Chapter 18 - Thermodynamics: Entropy, Free Energy, and Spontaneity

18.1 Spontaneous Processes

Thermochemistry: a field that deals with relationships between forms of energy

Thermodynamics - The study of the relationship between heat, work, and other forms of energy.

- Thermodynamics predicts whether a process will occur under the given conditions.

    – Processes that will occur are called **spontaneous**.

        - A process that, once started, proceeds on its own without a continuous external influence.

    - **Nonspontaneous** processes require energy input to go

Spontaneity is determined by comparing the chemical potential energy of the system before the reaction with the free energy of the system after the reaction.

If the system after reaction has less potential energy than before the reaction, the reaction is thermodynamically favorable.

Spontaneity ≠ fast or slow
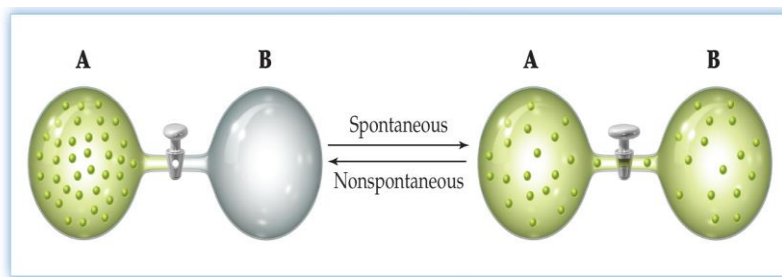
- Spontaneity reaction always moves a system toward equilibrium
- Spontaneity of a reaction does not identify the speed of reaction

As a second example, consider the combination of hydrogen and oxygen in the presence of a platinum catalyst:

$$H_{2(g)} + O_{2(g)} \xrightarrow{\text{cat.}} 2H_2O_{(l)}$$
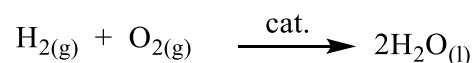
The forward reaction occurs spontaneously, but the reverse reaction, decomposition of water into its elements, does not occur no matter how long we wait.

- Spontaneous processes occur because they release energy from the system.

Any spontaneous process is irreversible because there is a net release of energy when it proceeds in that direction. It will proceed in only one direction.

A reversible process will proceed back and forth between the two end conditions and established at equilibrium. This results in no change in free energy.
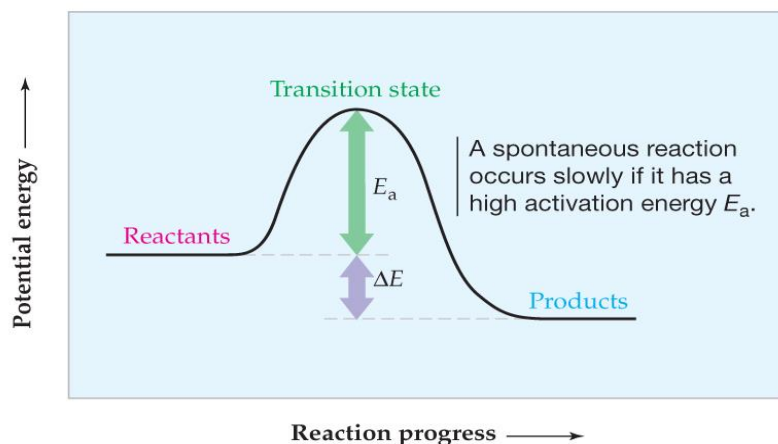
If a process is spontaneous in one direction, it must be nonspontaneous in the opposite direction.

Thermodynamics versus Kinetics

Thermodynamics tells us where a reaction is headed, but it says nothing about how long it takes to get there.


The rusting of these wheel rims is a slow but spontaneous reaction.

18.2 Enthalpy, Entropy, and Spontaneous Processes

Most spontaneous chemical reactions are accompanied by the conversion of potential energy to heat. For example, when methane burns in air, the potential energy stored in the chemical bonds of CH_4 and O_2 is partly converted to heat, which flows from the system (reactants plus products) to the surroundings:

$$CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(l)} \qquad \Delta H° = -890.3 \text{ kJ}$$
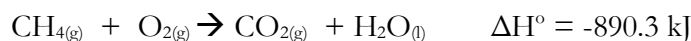
Because heat is lost by the system, the reaction is exothermic and the standard enthalpy of reaction is negative ($\Delta H° = -890.3$ kJ). The total energy is conserved, so all the energy lost by the system shows up as heat gained by the surroundings.

