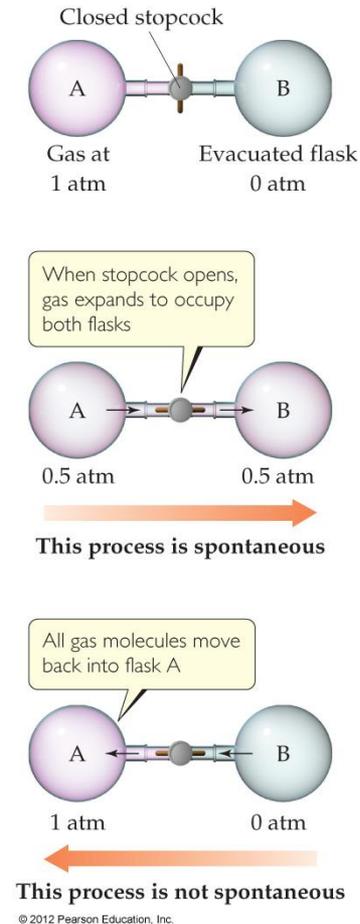


First Law of Thermodynamics

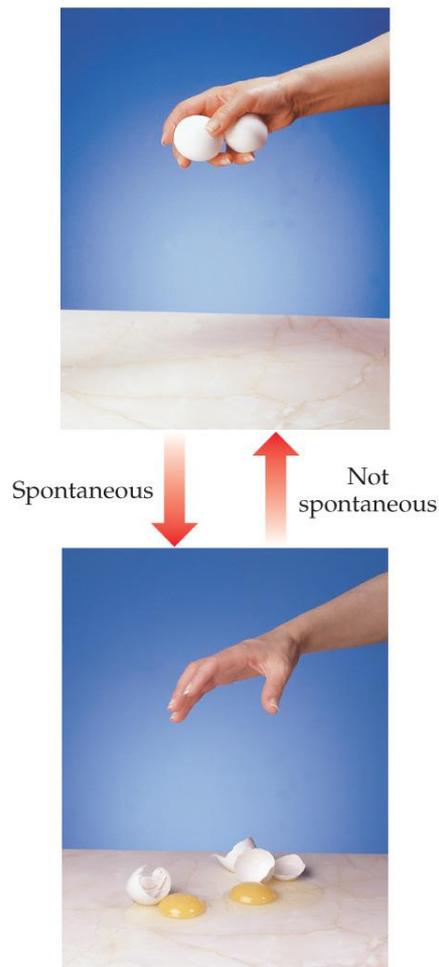
- You will recall from Chapter 5 that energy cannot be created or destroyed.
- Therefore, the total energy of the universe is a constant.
- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.

Spontaneous Processes

- **Spontaneous processes** are those that can proceed without any outside intervention.
- The gas in vessel B will spontaneously effuse into vessel A, but once the gas is in both vessels, it will *not* spontaneously return to vessel B.



Spontaneous Processes

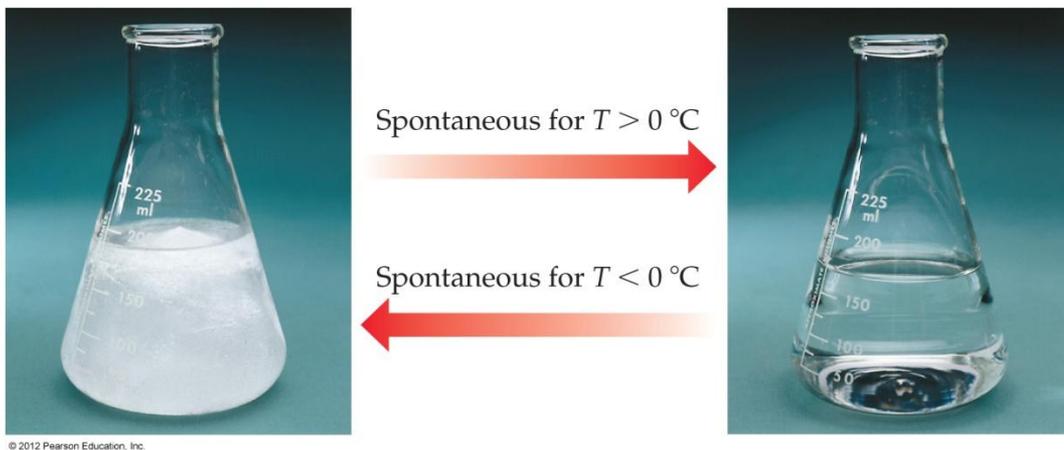


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Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

