Chemical Thermodynamics

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First Law of Thermodynamics

- **The First Law of Thermodynamics** was expressed in the study of thermochemistry. It is commonly known as the **Law Conservation of Energy**:

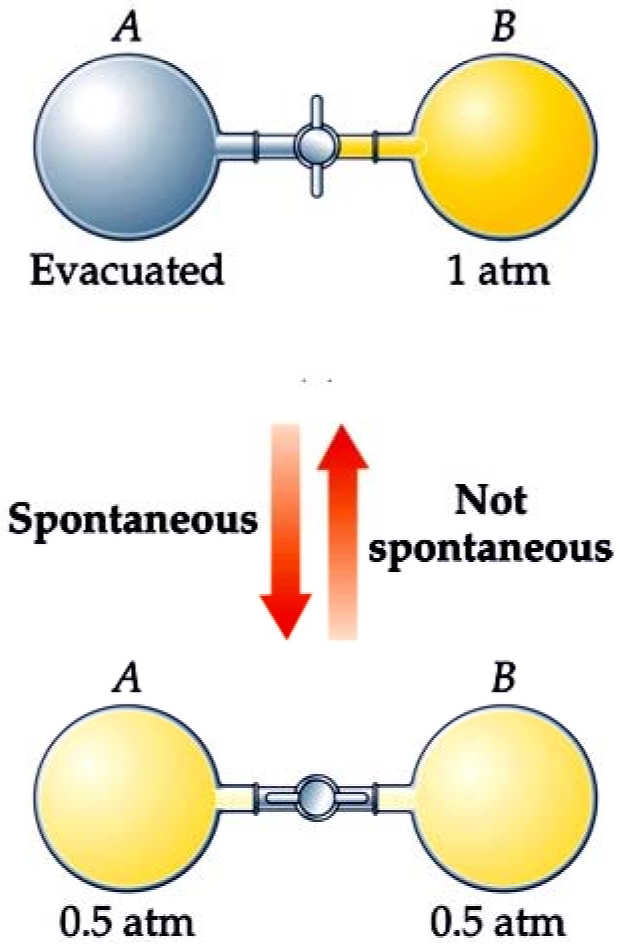
  The total energy of the universe is a constant.

  Energy cannot be created nor destroyed.

  Energy can 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, once started, can proceed without any outside intervention.**
- The term “spontaneous” has nothing to do with the time or rate of the process.
- In the diagram, when the valve is opened, the gas in flask *B* will spontaneously effuse into flask *A*, but once the gas is in both flasks, it will *not* spontaneously go back to one flask

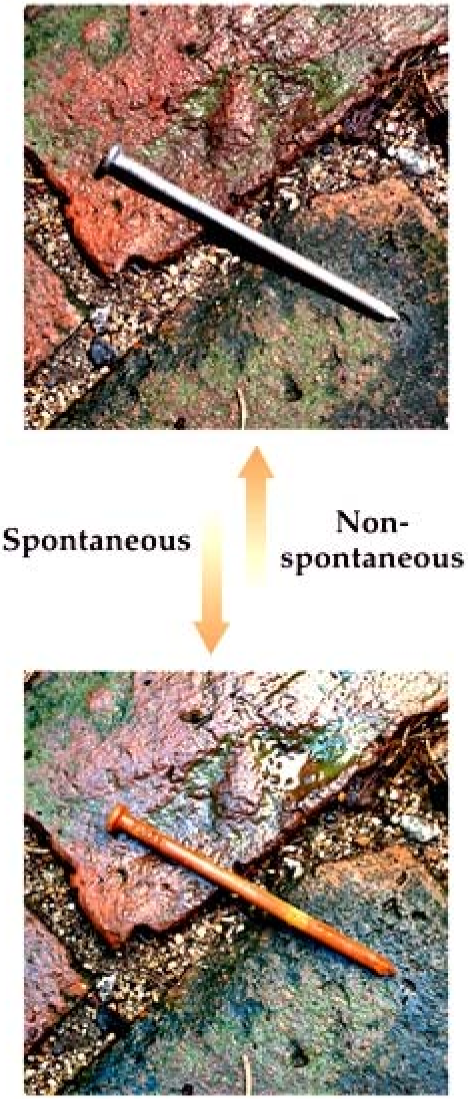


Spontaneous Processes

- Diamond is thermodynamically favored to convert to graphite, but not kinetically favored.

- Paper burns — a product-favored reaction. Also kinetically favored once reaction is begun.

Spontaneous Processes



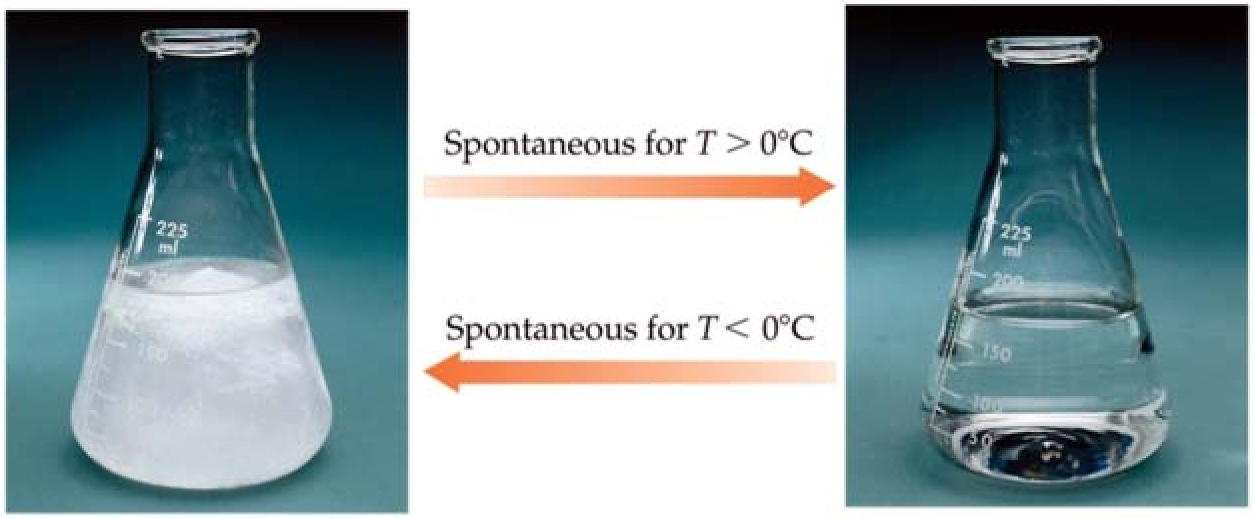
Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

In this example, an iron nail, in contact with the air, will rust.

To reverse the process something must be done to the system.

Spontaneous Processes

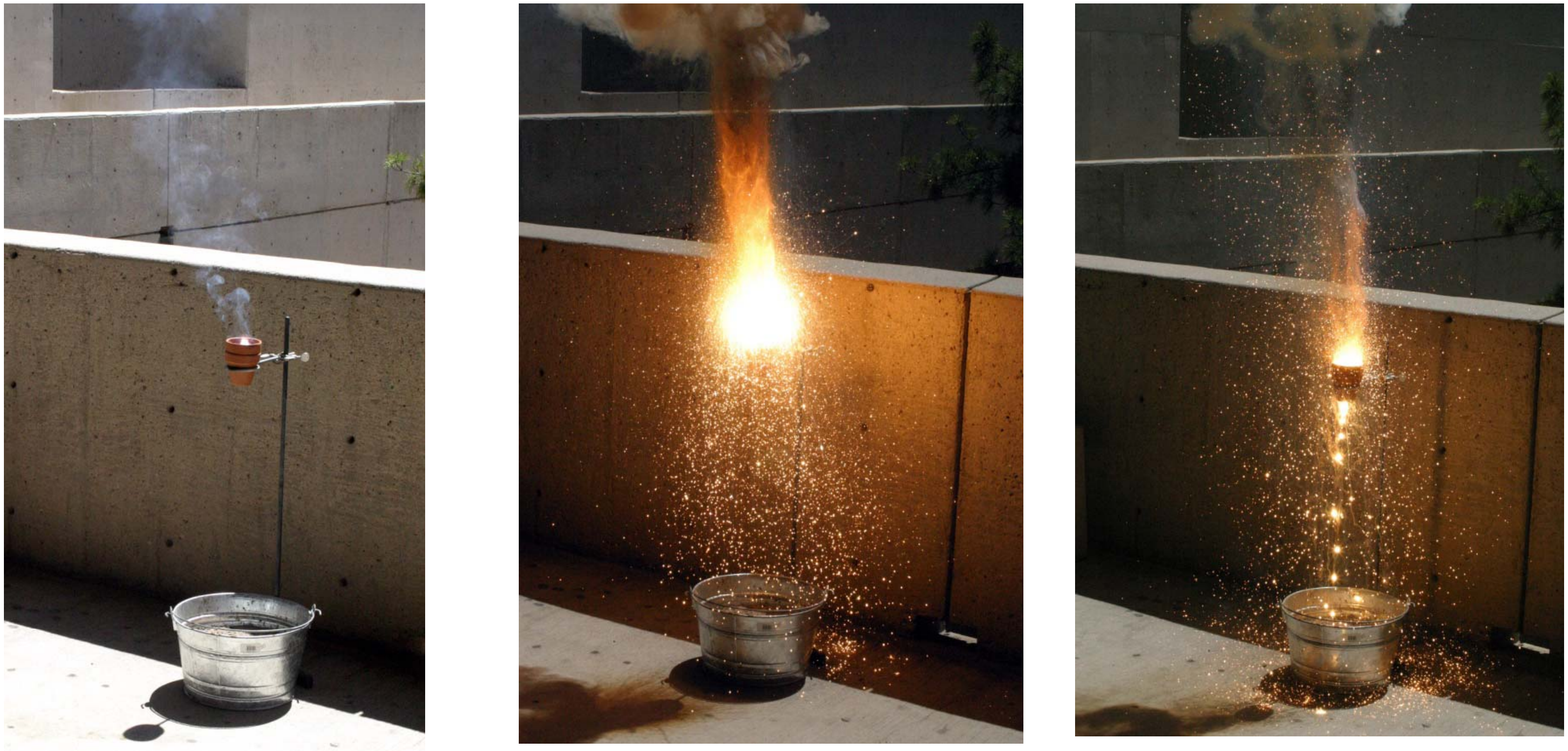
- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.



