Chapter 19
Chemical Thermodynamics

19.1 Spontaneous Processes

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.

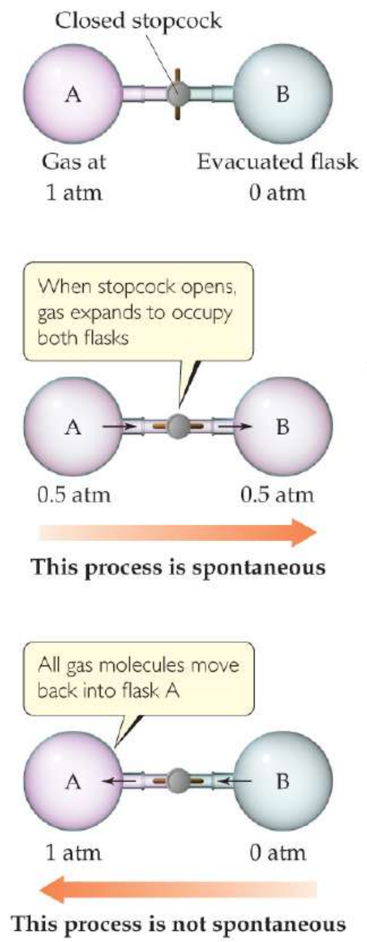
Enthalpy/Entropy

- Enthalpy is the heat absorbed by a system during a constant-pressure process.
- Entropy is a measure of the randomness in a system.
- Both play a role in determining whether a process is spontaneous.

Spontaneous Processes

- **Spontaneous processes** proceed without any outside assistance.
- The gas in vessel A will spontaneously effuse into vessel B, but it will *not* spontaneously return to vessel A.

⑩ Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

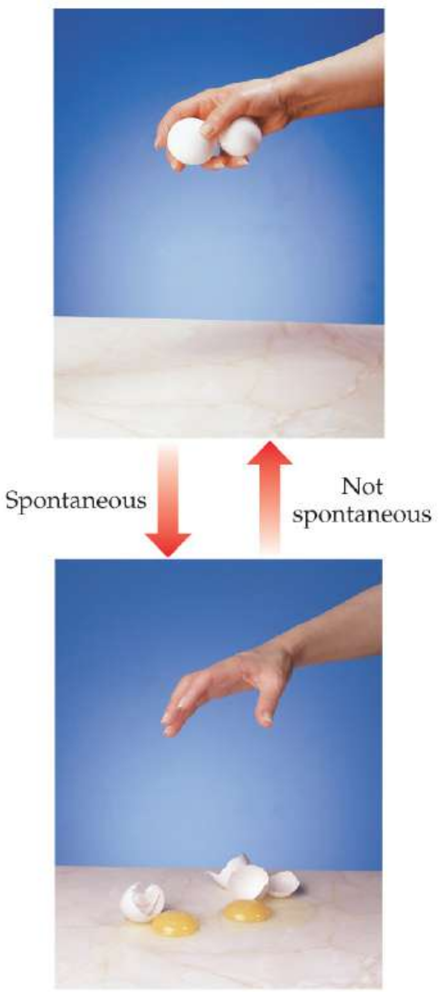


When stopcock opens, gas expands to occupy both flasks

This process is spontaneous

All gas molecules move back into flask A

This process is not spontaneous



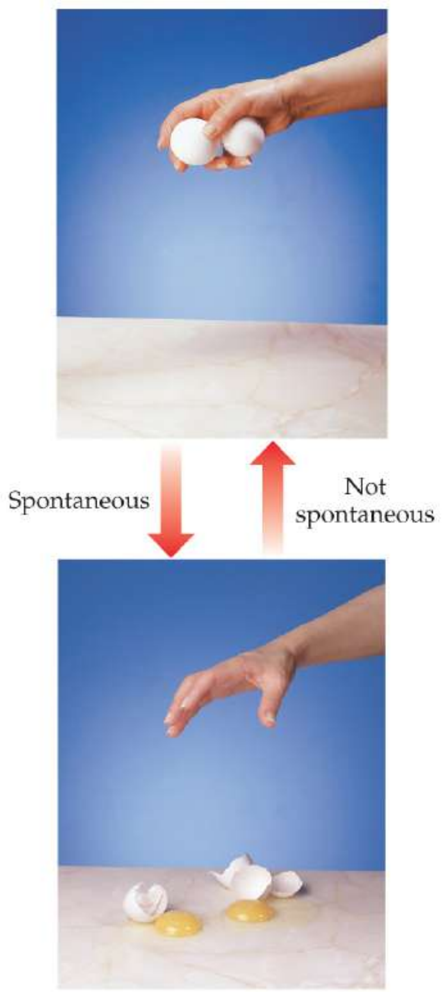
Does the potential energy of the eggs change during this process?