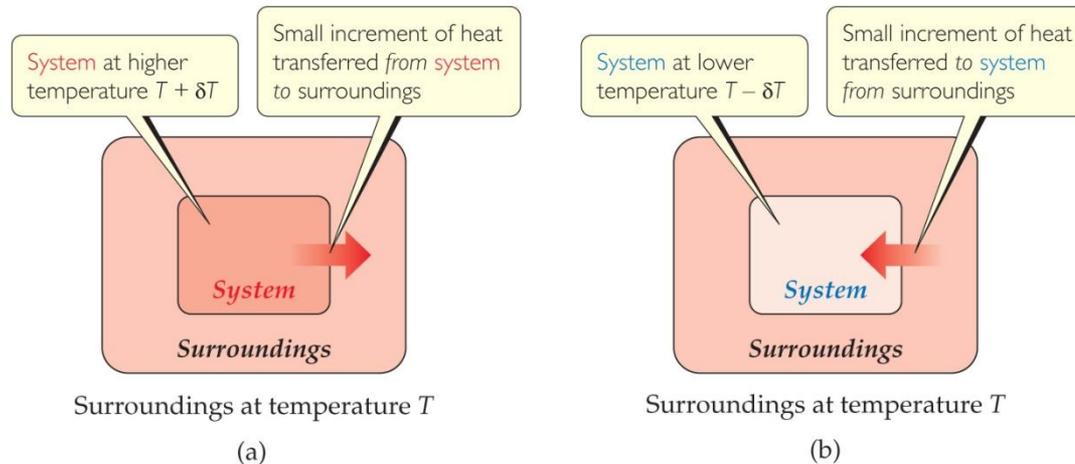
Spontaneous Processes

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0 °C, it is spontaneous for ice to melt.
- Below 0 °C, the reverse process is spontaneous.



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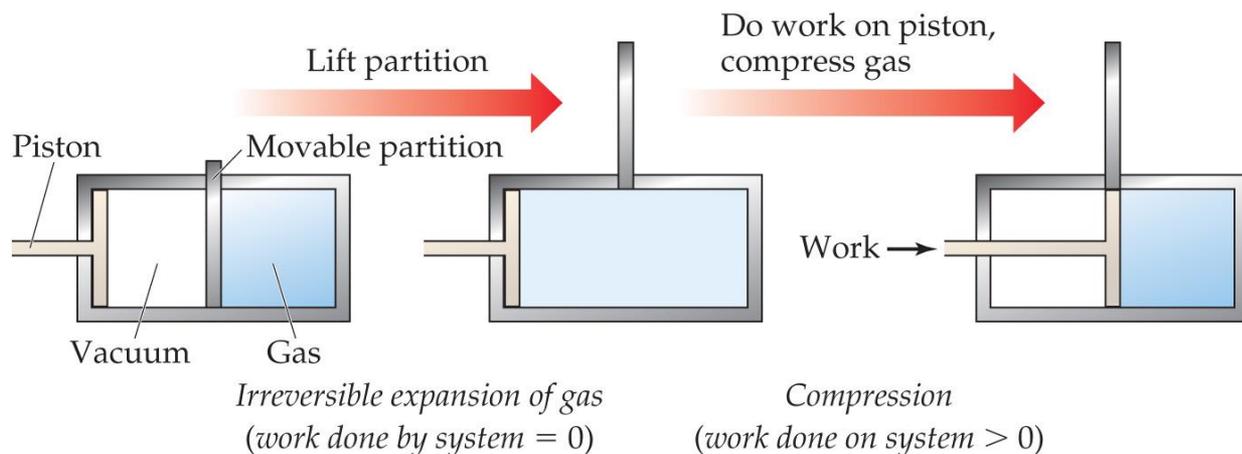
Reversible Processes



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In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

Irreversible Processes



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- Irreversible processes cannot be undone by exactly reversing the change to the system.
- Spontaneous processes are irreversible.

