

Chapter 19

Thermodynamics

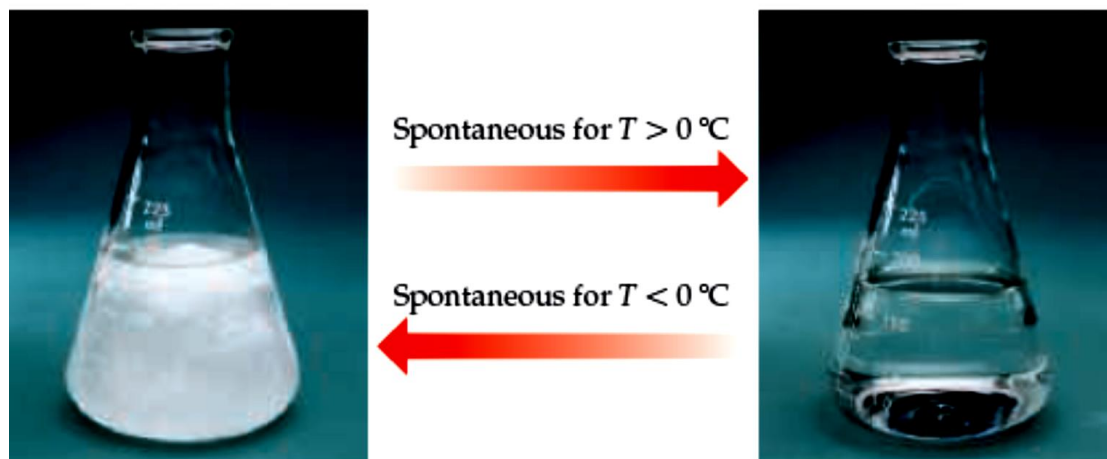
Thermodynamics studies how changes in energy, entropy and temperature affect the *spontaneity* of a process or chemical reaction.

Using thermodynamics we can predict the direction a reaction will go, and also the *driving force* of a reaction or system to go to equilibrium.

Spontaneity

A *spontaneous* process is one that occurs without outside intervention.

It **can release energy, require energy** (ice melting at temperatures above 0°C) or involve **no energy change** at all (two gases mixing).



▲ **Figure 19.2** Spontaneity can depend on temperature. At $T > 0^{\circ}\text{C}$, ice melts spontaneously to liquid water. At $T < 0^{\circ}\text{C}$, the reverse process, water freezing to ice, is spontaneous. At $T = 0^{\circ}\text{C}$ the two states are in equilibrium.

Spontaneity is **independent of the speed or rate** of a reaction.

A spontaneous process may proceed very slowly.

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

Predict whether each process is spontaneous as described, spontaneous in the reverse direction, or at equilibrium:

- (a) Water at 40 °C gets hotter when a piece of metal heated to 150 °C is added.
- (b) Water at room temperature decomposes into $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$.
- (c) Benzene vapor, $\text{C}_6\text{H}_6(\text{g})$, at a pressure of 101.3 kPa condenses to liquid benzene at the normal boiling point of benzene, 80.1 °C.

► **Practice Exercise 1**

The process of iron being oxidized to make iron(III) oxide (rust) is spontaneous. Which of these statements about this process is/are true? **(a)** The reduction of iron(III) oxide to iron is also spontaneous. **(b)** Because the process is spontaneous, the oxidation of iron must be fast. **(c)** The oxidation of iron is endothermic. **(d)** Equilibrium is achieved in a closed system when the rate of iron oxidation is equal to the rate of iron(III) oxide reduction. **(e)** The energy of the universe is decreased when iron is oxidized to rust.

► **Practice Exercise 2**

At 101.3 kPa pressure, $\text{CO}_2(\text{s})$ sublimates at $-78\text{ }^\circ\text{C}$. Is this process spontaneous at $-100\text{ }^\circ\text{C}$ and 101.3 kPa pressure?

Factors that can be combined to predict spontaneity:

- 1. Energy Change**
- 2. Temperature**
- 3. Entropy Change**

**19.2 | Entropy and the Second Law
of Thermodynamics**

Entropy

Entropy, **S**, is a measure of **randomness** or **disorder**. The natural tendency of things is to tend toward greater disorder. This is because there are many ways (or positions) that lead to disorder, but very few that lead to an ordered state.