a. Yes, as the eggs move downward

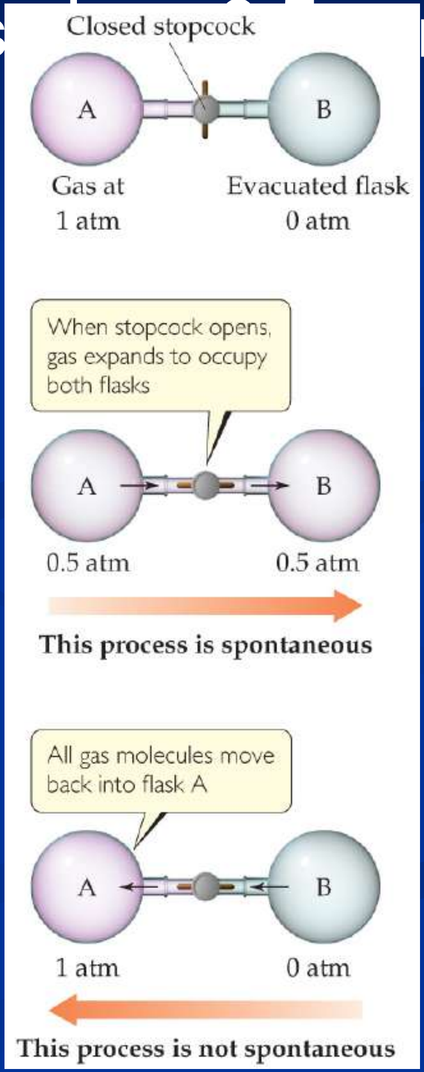
b. Yes, because the eggs undergo a change in velocity upon release.

c. No, because the eggs break upon hitting the surface.

d. No, the yellow yolk is a liquid and changes locations within the egg.



If flask B were smaller than flask A, would the final pressure after the stopcock is opened be greater than, equal to, or less m?



a. Greater than 0.5 atm

b. Equal to 0.5 atm

c. Less than 0.5 atm

Sample Exercise 19.1

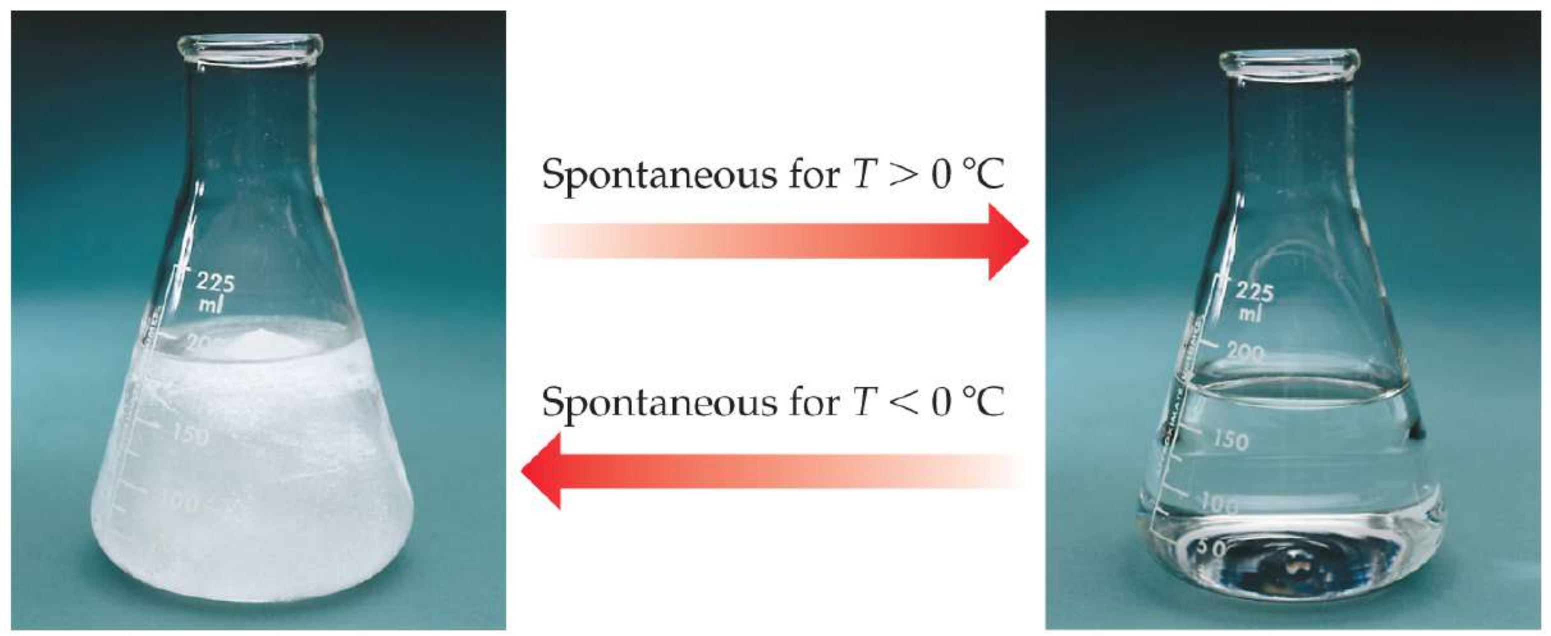
- Predict whether the following processes are spontaneous as described, spontaneous in the reverse direction, or in equilibrium:
  - A) When a piece of metal is heated to 150°C is added to water at 40°C and the water gets hotter
  - B) Water at room temperature decomposes into $H_{2(g)}$ and $O_{2(g)}$
  - C) Benzene vapor, $C_6H_{6(g)}$, at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, 80.1°C

