THERMODYNAMICS

Entropy

Concepts about Entropy

#1 - a thermodynamic function that increases as the number of energetically equivalent ways of arranging the components increases, S.

- Units are usually J/mol K

Concepts about Entropy

#2 – Random systems are more energetically stable, lower energy, than ordered systems

Concepts about Entropy

#3 – Increase in entropy of the universe is the driving force for spontaneous reactions.

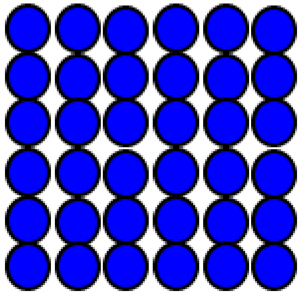
Concepts about Entropy

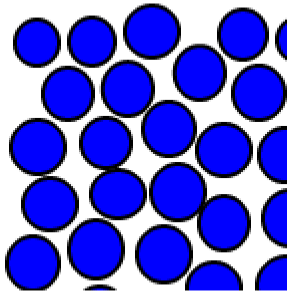
#4 – Nature proceeds toward the states that have the highest probabilities of existing.

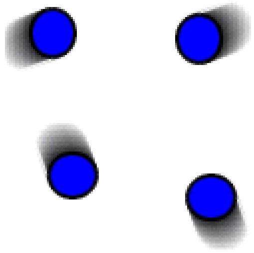
Positional Entropy

The probability of occurrence of a particular state depends on the number of ways (microstates) in which that arrangement can be achieved