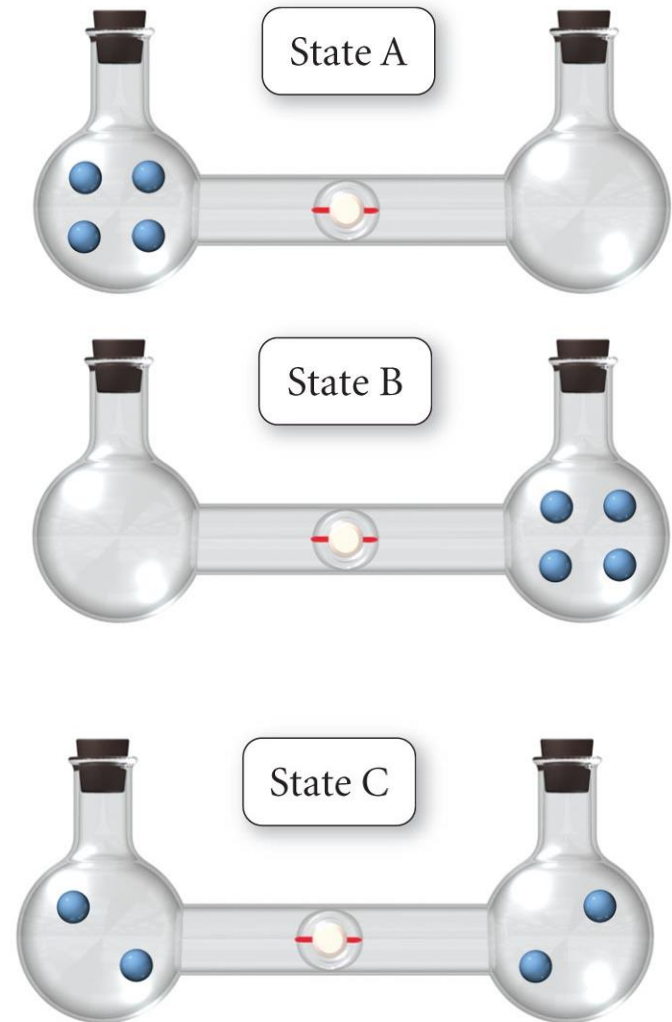
The entropy of a system is defined by the Boltzmann equation:

$$S = k \ln W$$

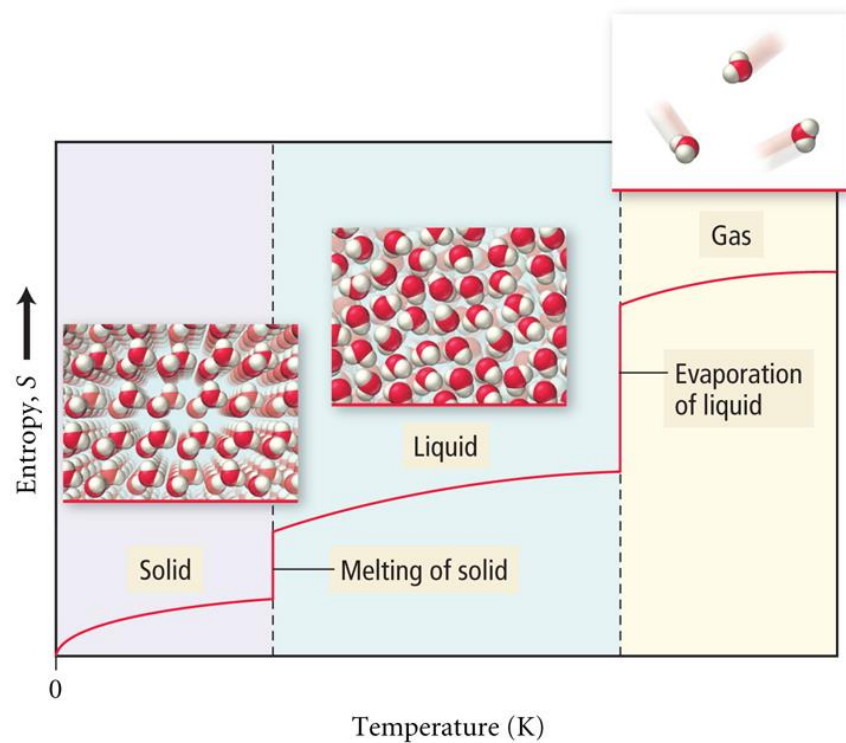
k is the Boltzmann constant, and W is the number of energetically equivalent ways to arrange the components of the system.