Entropy

- *Entropy* (S) is a term coined by Rudolph Clausius in the nineteenth century.
- Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered, $\frac{q}{T}$.

Entropy

- **Entropy** can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.

Entropy

- Like total energy, E , and enthalpy, H , entropy is a state function.
- Therefore,

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

Entropy

For a process occurring at constant temperature (an isothermal process), the change in entropy is equal to the heat that would be transferred if the process were reversible divided by the temperature:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Second Law of Thermodynamics

The second law of thermodynamics states that the entropy of the universe increases for spontaneous processes, and the entropy of the universe does not change for reversible processes.

Second Law of Thermodynamics

In other words:

For reversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For irreversible processes:

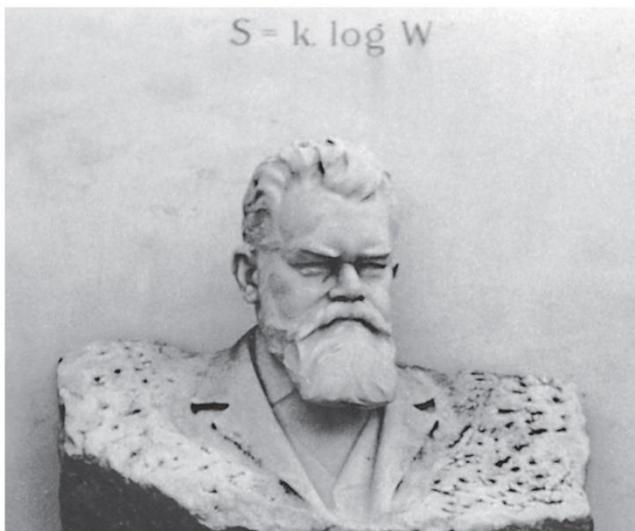
$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Second Law of Thermodynamics

These last truths mean that as a result of all spontaneous processes, the entropy of the universe increases.

Entropy on the Molecular Scale

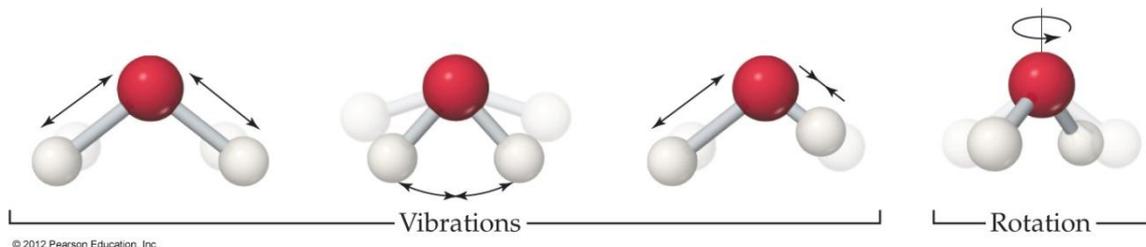
- Ludwig Boltzmann described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.



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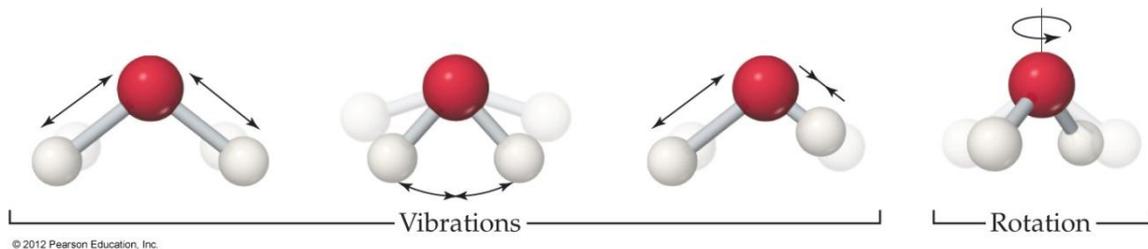
Entropy on the Molecular Scale

- 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 about an axis or rotation about σ bonds.