Spontaneous Processes

In general, spontaneous reactions are exothermic.

$Fe_2O_3(s) + 2\ Al(s) \rightarrow 2\ Fe(s) + Al_2O_3(s) \quad \Delta H_{rxn} = -848\ kJ$



Reversible Processes

Nicolas Léonard Sadi Carnot (1796 – 1832)

In an 1824 book *Réflexions sur la puissance motrice du feu* ("Reflections on the Motive Power of Fire"), he discussed the relation between heat and mechanical energy and presented an idealized steam engine that could be used to understand and clarify the fundamental principles that are of general applicability to all heat engines, independent of the particular design choices that might be made.

Reversible Processes

In Carnot’s idealized engine, a gas is allowed to expand to do work, absorbing heat in the process, and is expanded again without transfer of heat but with a temperature drop. The gas is then compressed, heat being given off, and finally it is returned to its original condition by another compression, accompanied by a rise in temperature.

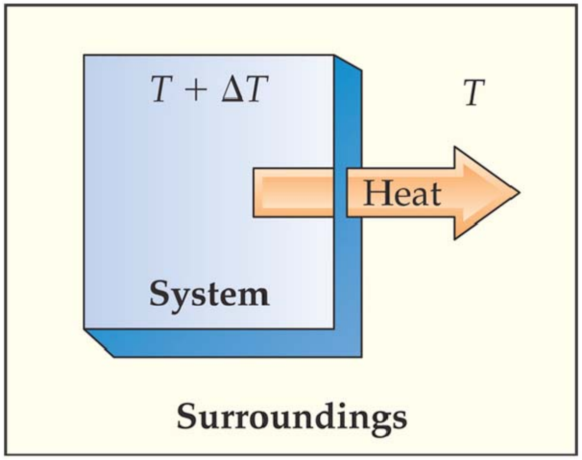
This series of operations is known as Carnot's cycle.

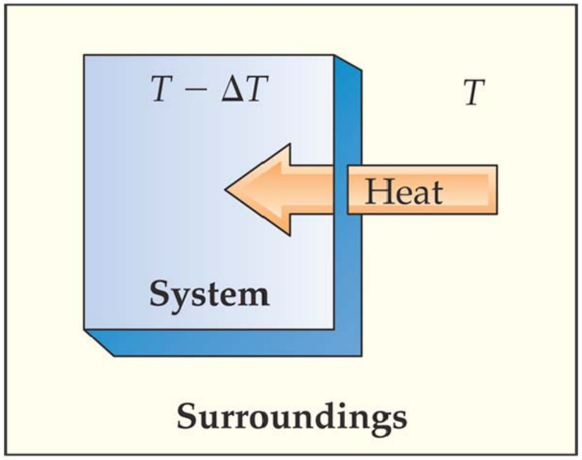
It shows that even under ideal conditions a heat engine cannot convert into mechanical energy all the heat energy supplied to it; some of the heat energy must be rejected.

Carnot’s statement lead to the second law of thermodynamics.

An animation of the Carnot Cycle by Michael Fowler and Jacquie Hui Wan Ching, Department of Physics, University of Virginia can be found at **http://galileoandeinstein.physics.virginia.edu/more_stuff/flashlets/carnot.htm**

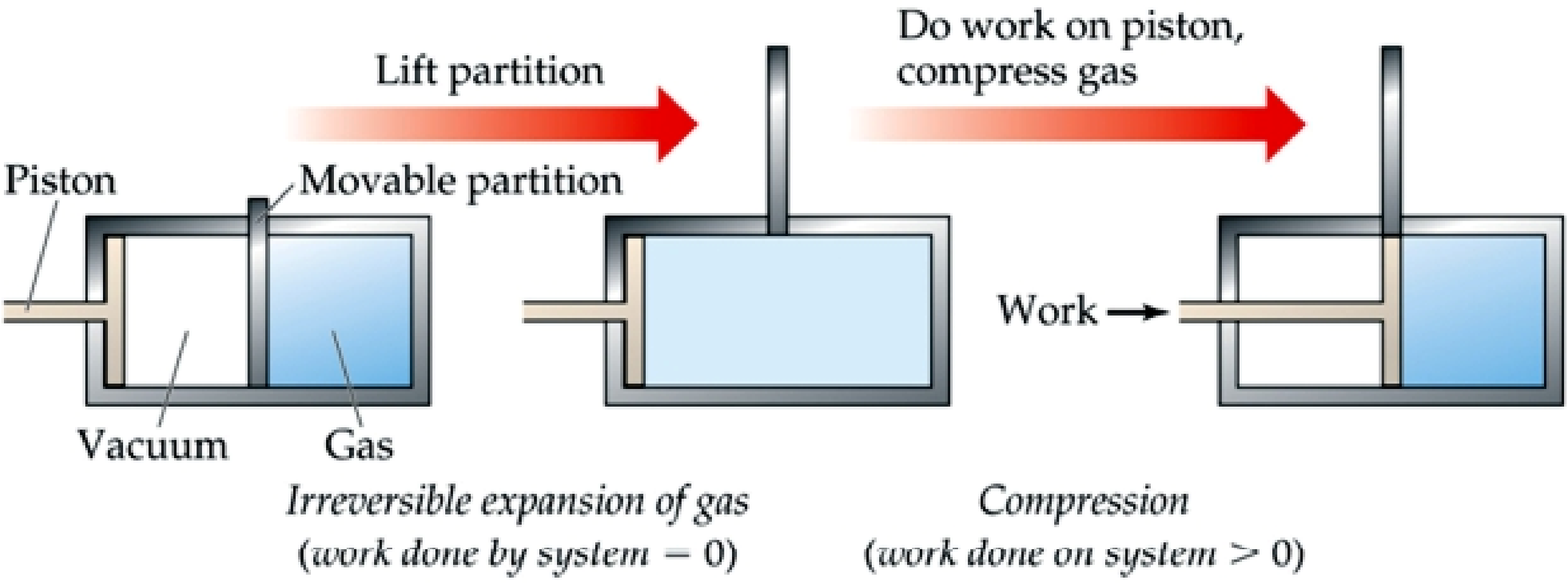
Reversible Processes





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



Irreversible expansion of gas
(*work done by system* = 0)

Compression
(*work done on system* > 0)

- Irreversible processes cannot be undone by exactly reversing the change to the system.
- Spontaneous processes are irreversible.
- This system can only be reversed by doing work on it.

Entropy

- *Entropy* (*S*) is a term coined by Rudolph Clausius (1822-1888)
- In an 1850 paper, "*On the mechanical theory of heat*", he stated:

  > "*the equivalent of the work done by heat is found in the mere transfer of heat from a hotter to a colder body, while the quantity of heat remains undiminished.*"

- This is the basic idea of the Second Law of Thermodynamics.

Entropy

- In an 1865 paper, Clausius introduced the concept of entropy.
- The modern form of his equation is $\Delta S = \frac{q}{T}$

"If we wish to designate *S* by a proper name we can say of it that it is the *transformation content* of the body, in the same way that we say of the quantity *U* that it is the *heat and work content* of the body. However, since I think it is better to take the names of such quantities as these, …, from the ancient languages, …, I proposed to name the magnitude *S* the *entropy* of the body, from the Greek word η τροπη, a transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*, since both these quantities, which are to be known by these names, are so nearly related to each other in their physical significance that a certain similarity in their names seemed to me advantageous."