The driving force for a spontaneous process is an **increase in the entropy of the universe.**

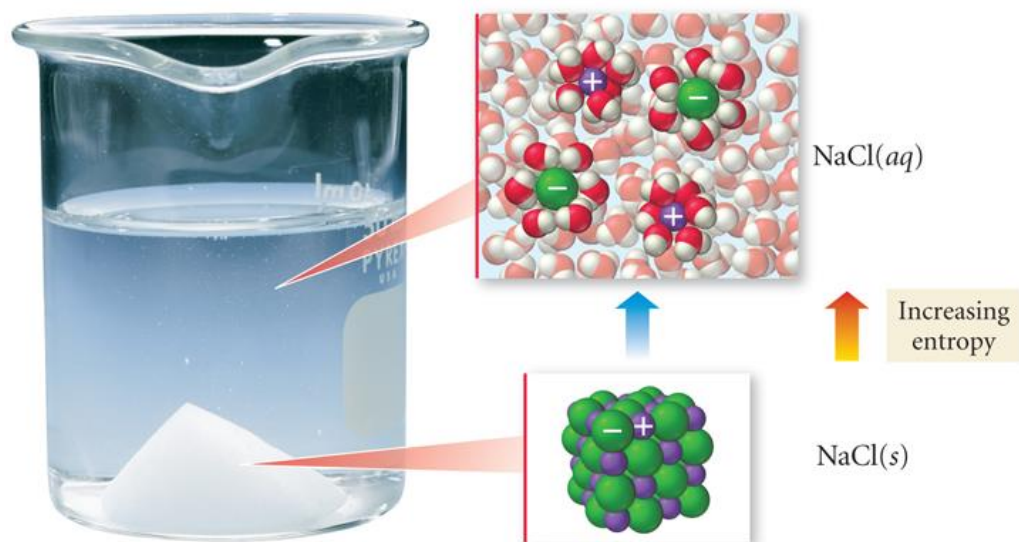
Gases will spontaneously and uniformly mix because the mixed state has more possible arrangements (a larger value of W and higher entropy) than the unmixed state.



ΔS° and Phase Changes



ΔS° and Mixtures

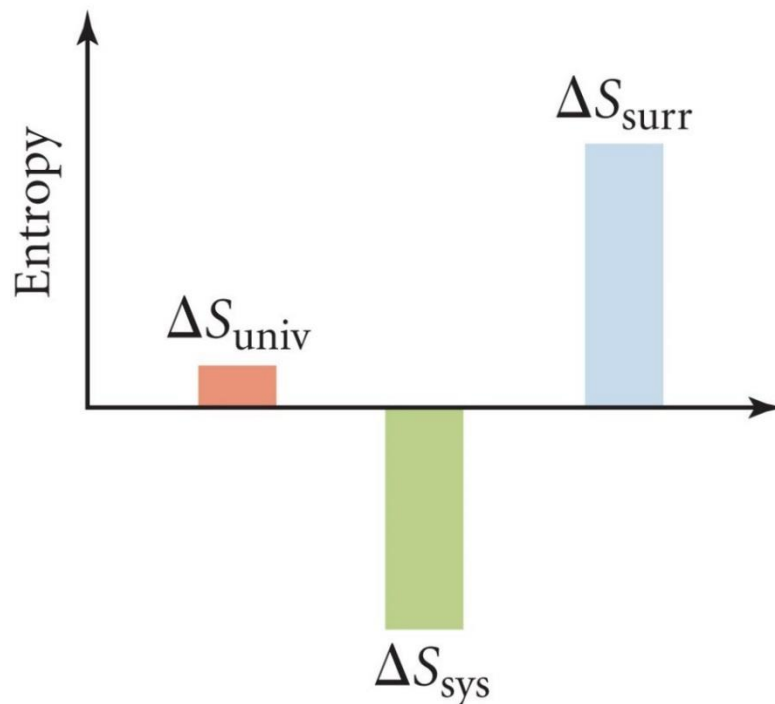


The 2nd Law of Thermodynamics

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

Water spontaneously freezes at a temperature below 0°C

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$



Δ S and Spontaneity

Signs of Entropy Changes

ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	<i>Process Spontaneous?</i>
+	+	+	Yes
—	—	—	No (reaction will occur in opposite direction)
<u>+</u>	—	?	Yes, if <u>ΔS_{sys}</u> has a larger magnitude than ΔS_{surr}
—	<u>+</u>	?	Yes, if <u>ΔS_{surr}</u> has a larger magnitude than ΔS_{sys}

Predicting the sign of ΔS°

For many chemical reactions or physical changes, it is relatively easy to predict if the entropy **of the system** is increasing or decreasing.

