17.1 - Entropy

BIG IDEA 5

The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.

Enduring understanding: Chemical or physical processes are driven by a decrease in enthalpy or an increase in entropy or both.

Thermodynamics versus Kinetics

Kinetics: Study of interactions between particles involved in a reaction.

　Rate of a reaction depends on the pathway from reactants to products.

Thermodynamics: Study of energetic transfer between particles.

　Provides information on whether a reaction is spontaneous based only on the properties of the reactants and products.

Spontaneous process: Occurs without external intervention, can be fast or slow.

Entropy (Symbol = S)

Thermodynamic function that describes the number of arrangements that are available to a system existing in a given state.

Measure of molecular randomness or disorder.

Colloquially, entropy is used to describe general disorder in a situation, like a messy bedroom.

The Expansion of an Ideal Gas into an Evacuated Bulb

Nature spontaneously proceeds toward the states that have the highest probabilities of existing.
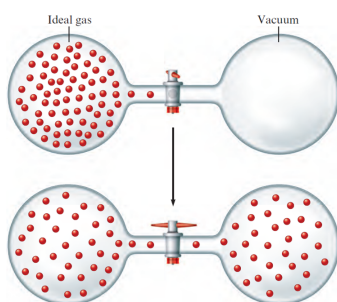
Microstates

Possible configuration of particles in a system are microstates. The more possible microstates, the greater the entropy value that the system has.
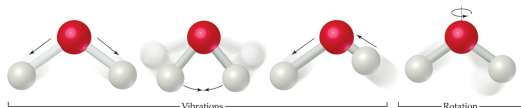
Entropy on the Molecular Scale

Molecules exhibit several types of motion:

Translational: Movement of the entire molecule from one place to another.

Vibrational: Periodic motion of atoms within a molecule.

Rotational: Rotation of the molecule on about an axis or rotation about s bonds.

Entropy on the Molecular Scale

The number of microstates and, therefore, the entropy tends to increase with increases in

Temperature.

Volume.

The number of independently moving molecules.

Positional Probability

Depends on the number of configurations in space that yield a particular state.

Gas expands into a vacuum to give a uniform distribution.

Expanded state has the highest positional probability of the states available to the system.

Positional entropy increases when going from solid to gaseous state.

S_{solid} < S_{liquid} ≪ S_{gas}

Positional Entropy and Solutions

Entropy change when mixing two pure substances is expected to be positive.

Result of the presence of more microstates for the mixed condition.

Caused due to the increased volume available to a given particle after mixing occur.

Formation of solutions is favored by an increase in positional entropy that is associated with mixing.

1. Positional Entropy Example

For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature and explain why.

A. 1 gram of solid CO_2 and 1 gram of gaseous CO_2.

Gaseous CO_2, particles are far apart.

B. 1 mole of N_2 gas at 1 atm and 1 mole N_2 gas at 1.0×10^{-2} atm.

N_2 gas at 1.0×10^{-2} atm - much bigger volume.

2. Predicting Entropy Change Example

Predict the sign of the entropy change for each of the following processes.

A. Solid sugar is added to water to form a solution.

Positive - as sugar dissolves particles are free to move around.

B. Iodine vapor condenses on a cold surface to form crystals.

Negative - greater order is established as crystals form.

Second Law of Thermodynamics

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

First law of thermodynamics:

Energy of the universe is constant,

Energy is conserved, entropy is not.

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

Changes in Entropy of the Universe

ΔS_{univ} is positive:

Entropy of the universe increases,

Process is spontaneous in the direction written.

ΔS_{univ} is negative:

Process is spontaneous in the opposite direction.

ΔS_{univ} is zero:

Process has no tendency to occur,

System is at equilibrium.

Entropy Changes in Surroundings

Entropy is a term coined by Rudolph Clausius in the 19th century.

Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered:

$$magnitude\ of\ entropy\ change\ of\ surroundings = \frac{q}{T}$$

Heat that flows into or out of the system changes the entropy of the surroundings.

For an isothermal (same temperature) process:

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

Entropy Changes in Surroundings (ΔS_{surr})

ΔS_{surr} is determined by flow of energy as heat.

Exothermic process increases ΔS_{surr}.

  Important driving force for spontaneity.

Endothermic process decreases ΔS_{surr}.

Impact of transfer of energy as heat to or from the surroundings is greater at lower temperatures.

Entropy Changes in Surroundings (ΔS_{surr})

Sign of ΔS_{surr} depends on the direction of the heat flow.

At constant temperature:

ΔS_{surr} for exothermic processes is positive,

ΔS_{surr} for endothermic processes is negative,

Magnitude of ΔS_{surr} depends on the temperature.

$$\begin{array}{l}
\text{Driving force} \\
\text{provided by} \\
\text{the energy flow} \\
\text{(heat)}
\end{array} = \begin{array}{l}\text{magnitude of the}\\ \text{entropy change of}\\ \text{the surroundings}\end{array} = \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

Summary of Characteristics: Surroundings Entropy Changes

Exothermic process: $\Delta S_{surr} = +\dfrac{\text{quantity of heat (J)}}{\text{temperature (K)}}$

Endothermic process: $\Delta S_{surr} = -\dfrac{\text{quantity of heat (J)}}{\text{temperature (K)}}$

ΔS_{surr} and ΔH

Reaction takes place under conditions of constant temperature (in Kelvins) and pressure:

$$\Delta S_{surr} = -\frac{\Delta H}{T} \quad \begin{array}{l} H = kJ \\ T = \text{Kelvins} \end{array}$$

If the reaction is exothermic:

ΔH has a negative sign.

