^3 + q^4$

The 1st Law: Tracking Energy Exchanges Between the System and the Surroundings

Electrical Motor:	Electrical Energy → Mechanical Work
Automobile Engine:	Chemical Energy → Mechanical Work
Steam Engine:	Thermal Energy → Mechanical Work

$$\Delta E = q + w$$

The Change in the Energy of the System (ΔE) equal to the heat transfer (q) and work (w)

$\Delta E = q$ (heat transfer, no work)

$\Delta E = w$ (work, no heat transfer)

$\Delta E = 0 \quad q = -w$ (heat transfer = - work)

Next Time - State Functions

What is a Thermodynamic State?

- When a system is at equilibrium, state variables have well-defined values.

What are Examples of State Variables?

- Temperature, Pressure, Volume, Enthalpy (H)
- Entropy (S) and Gibbs Energy (G) are also functions of state.

Changes in State Variables Depend Only on the Difference in the Values of the Initial and Final States.