Practice Exercise 2

- Under 1 atm pressure, $CO_{2(s)}$ sublimes at -78°C. Is the transformation of $CO_{2(s)}$ to $CO_{2(g)}$ a spontaneous process at -100°C and 1 atm pressure.

Experimental Factors Affect Spontaneous Processes

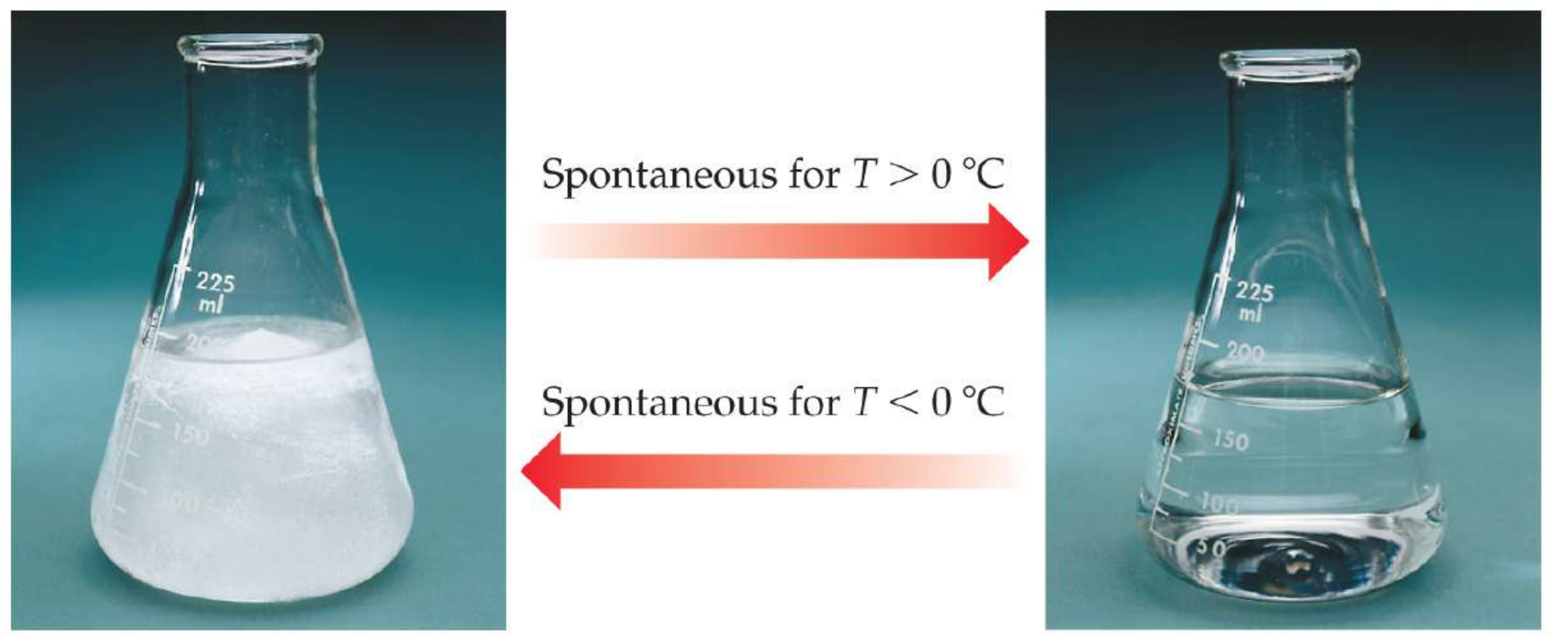
- Temperature and pressure can affect spontaneity.
- An example of how temperature affects spontaneity is ice melting or freezing.