For chemical reactions, it is sometimes possible to **compare the randomness of products versus reactants.**



The production of a gaseous product from a solid reactant will have a positive value of ΔS° .

Entropy Values of Common Substances

Since entropy is a measure of randomness, it is possible to calculate absolute entropy values. This is in contrast to enthalpy values, where we can only calculate changes in enthalpy. **A perfect crystal at absolute zero has an entropy value (S) = 0.** All other substances have positive values of entropy due to some degree of disorder.

TABLE 17.1 Standard Molar Entropies for Some Common Substances at 25°C

Substance	Formula	S° [J/(K · mol)]	Substance	Formula	S° [J/(K · mol)]
<i>Gases</i>			<i>Liquids</i>		
Acetylene	C ₂ H ₂	200.8	Acetic acid	CH ₃ CO ₂ H	160
Ammonia	NH ₃	192.3	Ethanol	CH ₃ CH ₂ OH	161
Carbon dioxide	CO ₂	213.6	Methanol	CH ₃ OH	127
Carbon monoxide	CO	197.6	Water	H ₂ O	69.9
Ethylene	C ₂ H ₄	219.5	<i>Solids</i>		
Hydrogen	H ₂	130.6	Calcium carbonate	CaCO ₃	92.9
Methane	CH ₄	186.2	Calcium oxide	CaO	39.7
Nitrogen	N ₂	191.5	Diamond	C	2.4
Nitrogen dioxide	NO ₂	240.0	Graphite	C	5.7
Dinitrogen tetroxide	N ₂ O ₄	304.2	Iron	Fe	27.3
Oxygen	O ₂	205.0	Iron(III) oxide	Fe ₂ O ₃	87.4

Entropy Values

For comparable structures, the entropy increases with increasing mass

For molecules with similar masses, the more complex molecule has greater entropy. The molecule with more bonds has additional ways to absorb energy, and thus greater entropy.

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

	Molar Mass (g/mol)	S° (J/mol · K)
CO(g)	28.01	197.7
C ₂ H ₄ (g)	28.05	219.3

Entropy, temperature and heat flow all play a role in spontaneity. A thermodynamic quantity, the ***Gibbs Free Energy*** (**G**), combines these factors to predict the spontaneity of a process.

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

If a process releases heat (ΔH is negative) and has an increase in entropy (ΔS is positive), it will always be spontaneous.

The value of ΔG for spontaneous processes is negative.

Spontaneity

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

If $\Delta G < 0$, the process is spontaneous

If $\Delta G > 0$, the process is non-spontaneous

If $\Delta G = 0$, the system is at equilibrium.

Case
ΔS positive, ΔH negative
ΔS positive, ΔH positive
ΔS negative, ΔH negative
ΔS negative, ΔH positive

Result?