Ice, for example, spontaneously absorbs heat from the surroundings and melts at temperatures above 0 °C. Similarly, liquid water absorbs heat and spontaneously boils at temperatures above 100 °C.

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \qquad\qquad \Delta H_{fus} = +6.01 \text{ kJ}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad\qquad H_{vap} = +40.7 \text{ kJ}$$

Because some spontaneous reactions are exothermic and others are endothermic, enthalpy alone can't account for the direction of spontaneous change; a second factor must be involved. This second determinant of spontaneous change is nature's tendency to move to a condition of maximum randomness

Entropy (S): The amount of molecular randomness of a system

- The randomness (or disorder) of a system comes about because the particles in the system (atoms, ions, and molecules) are in constant motion, moving about in the accessible volume, colliding with each other and continually exchanging energy.

- Entropy is a state function (Section 9.2), and the entropy change ΔS for a process thus depends only on the initial and final states of the system:

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

Dang2

When the randomness of a system increases, **ΔS** has a positive value; when randomness decreases, **ΔS** is negative.

Entropy increases as one goes from a solid to a liquid, or a liquid to a gas

Entropy increases if a solid or liquid is if a solid or liquid is dissolved in a solvent

Entropy increases as the number of particles (molecules) in a system increases.

The entropy of any material increases with increasing temperature

Entropy is higher for weakly bonded compounds than for compounds with very strong covalent
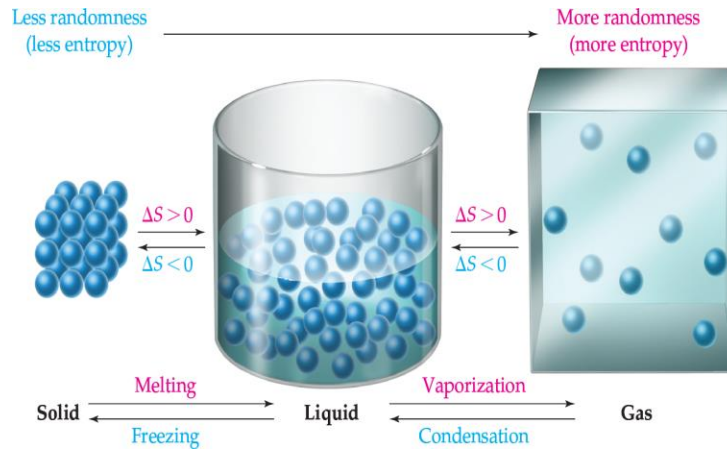
The entropy change that occurs on dissolving sodium chloride in water occurs because the crystal structure of solid NaCl is disrupted and the Na$^+$ and Cl$^-$ ions become hydrated, or surrounded by an ordered shell of solvent water molecules
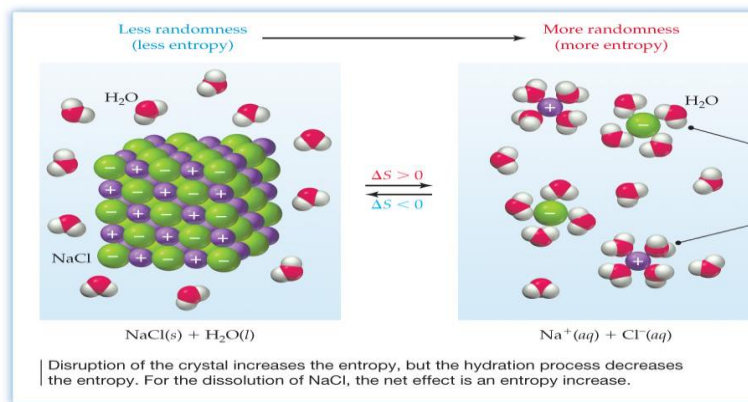

18.3 Entropy and Probability

Thus entropy—is a probability concept, related to the number of ways that a particular state of a system can be achieved. A particular state of a macroscopic system, characterized by its temperature, pressure, volume, and number of particles, can be achieved in a vast number of ways in which the fluctuating positions and energies of the individual particles differ but the volume and total energy are constant.