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,

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

Standard entropy values in J/mol-K can be found in a table of thermodynamic values in the appendix of most textbooks.

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:

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

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:

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

For irreversible processes:

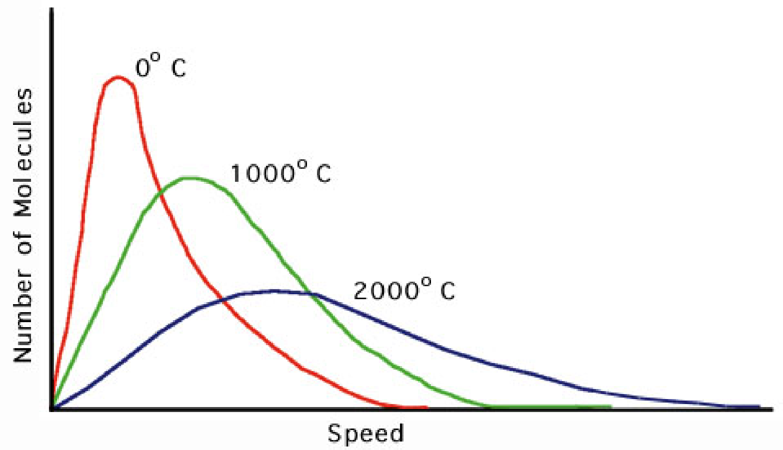
$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

To summarize:

as a result of all spontaneous processes the entropy of the universe increases.

Entropy on the Molecular Scale

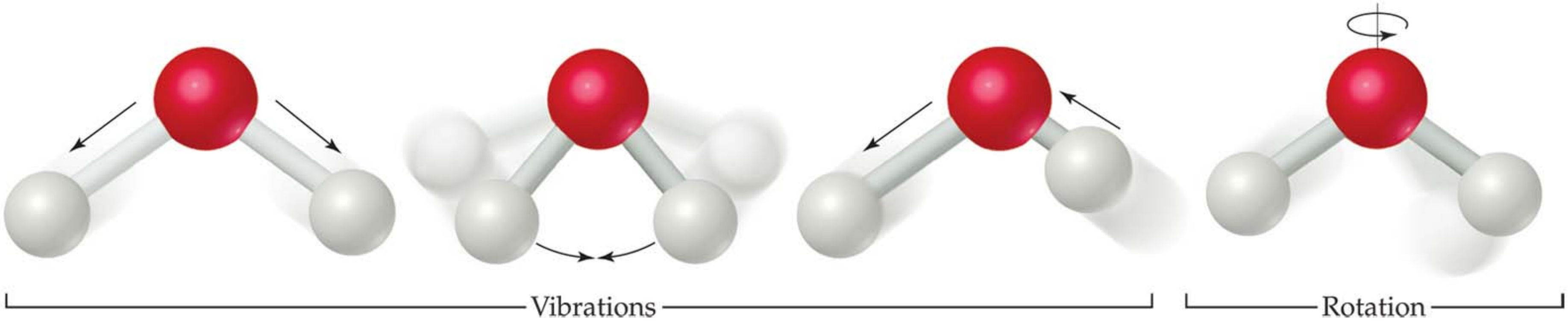
- Ludwig Boltzmann (1844-1906) described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.



An animation of the Maxwell-Boltzman distribution for molecular speeds in a gas can be found at http://www.chm.davidson.edu/chemistryapplets/KineticMolecularTheory/Maxwell.html

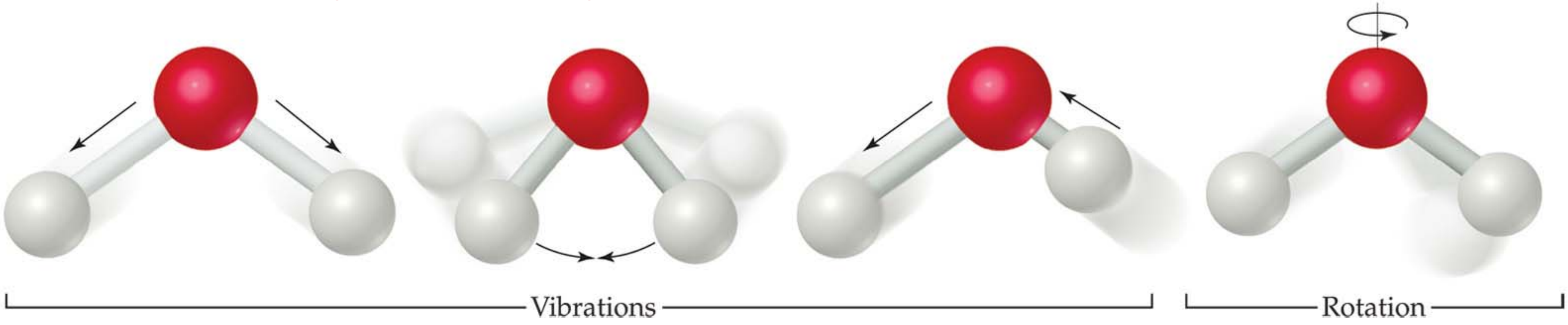
Entropy on the Molecular Scale

- 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 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.

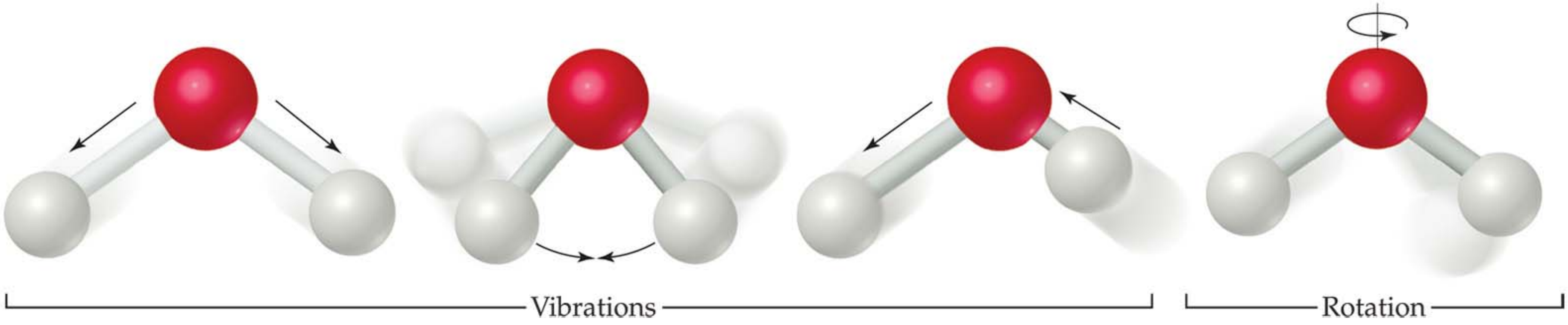


Entropy on the Molecular Scale

- 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

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

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

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

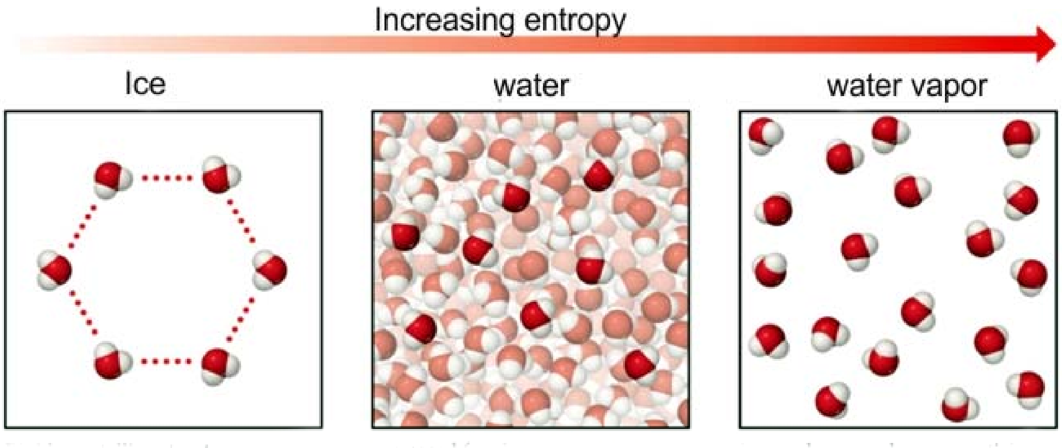
Entropy on the Molecular Scale

- 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.**
  - **Ice: vibrational motion only**
  - **Water: vibrational, rotational, and limited translational motion**
  - **Water vapor: vibrational, rotational, and translational motion**
- **Therefore,**