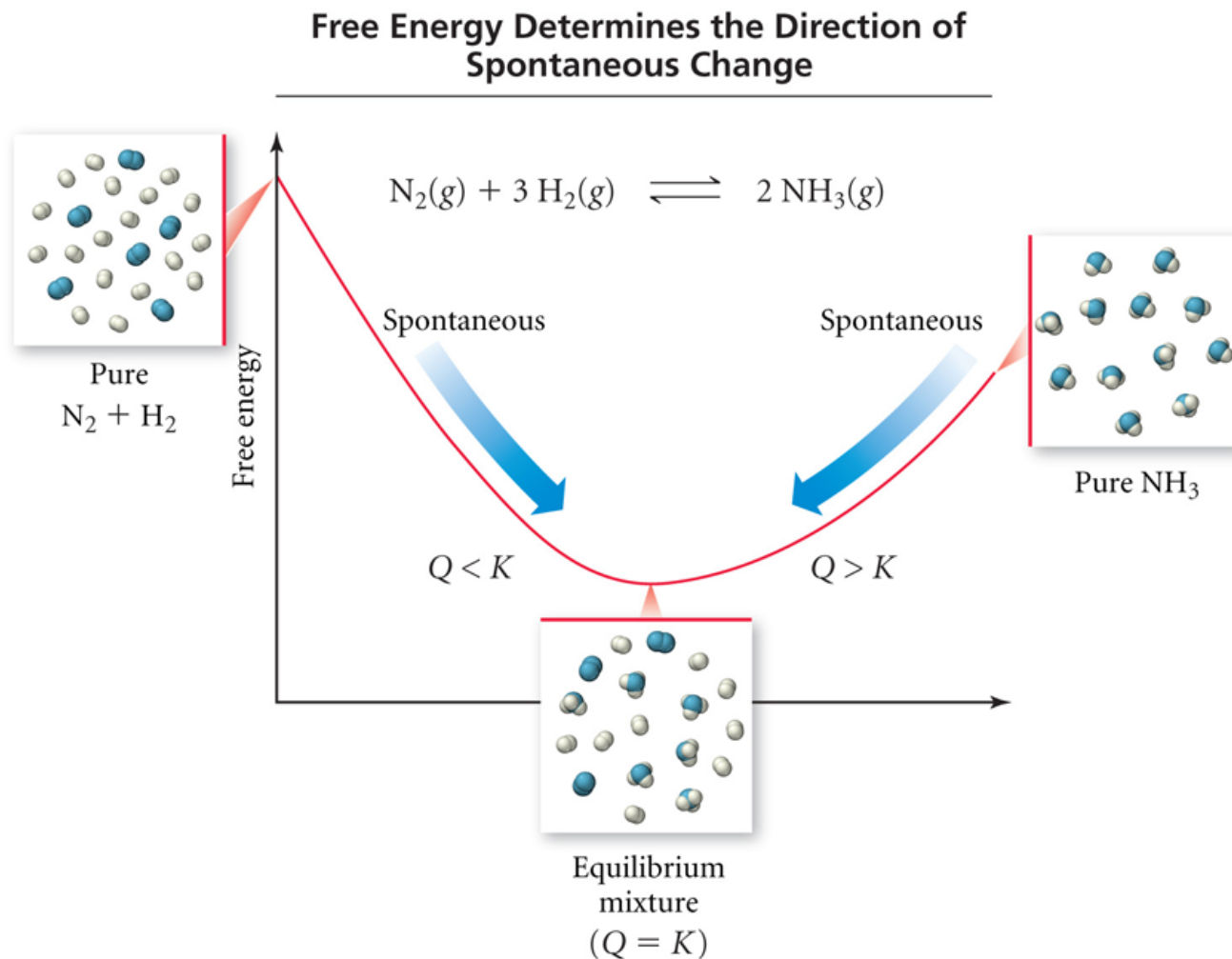
ΔG

Although ΔG can be used to predict in which direction a reaction will proceed, it does not predict the rate of the reaction.

For example, the conversion of diamond to graphite has a $\Delta G^\circ = -3 \text{ kJ}$, so diamonds should spontaneously change to graphite at standard conditions. However, **kinetics shows that the reaction is extremely slow.**

The Significance of ΔG

ΔG represents the driving force for the reaction to proceed to equilibrium.



ΔG and Equilibrium Constant

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

At equilibrium, ΔG is equal to zero, and $Q = K$.

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

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

Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Standard Molar Free Energies of Formation (ΔG_f°) for Selected Substances at 298 K

Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)
H ₂ (g)	0	CH ₄ (g)	−50.5
O ₂ (g)	0	H ₂ O(g)	−228.6
N ₂ (g)	0	H ₂ O(l)	−237.1
C(s, graphite)	0	NH ₃ (g)	−16.4
C(s, diamond)	2.900	NO(g)	+87.6
CO(g)	−137.2	NO ₂ (g)	+51.3
CO ₂ (g)	−394.4	NaCl(s)	−384.1

Calculate, ΔG° and K at 25°C for:



$$\begin{aligned}
 \Delta G^\circ &= (1 \text{ mol}) \Delta G_f^\circ \text{ (graphite)} - (1 \text{ mol}) \Delta G_f^\circ \text{ (diamond)} \\
 &= 0 - (1 \text{ mol})(2.900 \text{ kJ/mol}) \\
 &= -2.900 \text{ kJ}
 \end{aligned}$$

The reaction is spontaneous at 25°C.