(a) The perfectly ordered "heads-up" structure.

20 "heads"
0 "tails"

(b) The molecules arranged randomly in one of the 2^{20} ways in which a disordered structure can be obtained.
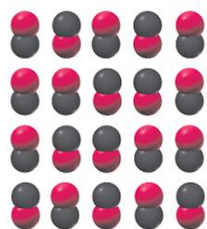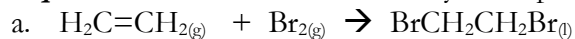

9 "heads"
11 "tails"

$$S = k \ln W$$

$$k = \text{Boltzmann's constant}$$

W = The number of ways that the state can be achieved

- The microstate (W) or the more ways that the energy can be distributed the greater the randomness of the state and higher the entropy

Example: Predict whether ΔS° is likely to be positive or negative for each of the following reactions

   a. $H_2C=CH_{2(g)} + Br_{2(g)} \rightarrow BrCH_2CH_2Br_{(l)}$
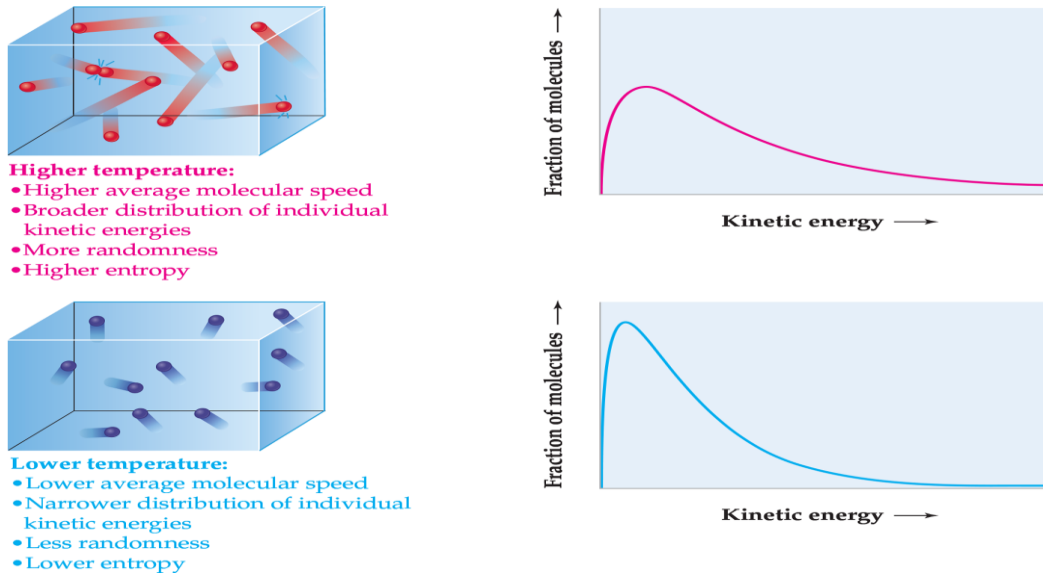
   b. Solid carbon dioxide sublimes.

   d. Consider the following figure

Reaction
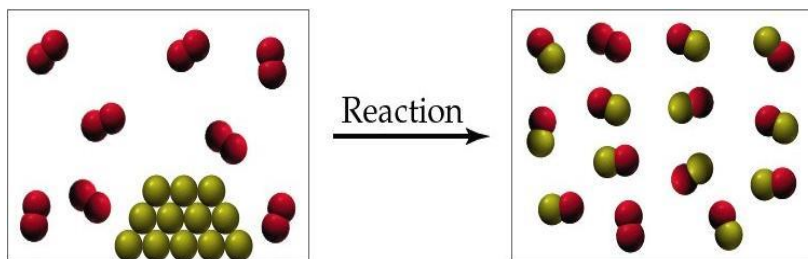
18.4 Entropy and Temperature

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases

At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature

Higher temperature:
- Higher average molecular speed
- Broader distribution of individual kinetic energies
- More randomness
- Higher entropy