ΔS_{surr} is positive since heat flows into the surroundings.

ΔS_{sys} and ΔS_{surr} vs. ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Process Spontaneous?
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

3. ΔS_{surr} Example

Carbon is used as the reducing agent for oxide ores:

$$Sb_4O_6(s) + 6C(s) \rightarrow 4Sb(s) + 6CO(g) \quad \Delta H = 778 \text{ kJ}$$
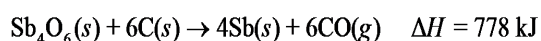
Calculate ΔS_{surr} for this reaction at 25°C and 1 atm

$$\Delta S_{surr} = -\frac{\Delta H}{T} = -\frac{778\,kJ}{298\,K} = -2.61\frac{kJ}{K}$$

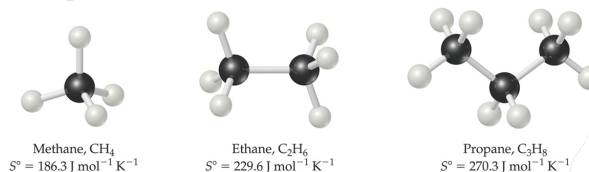## Standard Entropy

These are molar entropy values of substances in their standard states - just like standard enthalpy.

Use Resources in Appendix 4!

Standard entropy tends to increase with increasing molar mass.

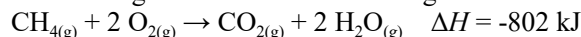Larger and more complex molecules have a greater entropy.

Methane, CH_4
$S° = 186.3$ J mol^{-1} K^{-1}

Ethane, C_2H_6
$S° = 229.6$ J mol^{-1} K^{-1}

Propane, C_3H_8
$S° = 270.3$ J mol^{-1} K^{-1}

Entropy Changes

Entropy changes for a reaction can be estimated in a manner analogous to that by which DH is estimated:

$$\Delta S = \Sigma\, n\, \Delta S°_{products} - \Sigma\, m\, \Delta S°_{reactants}$$

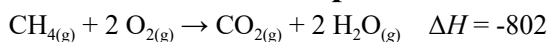where n and m are the coefficients in the balanced chemical equation.

4. ΔS Example

Predict the sign of $\Delta S°$ for the following reaction:
$$CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(g)} \quad \Delta H = -802 \text{ kJ}$$

Calculate $\Delta S°$ for the reaction: find the following information in Appendix 4 (Pages A19 - A 22):

	$\Delta S°$ (J/K mol)
$CH_{4(g)}$	186
$O_{2(g)}$	205
$CO_{2(g)}$	214
$H_2O_{(g)}$	189

4. ΔS Example

$$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)} \quad \Delta H = -802$$

$\Delta S°$ (J/K mol)

$CH_{4(g)}$	186
$O_{2(g)}$	205
$CO_{2(g)}$	214
$H_2O_{(g)}$	189

$\Delta S = \Sigma\ n\ \Delta S°_{products} - \Sigma\ m\ \Delta S°_{reactants}$

$\Delta S = 214$ J/K mol $+ 2(189$ J/K mol$) - 186$ J/K mol
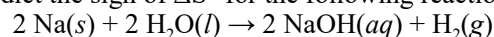$- 2(205$ J/K mol$) = -4$ J/K mol

Our prediction may have been inaccurate! Why?

Redistribution of atoms leads to more massive molecules, which move slower and have less entropy.

5. ΔS Example

Predict the sign of $\Delta S°$ for the following reaction:
$$2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + H_2(g)$$
Positive - the system releases gas, and a dissolved entity (inherently high entropy), resulting from the interactions of a solid an liquid (low entropy).

Calculate $\Delta S°$ for the reaction: find the following information in Appendix 4 (Pages A19 - A 22):

$\Delta S°$ (J/K mol)

Na(s)	51
H_2O(l)	70
NaOH(aq)	50
H_2(g)	131

5. ΔS Example

$$2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + H_2(g)$$
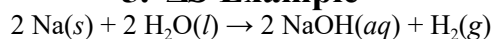
$\Delta S°$ (J/K mol)

Na(s)	51
H_2O(l)	70
NaOH(aq)	50
H_2(g)	131

$\Delta S = \Sigma\ n\ \Delta S°_{products} - \Sigma\ m\ \Delta S°_{reactants}$

$\Delta S = 2(50$ J/K mol$) + 131$ J/K mol $- 2(51$ J/K mol$)$
$- 2(70$ J/K mol$) = -11$ J/K mol

Our prediction was inaccurate! Why? - More research needed (MRN)!

Homework

Read 17.2 in your textbook

17.1 Problems in your Booklet
Due: Next Class.