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





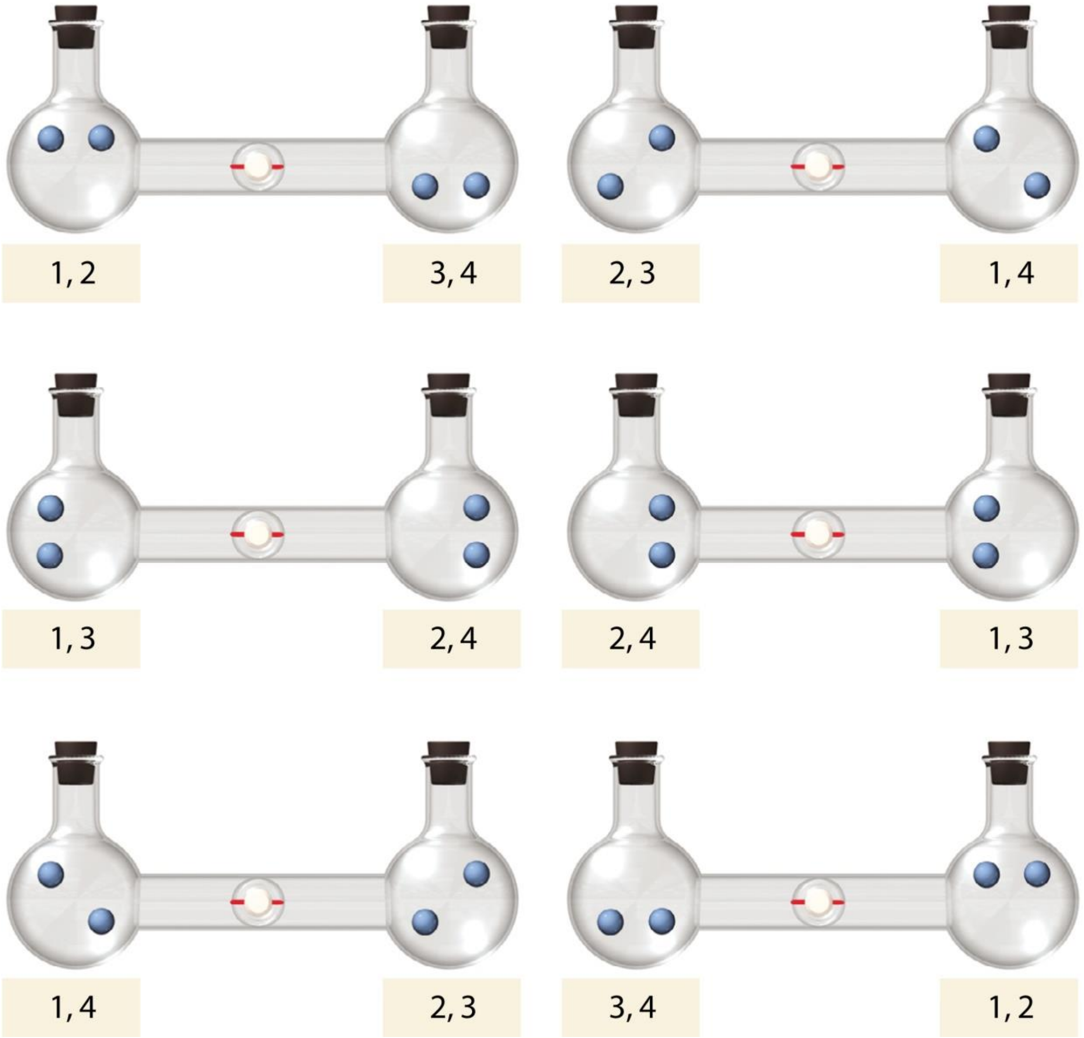


Macrostate State vs Microstate

- These microstates all have the same macrostate.

- So there are six different particle arrangements that result in the same macrostate.

- The individual unique particles make up the microstate, the overall “big picture” is the macrostate



Changes in Entropy

$$\Delta S = S_{final} - S_{initial}$$

Entropy change is favorable when the result is a more random system.

- When ΔS is positive.

Changes in Entropy

Some changes that increase entropy:

#1 - Rxn’s whose products are in a more random state

Changes in Entropy

Some changes that increase entropy:

#2 - Rxn’s that have larger numbers of product molecules than reactant molecules

Changes in Entropy

Some changes that increase entropy:

#3 - Rxn’s that have an increase in temperature (exothermic)

Changes in Entropy

Some changes that increase entropy:

#4 - Rxn’s that have solids dissociating into ions

Changes in Entropy - Examples

State of Matter

	$S°$(J/mol·K)
$H_2O(l)$	70.0
$H_2O(g)$	188.8

(at a particular temperature)

Changes in Entropy - Examples

Molar Mass

- The larger the molar mass, the larger the entropy.
- Seems a little counter intuitive…its complicated
  - Available energy states are more closely spaced, allowing more dispersal of energy through the states.

	$S°$ (J/mol·K)
He(g)	126.2
Ne(g)	146.1
Ar(g)	154.8
Kr(g)	163.8
Xe(g)	169.4

Changes in Entropy - Examples

Molecular Complexity

- Larger, more complex molecules generally have larger entropy. – *Larger/Complex doesn't always mean molar mass!*
- More energy states are available, allowing more dispersal of energy through the states.

	Molar Mass (g/mol)	S°(J/mol–K)
Ar(g)	39.948	154.8
NO(g)	30.006	210.8

	Molar Mass (g/mol)	S°(J/mol–K)
CO(g)	28.01	197.7
C_2H_4(g)	28.05	219.3

Changes in Entropy - Examples

Dissolution

- Dissolved solids generally have larger entropy, distributing particles throughout the mixture.

	S°(J/mol~K)
$KClO_3(s)$	143.1
$KClO_3(aq)$	265.7

2nd Law of Thermodynamics

The total entropy change of the universe must be positive for a process to be spontaneous

Reversible process - $\Delta S_{univ} = 0$
Irreversible spontaneous process - $\Delta S_{univ} > 0$

2nd Law of Thermodynamics

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

- If the entropy of the system ↓
  Then the entropy of the surroundings must ↑ by a larger amount.

2^{nd} Law of Thermodynamics

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

- When ΔS_{system} is negative, $\Delta S_{surroundings}$ must be positive and bigger for a spontaneous process.

Relating Entropy to Heat Energy

The entropy change in the surroundings is proportional to the amount of heat gained or lost.

$$q_{\text{surroundings}} = -q_{\text{system}}$$

(Equal but opposite sign)

(Sometimes it is easier to measure surroundings than the system, or vice versa – our lab experiments can exploit this fact sometimes to make our life more convenient.)

Relating Entropy to Heat Energy

The entropy change in the surroundings is also inversely proportional to its temperature.

At constant pressure and temperature:

$$\Delta S_{\text{surroundings}} = \frac{-q_{\text{system}}}{\text{T}} = \frac{-\Delta H_{\text{system}}}{\text{T}}$$

Standard Entropy Change, $\Delta S°$

Standard entropy change - the difference in absolute entropy between the reactants and products under standard conditions.

$$\Delta S^o_{reaction} = \sum n_p S^o_{products} - \sum n_r S^o_{reactants}$$

Remember - although the standard enthalpy of formation, $\Delta H_f°$, of an element is 0 kJ/mol, the absolute entropy at 25 °C, $S°$, is always positive, not zero!