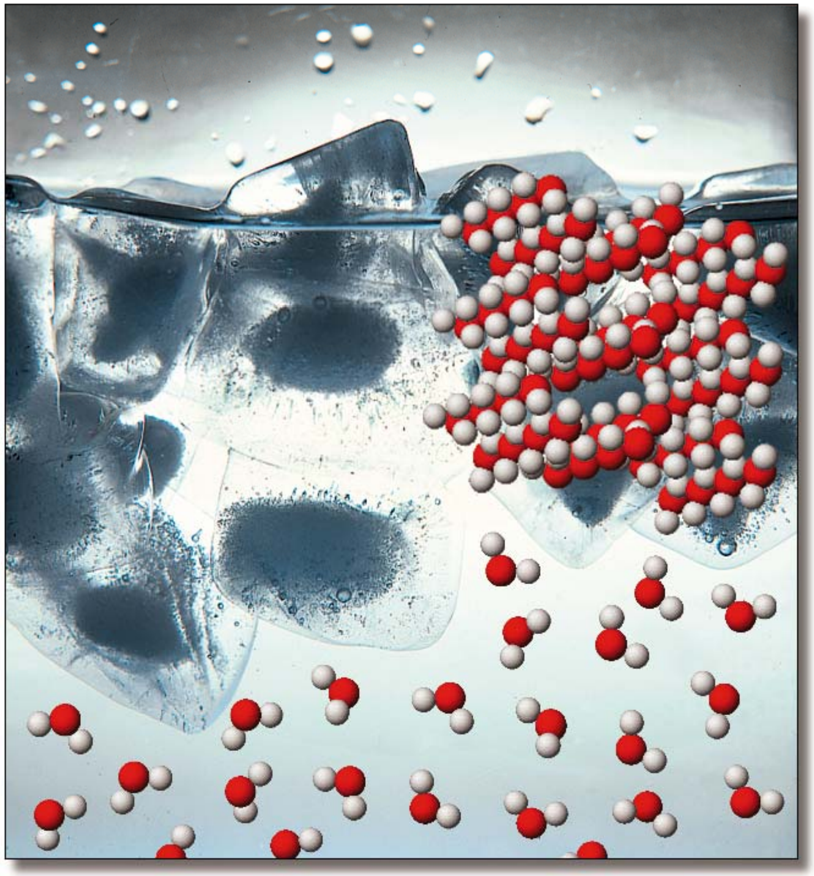
$S(g) > S(l) > S(s)$

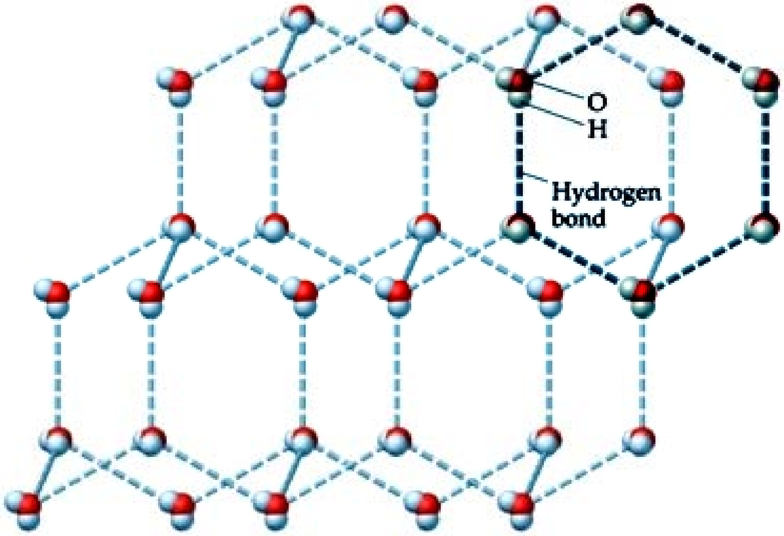


	S^o (J/K•mol)
$H_2O_{(liq)}$	69.95
$H_2O_{(gas)}$	188.8

Entropy and Physical States

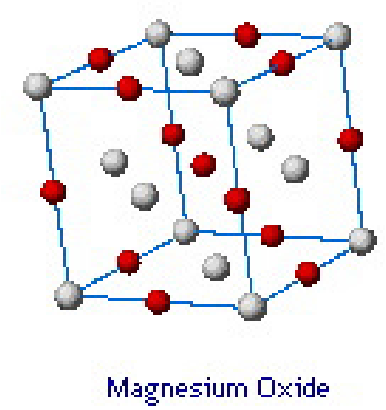
- The entropy of liquid water is greater than the entropy of solid water (ice) at 0˚ C.
- Energy is more dispersed in liquid water than in solid water.

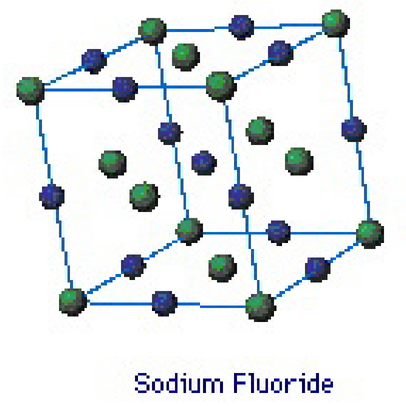




Entropy

Entropies of ionic solids depend on coulombic attractions.