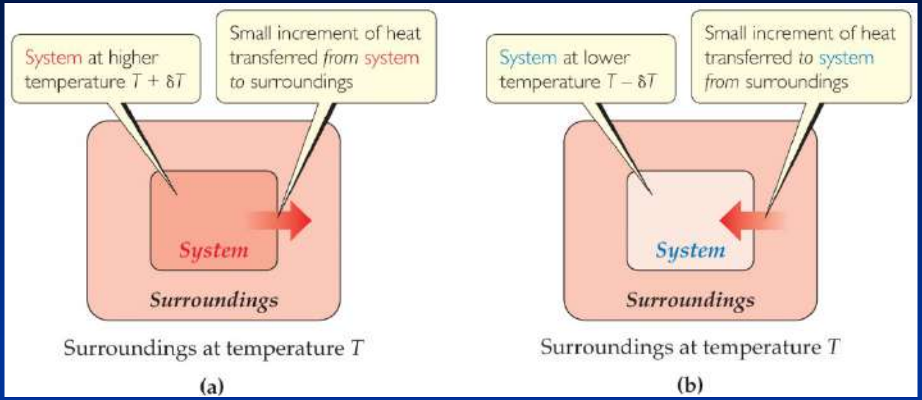
In which direction is this process exothermic?

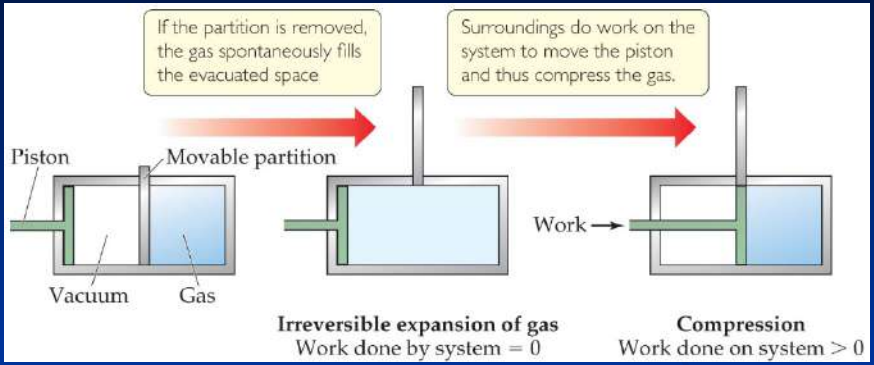
a. Freezing of liquid water to ice

b. Melting of ice to liquid water



Reversible and Irreversible Processes

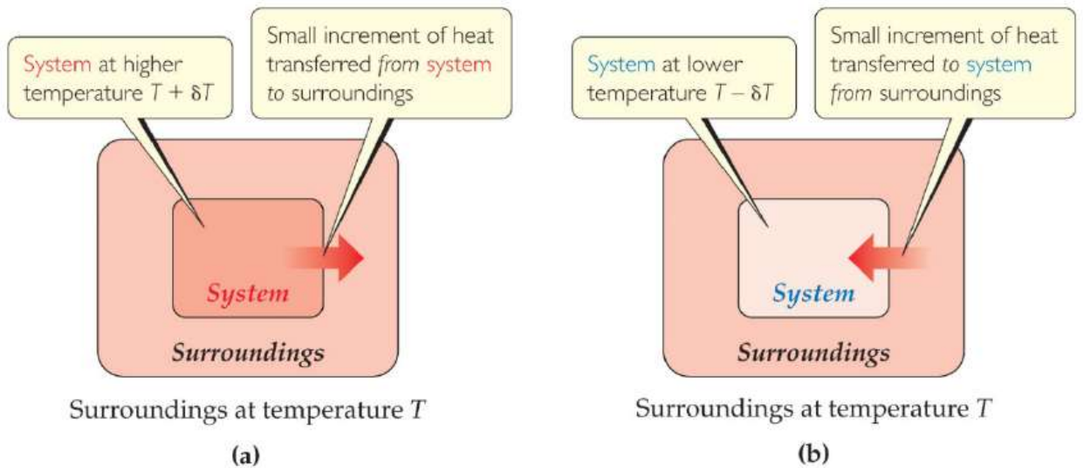




Reversible process: The system changes so that the system and surroundings can be returned to the original state by exactly reversing the process. This maximizes work done by a system *on* the surroundings.