Lower temperature:
- Lower average molecular speed
- Narrower distribution of individual kinetic energies
- Less randomness
- Lower entropy

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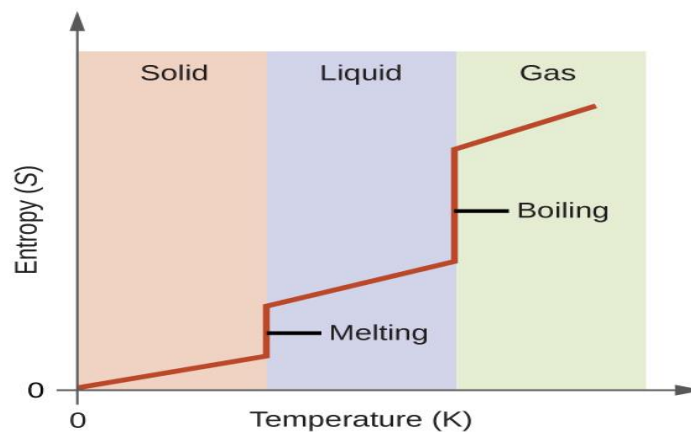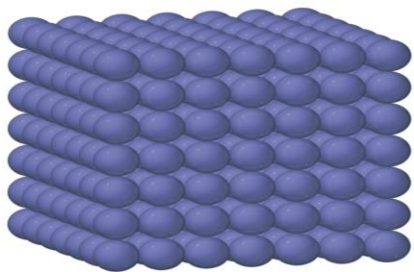

Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The Third Law of Thermodynamics: Absolute Entropy

The relationship between entropy and disorder of in system is **S= k lnW**

Perfect crystal at 0 K
$W = 1 \quad S = 0$

The **absolute entropy** of a substance is the amount of energy it has due to dispersion of energy through its particles.

The third law states that for a perfect crystal at absolute zero, the absolute entropy = 0 J/mol · K.

- Therefore, every substance that is not a perfect crystal at absolute zero has some energy from entropy.

- Therefore, the absolute entropy of substances is always positive.

18.5 Standard Molar Entropies and Standard Entropies of Reaction

The change entropy change can be determined by two approaches: (1) calculations based on Boltzmann's equation and (2) experimental measurements of heat capacities (Section 9.7) down to very low temperatures.

Standard Molar Entropy ($S°$): The entropy of 1 mole of a pure substance at 1 atmosphere pressure and a specified temperature

Standard molar entropies make it possible to compare the entropies of different substances under the same conditions of temperature and pressure.

Substance	Formula	$S°$ [J/(K · mol)]	Substance	Formula	$S°$ [J/(K · mol)]
Gases			**Liquids**		
Acetylene	C_2H_2	200.8	Acetic acid	CH_3CO_2H	160
Ammonia	NH_3	192.3	Ethanol	CH_3CH_2OH	161
Carbon dioxide	CO_2	213.6	Methanol	CH_3OH	127
Carbon monoxide	CO	197.6	Water	H_2O	69.9
Ethylene	C_2H_4	219.5	**Solids**		
Hydrogen	H_2	130.6	Calcium carbonate	$CaCO_3$	91.7
Methane	CH_4	186.2	Calcium oxide	CaO	38.1
Nitrogen	N_2	191.5	Diamond	C	2.4
Nitrogen dioxide	NO_2	240.0	Graphite	C	5.7
Dinitrogen tetroxide	N_2O_4	304.3	Iron	Fe	27.3
Oxygen	O_2	205.0	Iron(III) oxide	Fe_2O_3	87.4

The standard entropy change is the difference in absolute entropy between the reactants and products under standard conditions.

$$\Delta S°_{reaction} = \left(\sum n_p S°_{products}\right) - \left(\sum n_r S°_{reactants}\right)$$

Example: Calculate the standard entropy change for the combustion of methanol, CH_3OH:
$$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)}$$
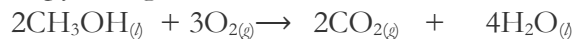
18.6 Entropy and the Second law of Thermodynamic

First law of thermodynamics

In any process, spontaneous or nonspontaneous, the total energy of a system and its surroundings is constant.