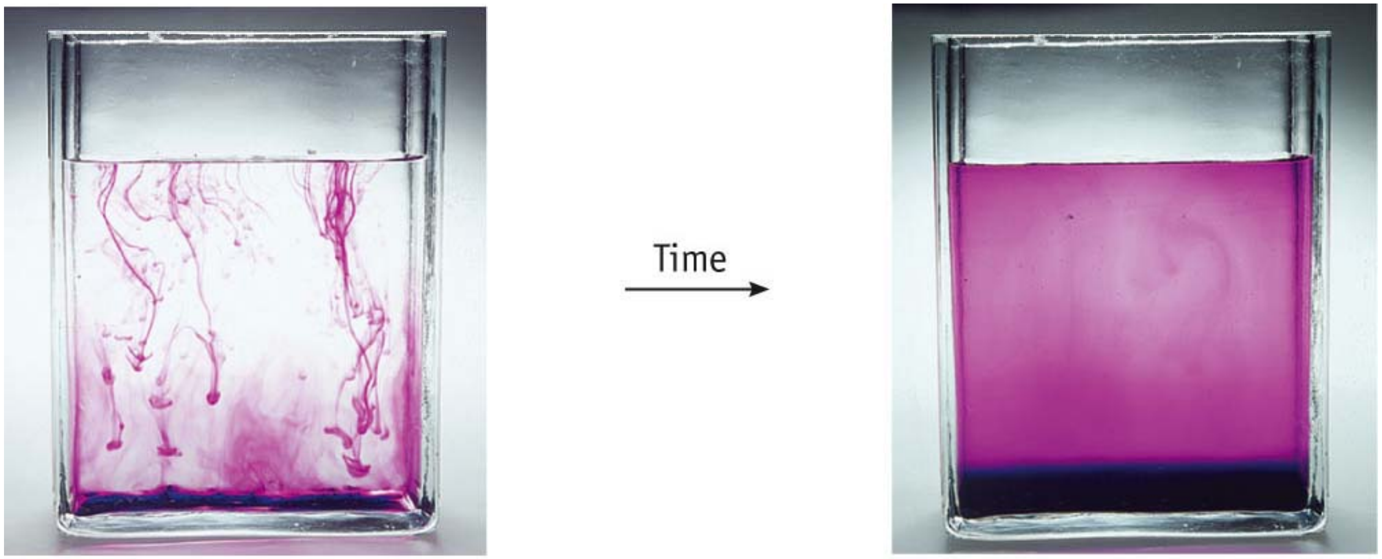
Mg^{2+} & O^{2-}

Na^{+} & F^{-}

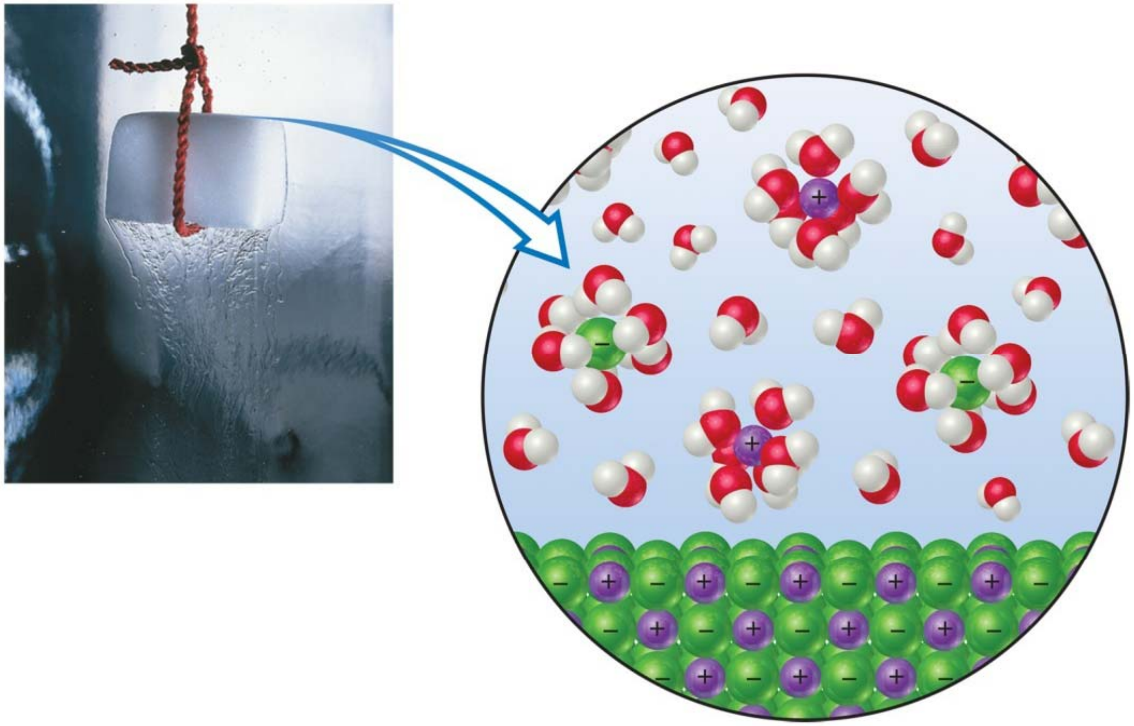
	S^o (J/K•mol)
MgO	26.9
NaF	51.5

Entropy

Liquids or solids dissolve in a solvent in a spontaneous process owing to the increase in entropy. Matter (and energy) are more dispersed.



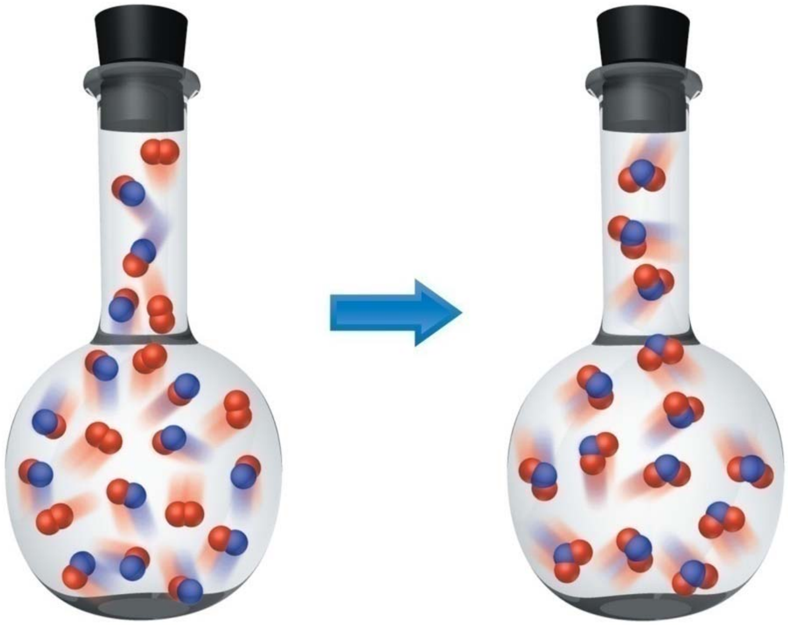
Solutions



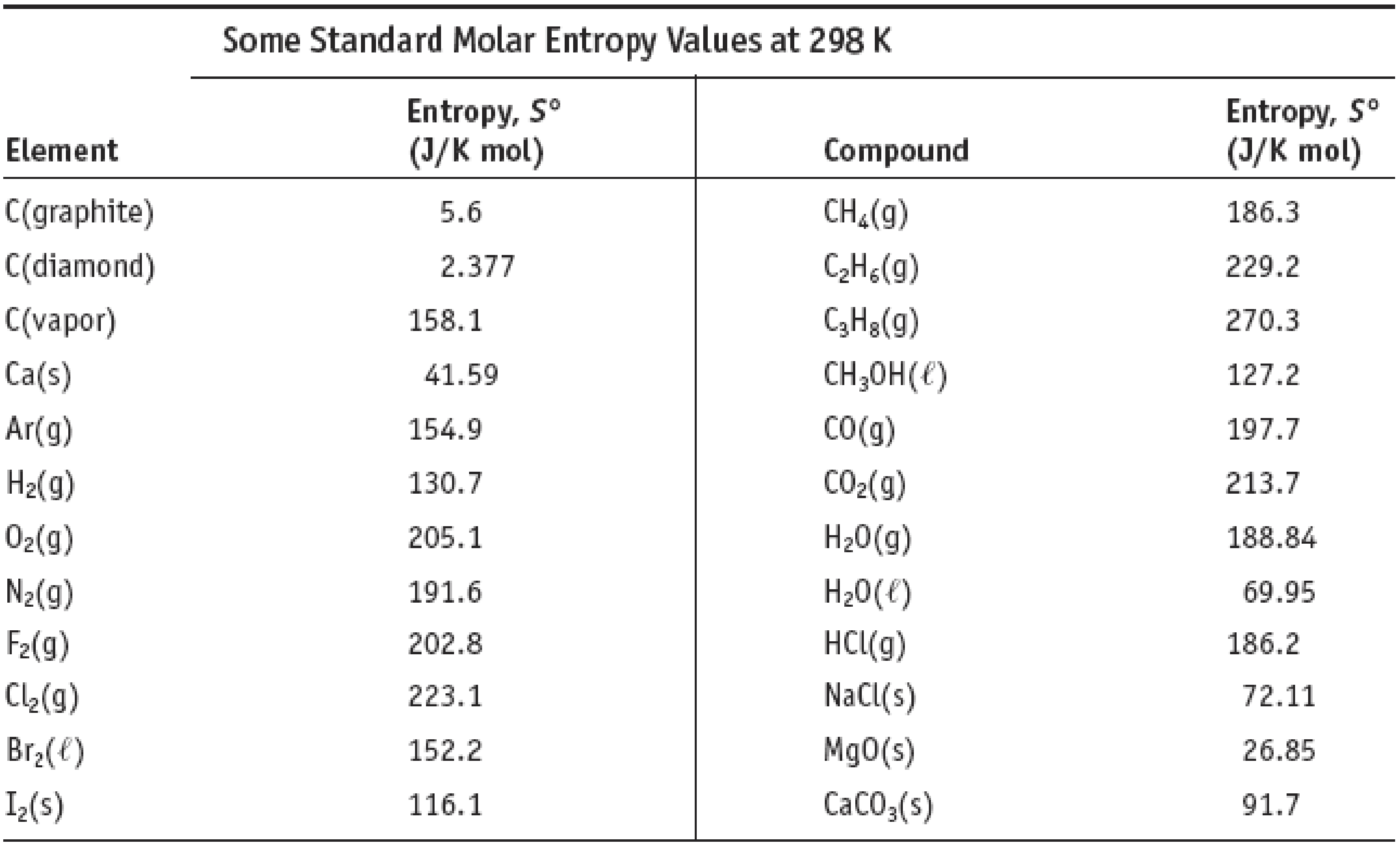
Generally, when a solid is dissolved in a solvent, entropy increases.

Entropy

- 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.



Standard Molar Entropies

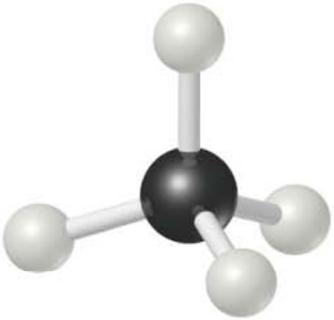


Some Standard Molar Entropy Values at 298 K

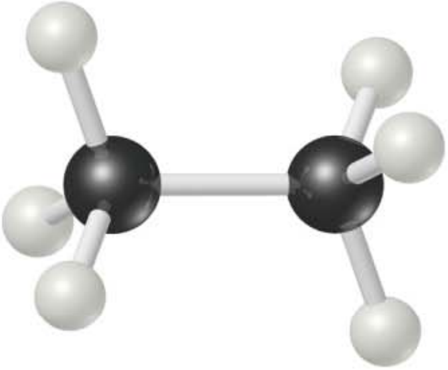
Element	Entropy, $S°$ (J/K mol)	Compound	Entropy, $S°$ (J/K mol)
C(graphite)	5.6	$CH_4(g)$	186.3
C(diamond)	2.377	$C_2H_6(g)$	229.2
C(vapor)	158.1	$C_3H_8(g)$	270.3
Ca(s)	41.59	$CH_3OH(\ell)$	127.2
Ar(g)	154.9	CO(g)	197.7
$H_2(g)$	130.7	$CO_2(g)$	213.7
$O_2(g)$	205.1	$H_2O(g)$	188.84
$N_2(g)$	191.6	$H_2O(\ell)$	69.95
$F_2(g)$	202.8	HCl(g)	186.2
$Cl_2(g)$	223.1	NaCl(s)	72.11
$Br_2(\ell)$	152.2	MgO(s)	26.85
$I_2(s)$	116.1	$CaCO_3(s)$	91.7

Standard Entropies

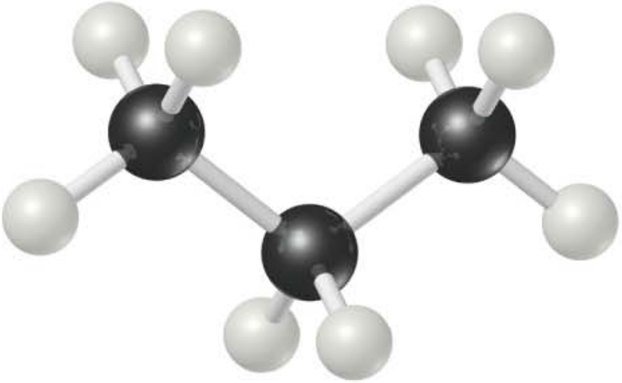
Larger and more complex molecules have greater entropies.