Entropy on the Molecular Scale

- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
 - This would be akin to taking a snapshot of all the molecules.
- He referred to this sampling as a **microstate** of the thermodynamic system.

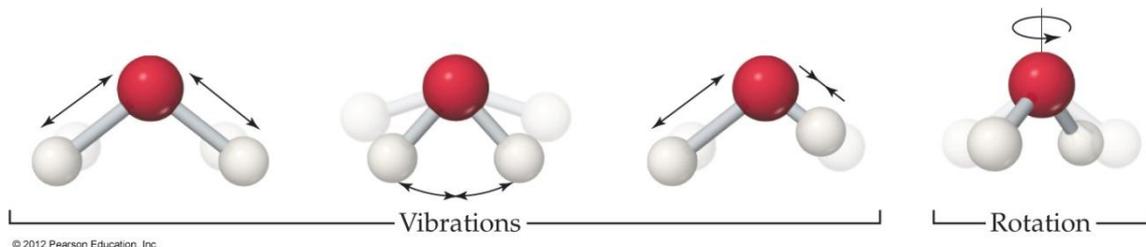


Entropy on the Molecular Scale

- Each thermodynamic state has a specific number of microstates, W , associated with it.
- Entropy is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.



Entropy on the Molecular Scale

- The change in entropy for a process, then, is

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}}$$

$$\Delta S = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$

- Entropy increases with the number of microstates in the system.

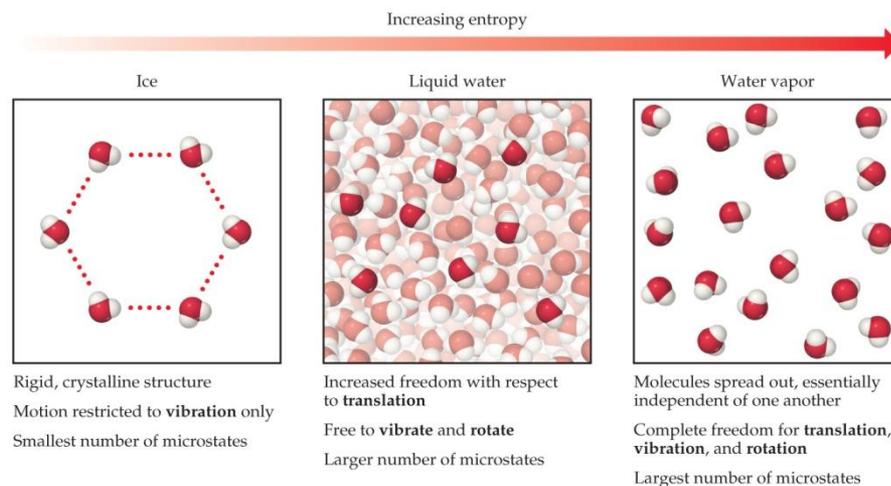
Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy, tends to increase with increases in
 - Temperature
 - Volume
 - The number of independently moving molecules.