- It says that energy (or enthalpy) can flow between a system and its surroundings but the total energy of the system plus the surroundings always remains constant
- but it doesn't tell us whether a particular reaction will be spontaneous or nonspontaneous.

Second law of thermodynamics

In any spontaneous process, the total entropy of a system and its surroundings always increases.

- Provide a clear cut criterion of spontaneity
- Direction of spontaneous change is always determined by the sign of the total entropy change
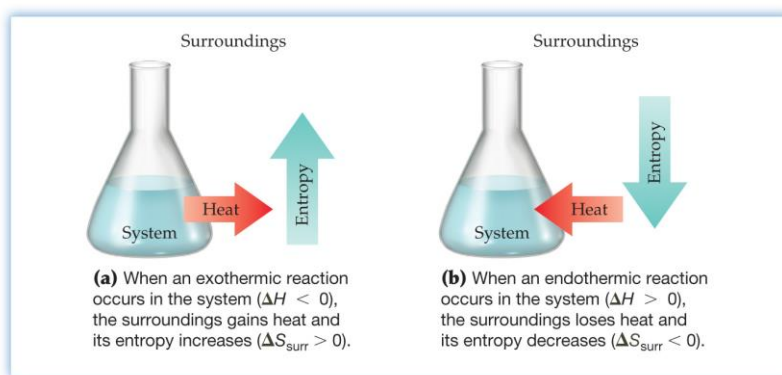- In any spontaneous process, there is always an increase in the entropy of the universe.

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

$\Delta S_{total} > 0$	The reaction is spontaneous.
$\Delta S_{total} < 0$	The reaction is nonspontaneous.
$\Delta S_{total} = 0$	The reaction mixture is at equilibrium.

The entropy change in the surroundings is directly proportional to the enthalpy change for the reaction and inversely proportional to the kelvin temperature (T) of the surroundings, according to the equation

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

Recall: $\quad \Delta H°_{reaction} = \sum \Delta H_f°(products) \ - \ \sum \Delta H_f°(reactants)$

(a) When an exothermic reaction occurs in the system ($\Delta H < 0$), the surroundings gains heat and its entropy increases ($\Delta S_{surr} > 0$).

(b) When an endothermic reaction occurs in the system ($\Delta H > 0$), the surroundings loses heat and its entropy decreases ($\Delta S_{surr} < 0$).

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

$$\Delta S_{surroundings} \ \alpha \ -\Delta H_{system}$$

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

$$\Delta S_{surr} \; \alpha \; \frac{1}{T}$$

If the surroundings has a low temperature, it has only a small amount of randomness.

If the surroundings has a high temperature, it already has a large amount of randomness

Adding heat to cold surroundings is analogous to tossing a rock into calm waters. Both processes produce a considerable increase in the amount of motion and thus a relatively large increase in entropy.

Adding heat to hot surroundings is analogous to tossing a rock into rough waters. Both processes produce a relatively small increase in the amount of motion and thus a relatively small increase in entropy.
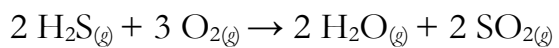
Example: **Will Ice Spontaneously Melt?**

The entropy change for the process

$$H_2O(s) \longrightarrow H_2O(l)$$
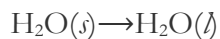
is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C?

Is it spontaneous at +10.00 °C?

Calculate **ΔS^o_{rxn}, ΔS^o_{surr}** and **ΔS^o_{total}** for the balanced chemical equation:

$2\ H_2S_{(g)} + 3\ O_{2(g)} \rightarrow 2\ H_2O_{(g)} + 2\ SO_{2(g)}$

	$H_2S(g)$	$O_2(g)$	$H_2O(g)$	$SO_2(g)$
S^o (J/mol K)	205.6	205.2	188.8	248.1
H^o (kJ/mol)	122	0	-241.8	248.1