Methane, CH_4
$S^\circ = 186.3$ J/mol-K



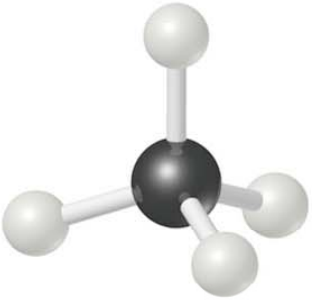
Ethane, C_2H_6
$S^\circ = 229.6$ J/mol-K



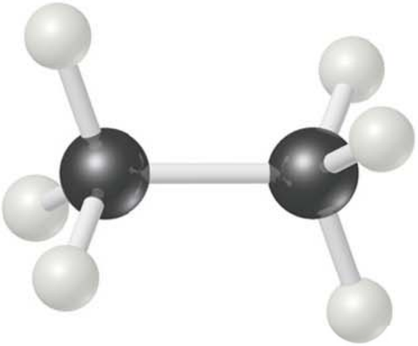
Propane, C_3H_8
$S^\circ = 270.3$ J/mol-K

Standard Entropies

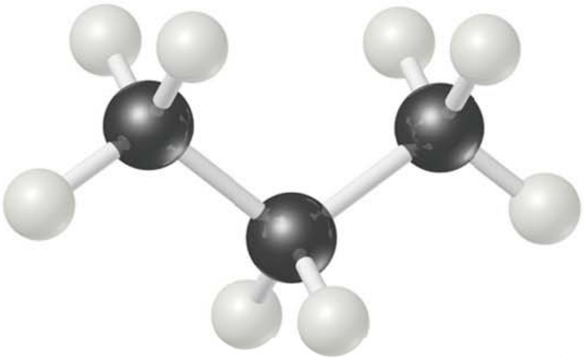
Larger and more complex molecules have greater entropies.



Methane, CH_4
$S^\circ = 186.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$



Ethane, C_2H_6
$S^\circ = 229.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$

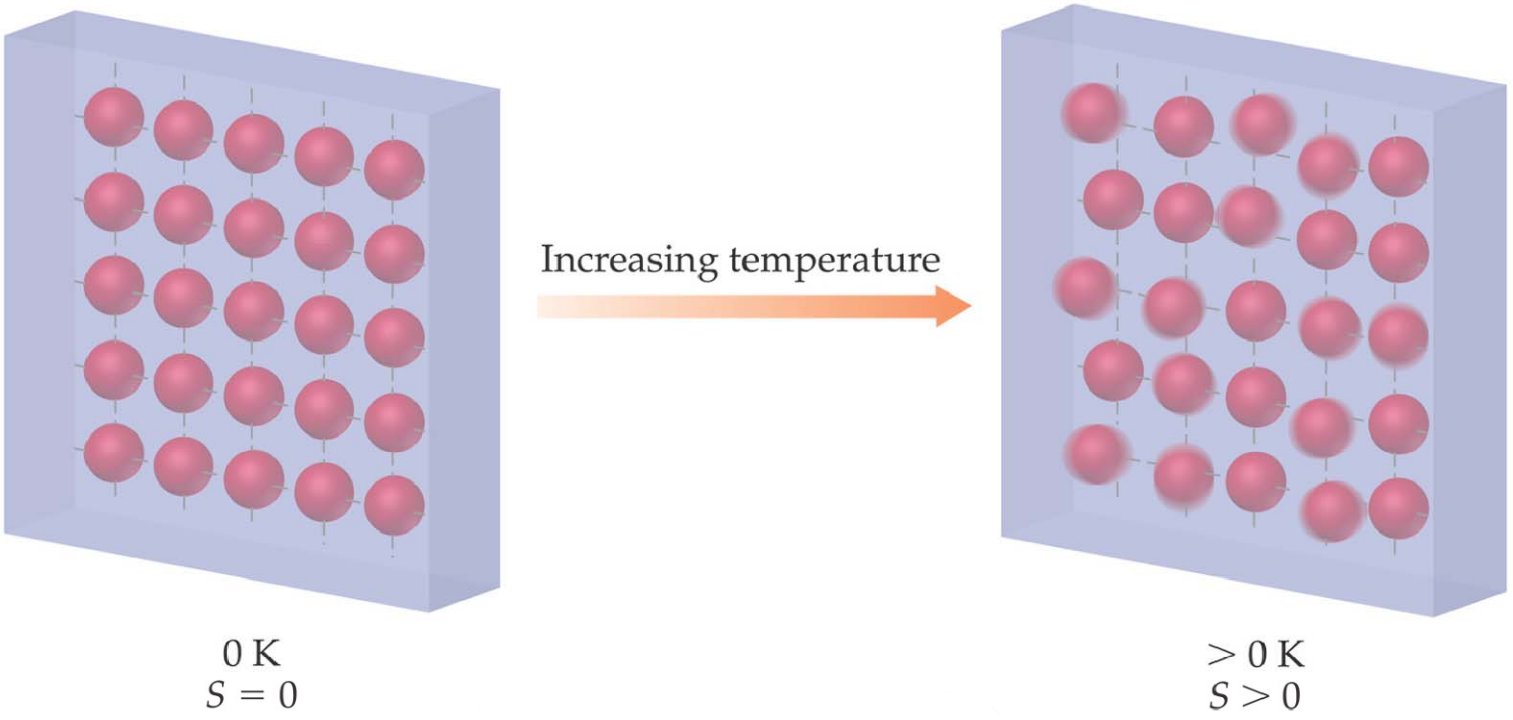


Propane, C_3H_8
$S^\circ = 270.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$

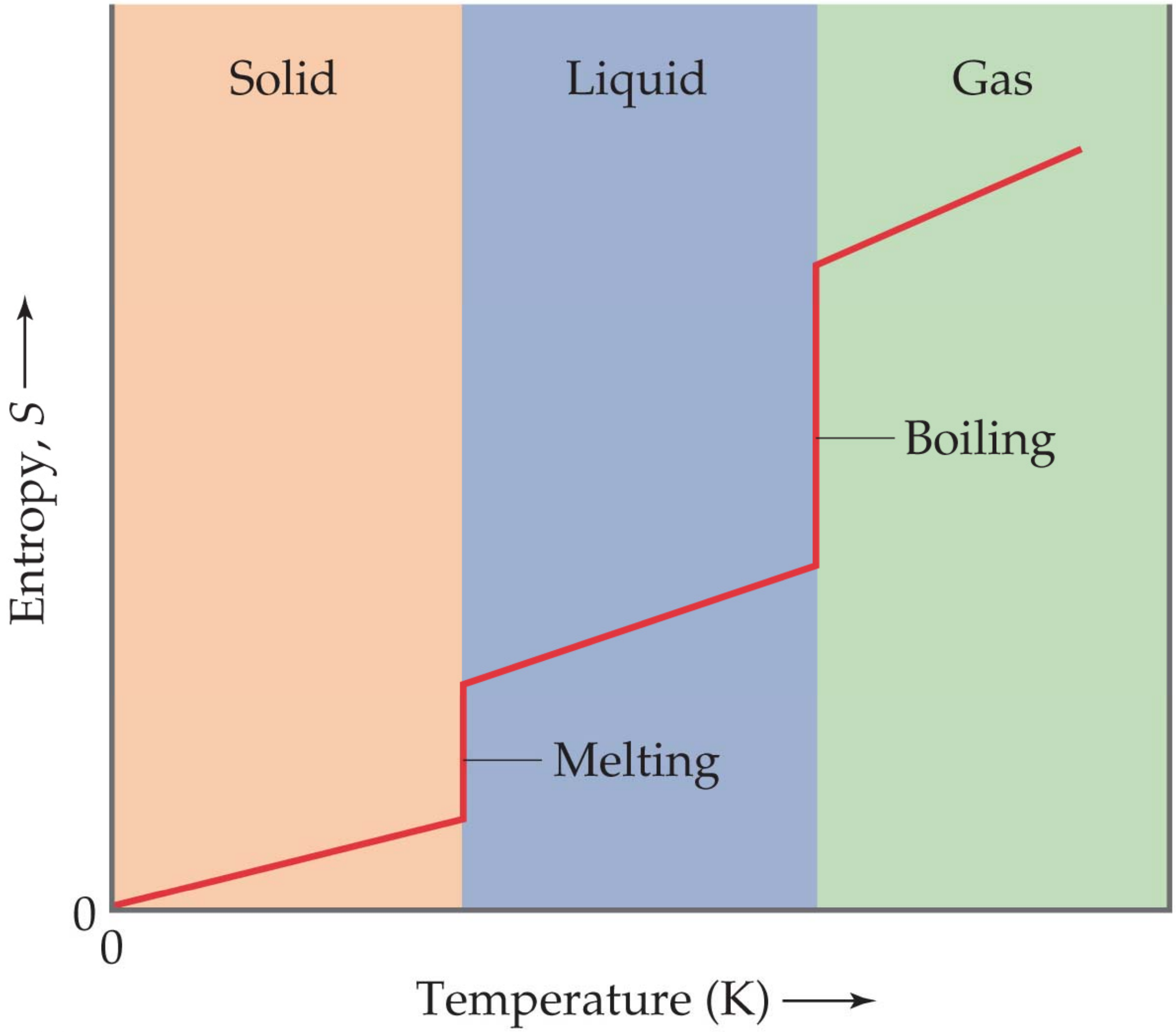
The number of degrees of freedom increases with increasing number of atoms – which also means increasing microstates.