Entropy and Physical States

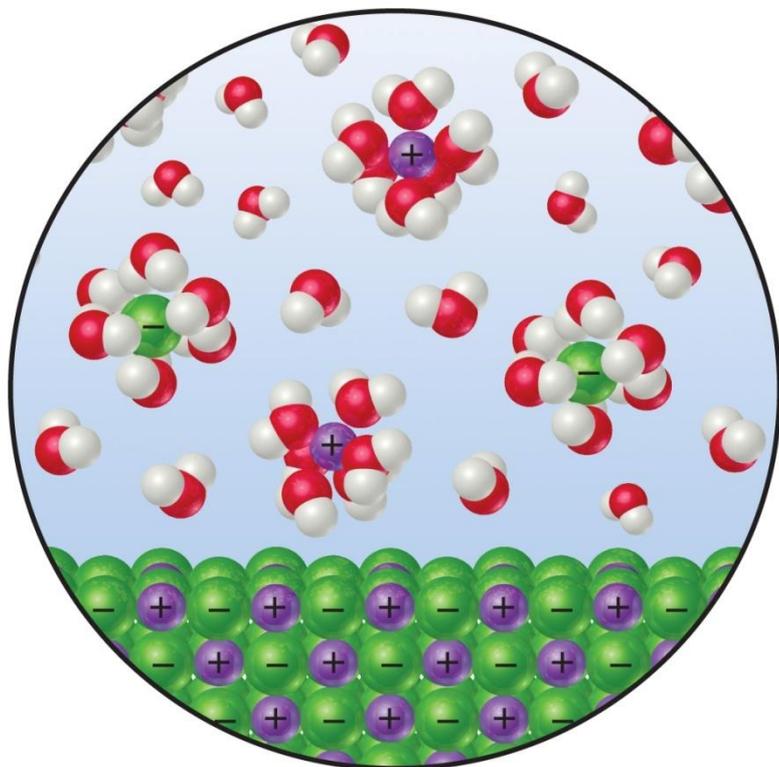
- Entropy increases with the freedom of motion of molecules.
- Therefore,

$$S(g) > S(l) > S(s)$$



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Solutions

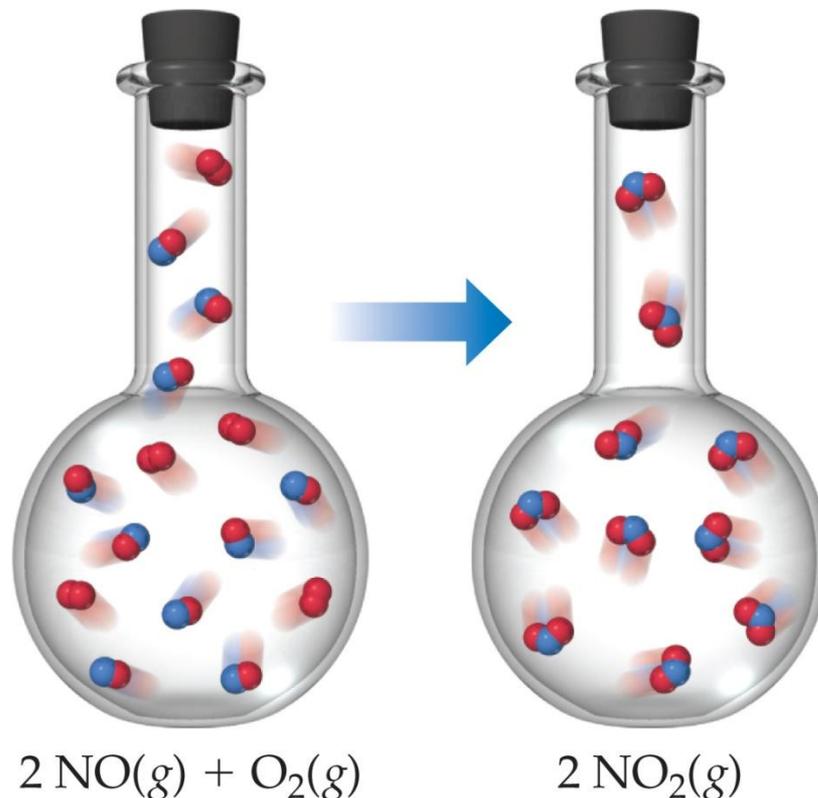


Generally, when a solid is dissolved in a solvent, entropy increases.