Third Law of Thermodynamics

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



Third Law of Thermodynamics



Entropy Changes

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

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

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 $\Delta H°$ for the system:

$$\Delta S_{\text{surr}} = \frac{-\Delta H°_{\text{sys}}}{T}$$

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

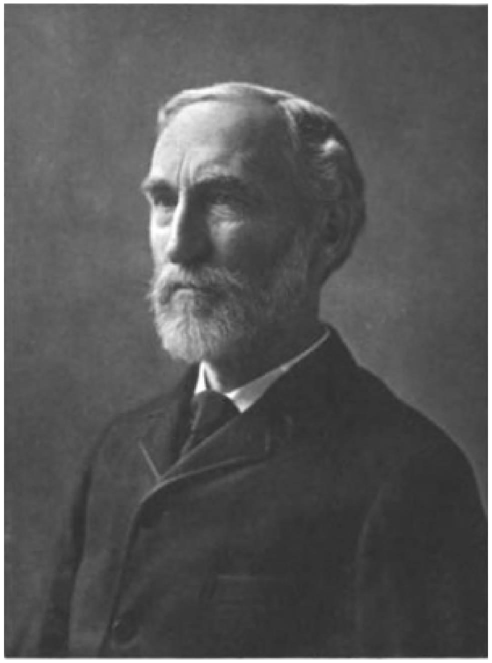
- This becomes:

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

Multiplying both sides by $-T$,

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

Gibbs Free Energy



- Josiah Willard Gibbs (1839-1903)
- Gibbs free energy, originally called *available energy*, was developed in 1873, in a footnote, Gibbs defined what he called the "available energy" of a body as such:

    " The greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition."

Gibbs Free Energy

- In the equation

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

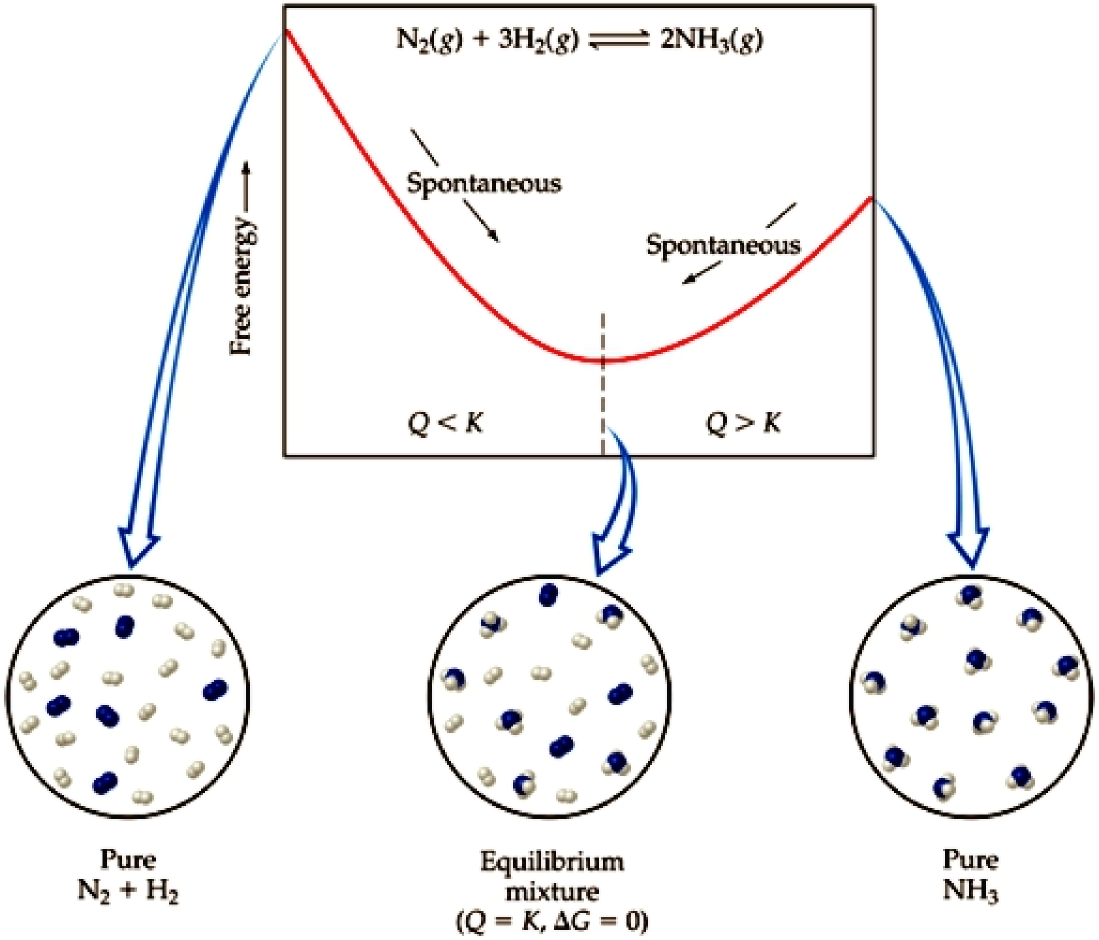
$-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG.

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

When $\Delta S_{\text{universe}}$ is positive, ΔG is negative.

Therefore, when ΔG is negative, a process is spontaneous.

Gibbs Free Energy



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°. (usually given at 298 K)

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

where *n* and *m* are the stoichiometric coefficients.

Free Energy and Temperature

At temperatures other than 298 K (25° C),

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

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, comes from the entropy term.

Free Energy and Temperature

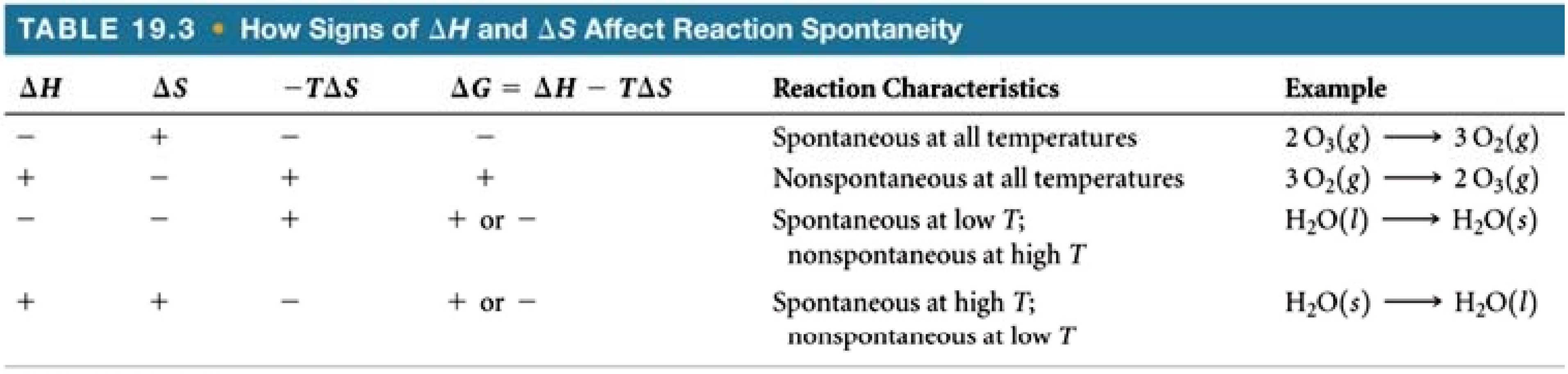


TABLE 19.3 • How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2\,O_3(g) \longrightarrow 3\,O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high T; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

Spontaneous or Not?

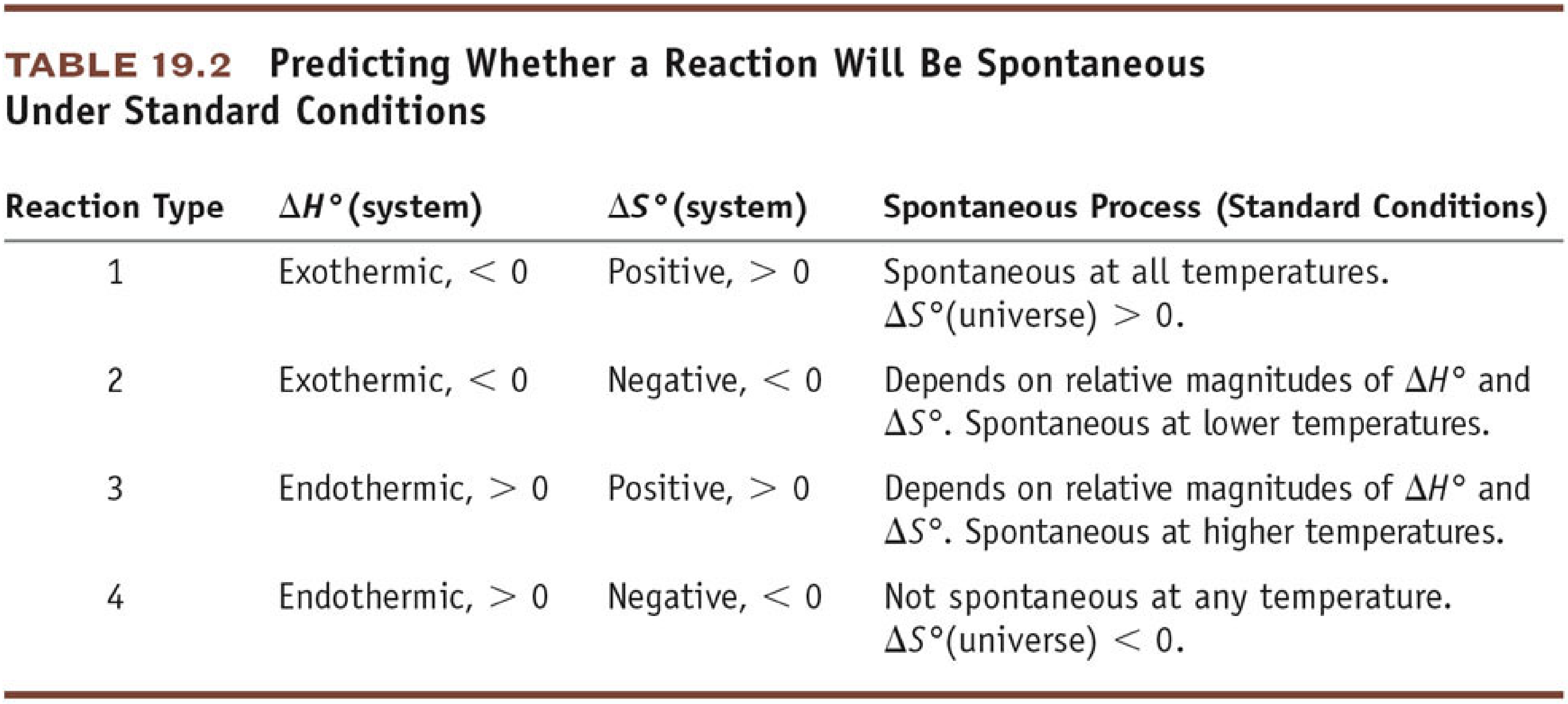


TABLE 19.2 Predicting Whether a Reaction Will Be Spontaneous Under Standard Conditions

Reaction Type	$\Delta H°$(system)	$\Delta S°$(system)	Spontaneous Process (Standard Conditions)
1	Exothermic, < 0	Positive, > 0	Spontaneous at all temperatures. $\Delta S°$(universe) > 0.
2	Exothermic, < 0	Negative, < 0	Depends on relative magnitudes of $\Delta H°$ and $\Delta S°$. Spontaneous at lower temperatures.
3	Endothermic, > 0	Positive, > 0	Depends on relative magnitudes of $\Delta H°$ and $\Delta S°$. Spontaneous at higher temperatures.
4	Endothermic, > 0	Negative, < 0	Not spontaneous at any temperature. $\Delta S°$(universe) < 0.

Free Energy and Equilibrium

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

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

where Q is the reaction quotient

R = the ideal gas constant, 8.314 J/mol-K

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

$$\Delta G = \Delta G^\circ$$

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

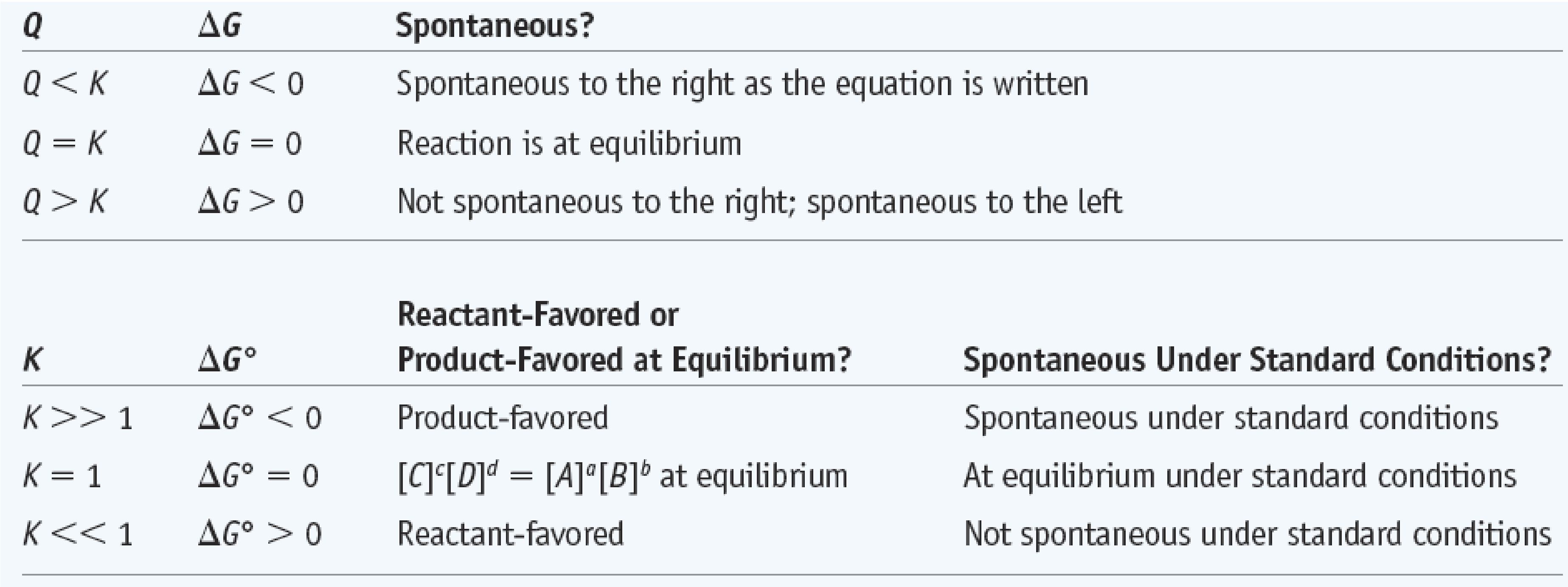
$$\Delta G^\circ = -RT \ln K$$

or,

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

A Summary

The relation of $\Delta_r G$, $\Delta_r G^\circ$, Q, K, reaction spontaneity, and product- or reactant favorability.



Q	ΔG	Spontaneous?
$Q < K$	$\Delta G < 0$	Spontaneous to the right as the equation is written
$Q = K$	$\Delta G = 0$	Reaction is at equilibrium
$Q > K$	$\Delta G > 0$	Not spontaneous to the right; spontaneous to the left

K	ΔG°	Reactant-Favored or Product-Favored at Equilibrium?	Spontaneous Under Standard Conditions?
$K >> 1$	$\Delta G^\circ < 0$	Product-favored	Spontaneous under standard conditions
$K = 1$	$\Delta G^\circ = 0$	$[C]^c[D]^d = [A]^a[B]^b$ at equilibrium	At equilibrium under standard conditions
$K << 1$	$\Delta G^\circ > 0$	Reactant-favored	Not spontaneous under standard conditions