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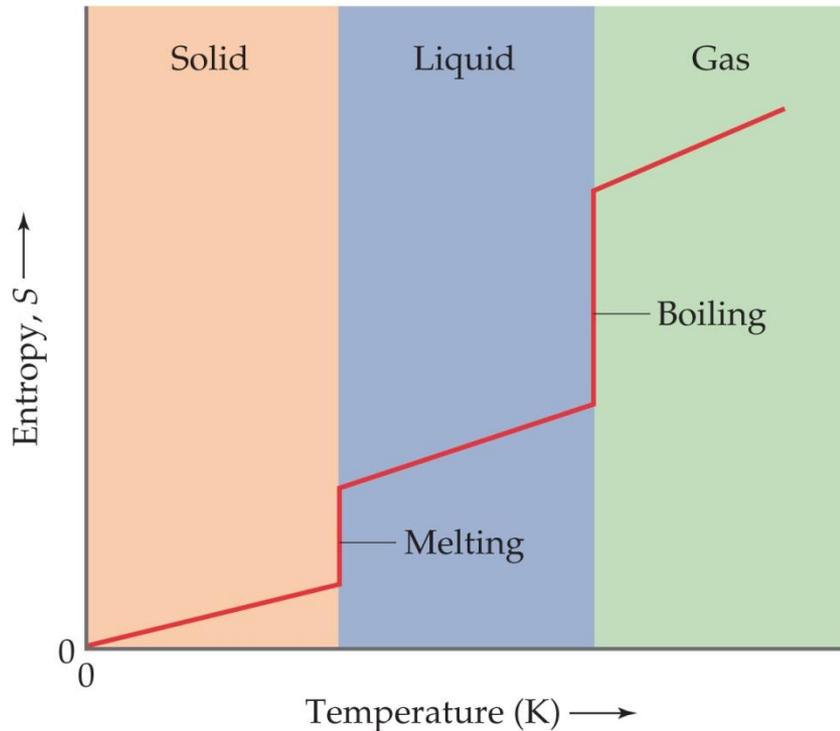
Entropy Changes

- In general, entropy increases when
 - Gases are formed from liquids and solids;
 - Liquids or solutions are formed from solids;
 - The number of gas molecules increases;
 - The number of moles increases.



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Third Law of Thermodynamics



The entropy of a pure crystalline substance at absolute zero is 0.

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Standard Entropies

- These are molar entropy values of substances in their standard states.
- Standard entropies tend to increase with increasing molar mass.

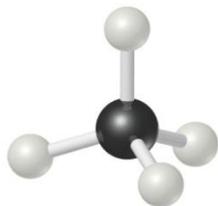
TABLE 19.1 • Standard Molar Entropies of Selected Substances at 298 K

Substance	S° (J/mol-K)
H ₂ (g)	130.6
N ₂ (g)	191.5
O ₂ (g)	205.0
H ₂ O(g)	188.8
NH ₃ (g)	192.5
CH ₃ OH(g)	237.6
C ₆ H ₆ (g)	269.2
H ₂ O(l)	69.9
CH ₃ OH(l)	126.8
C ₆ H ₆ (l)	172.8
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
FeCl ₃ (s)	142.3
NaCl(s)	72.3

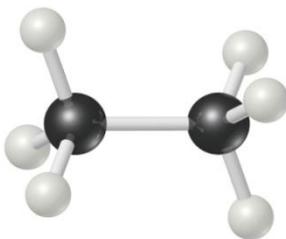
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Standard Entropies

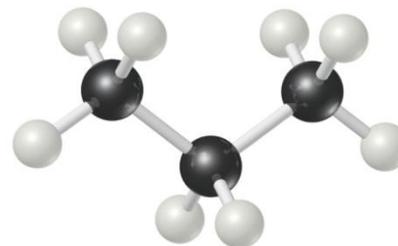
Larger and more complex molecules have greater entropies.



Methane, CH₄
 $S^\circ = 186.3 \text{ J/mol-K}$
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Ethane, C₂H₆
 $S^\circ = 229.6 \text{ J/mol-K}$



Propane, C₃H₈
 $S^\circ = 270.3 \text{ J/mol-K}$

Entropy Changes

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

$$\Delta S^\circ = \sum n \Delta S^\circ(\text{products}) - \sum m \Delta S^\circ(\text{reactants})$$

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

Entropy Changes in Surroundings

- Heat that flows into or out of the system changes the entropy of the surroundings.
- For an isothermal process:

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

- At constant pressure, q_{sys} is simply ΔH° for the system.

Entropy Change in the Universe

- The universe is composed of the system and the surroundings.
- Therefore,

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

- For spontaneous processes

$$\Delta S_{\text{universe}} > 0$$

Entropy Change in the Universe

- Since

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

and

$$q_{\text{system}} = \Delta H_{\text{system}}$$

This becomes:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \frac{-\Delta H_{\text{system}}}{T}$$

Multiplying both sides by $-T$, we get

$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

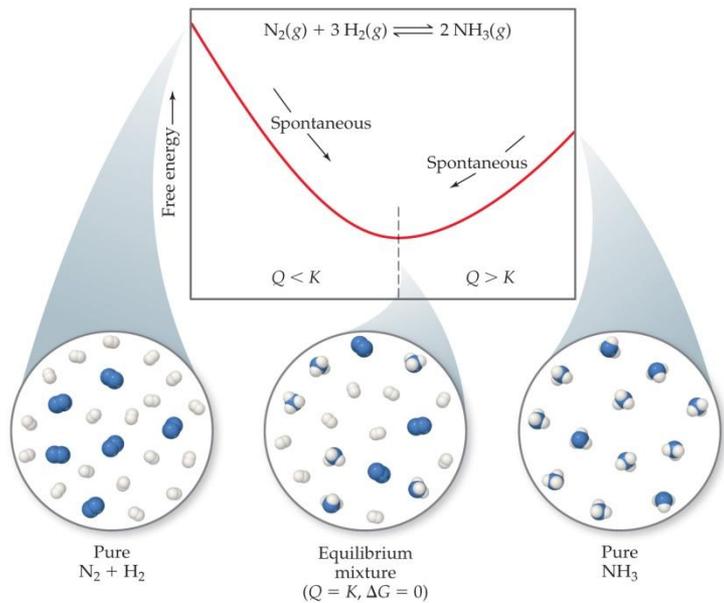
Gibbs Free Energy



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- $-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG .
- When $\Delta S_{\text{universe}}$ is positive, ΔG is negative.
- Therefore, when ΔG is negative, a process is spontaneous.

Gibbs Free Energy



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1. If ΔG is negative, the forward reaction is spontaneous.
2. If ΔG is 0, the system is at equilibrium.
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

Standard Free Energy Changes

Analogous to standard enthalpies of formation are standard free energies of formation, ΔG_f° :

$$\Delta G^\circ = \sum n \Delta G_f^\circ (\text{products}) - \sum m \Delta G_f^\circ (\text{reactants})$$

where n and m are the stoichiometric coefficients.

Free Energy Changes

At temperatures other than 25 °C,

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

How does ΔG° change with temperature?

Free Energy and Temperature

- There are two parts to the free energy equation:
 - ΔH° — the enthalpy term
 - $T\Delta S^\circ$ — the entropy term
- The temperature dependence of free energy then comes from the entropy term.

Free Energy and Temperature

TABLE 19.3 • How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	-	Spontaneous at all temperatures	$2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$
+	-	+	+	Nonspontaneous at all temperatures	$3 \text{O}_2(g) \longrightarrow 2 \text{O}_3(g)$
-	-	+	+ or -	Spontaneous at low T ; nonspontaneous at high T	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$
+	+	-	+ or -	Spontaneous at high T ; nonspontaneous at low T	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$

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Free Energy and Equilibrium

Under any conditions, standard or nonstandard, the free energy change can be found this way:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

(Under standard conditions, all concentrations are 1 *M*, so $Q = 1$ and $\ln Q = 0$; the last term drops out.)

Free Energy and Equilibrium

- At equilibrium, $Q = K$, and $\Delta G = 0$.
- The equation becomes

$$0 = \Delta G^\circ + RT \ln K$$

- Rearranging, this becomes

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{-\Delta G^\circ/RT}$$