Irreversible processes cannot be undone by exactly reversing the change to the system or cannot have the process exactly followed in reverse. Also, any spontaneous process is irreversible!

If the flow of heat into or out of the system is to be reversible, what must be true of



Surroundings at temperature T

(a)

Surroundings at temperature T

(b)

a. ΔT must be very large.

b. ΔT must be close to zero.

c. ΔT must be zero.

d. ΔT must be infinitesimally small.

19.1 Give It Some Thought

- If a process is nonspontaneous, does that mean the process cannot occur under any circumstances?
- Suppose you have a system made up of water only, with the container and everything beyond being the surroundings. Consider a process in which the water is first evaporated and then condensed back into its original container. Is this two-step process necessarily reversible?

19.2 Entropy and the Second Law of Thermodynamics

Entropy

- **Entropy** can be thought of as a measure of the randomness of a system.
- It is a state function:

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

- It can be found by heat transfer from surroundings at a given temperature:

$$\Delta S = \frac{q_{\text{rev}}}{T} \qquad (\text{constant } T)$$

Sample Exercise 19.2

- The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is -38.9°C, and its molar enthalpy of fusion is $\Delta H_{fus} = 2.29$ kJ/mol. What is the entropy change of the system when 50.0 g of $Hg_{(l)}$ freezes at the normal freezing point?

Practice Exercise 1

Do all exothermic phase changes have a negative value for the entropy change of the system?

(a) Yes, because the heat transferred from the system has a negative sign.

(b) Yes, because the temperature decreases during the phase transition.

(c) No, because the entropy change depends on the sign of the heat transferred to or from the system.

(d) No, because the heat transferred to the system has a positive sign.

(e) More than one of the previous answers is correct.

Practice Exercise 2

- The normal boiling point of ethanol, C_2H_5OH, is 78.3°C, and its molar enthalpy of vaporization is 38.56 kJ/mol. What is the change in entropy in the system when 68.3 g of $C_2H_5OH_{(g)}$ at 1 atm condenses to liquid at the normal boiling point?

Second Law of Thermodynamics

- The entropy of the universe increases in any spontaneous processes.
- This results in the following relationships:

Reversible Process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

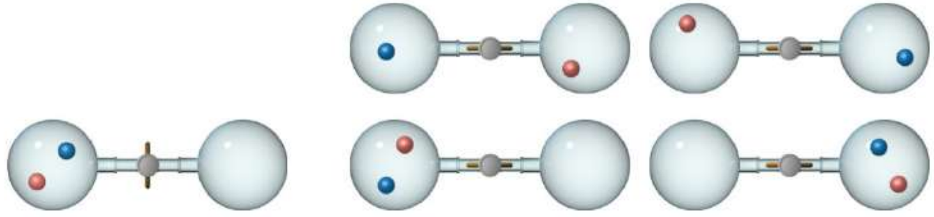
Irreversible Process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

19.2 Give It Some Thought

- How can S be a state function when ΔS depends on *q*, which is not a state function?
- The rusting of iron is spontaneous and is accompanied by a decrease in the entropy of the system (the iron and oxygen). What can we conclude about the entropy change of the surroundings?

19.3 The Molecular Interpretation of Entropy and the Third Law of Thermodynamics

Entropy on the Molecular Scale



(a)
The two molecules are colored
red and blue to keep track of them.

(b)
Four possible arrangements (microstates)
once the stopcock is opened.

- Boltzmann described entropy on the molecular level.
- Gas molecule expansion: Two molecules are in the apparatus above; both start in one side. What is the likelihood they both will end up there? $(1/2)^2$
- If one mole is used? $(1/2)^{6.02\times1023}$! (*No* chance!)
- Gases spontaneously expand to fill the volume given.
- Most probable arrangement of molecules: approximately equal molecules in each side

Statistical Thermodynamics

- Thermodynamics looks at bulk properties of substances (the *big* picture).
- We have seen what happens on the molecular scale.
- How do they relate?
- We use statistics (probability) to relate them. The field is called statistical thermodynamics.
- Microstate: A single possible arrangement of position and kinetic energy of molecules

Boltzmann's Use of Microstates

- Because there are so many possible microstates, we can't look at every picture.
- *W* represents the number of microstates.
- Entropy is a measure of how many microstates are associated with a particular macroscopic state.
- The connection between the number of microstates and the entropy of the system is:

$$S = k \ln W$$

Entropy Change

- Since entropy is a state function, the final value minus the initial value will give the overall change.
- In this case, an increase in the number of microstates results in a positive entropy change (more disorder).

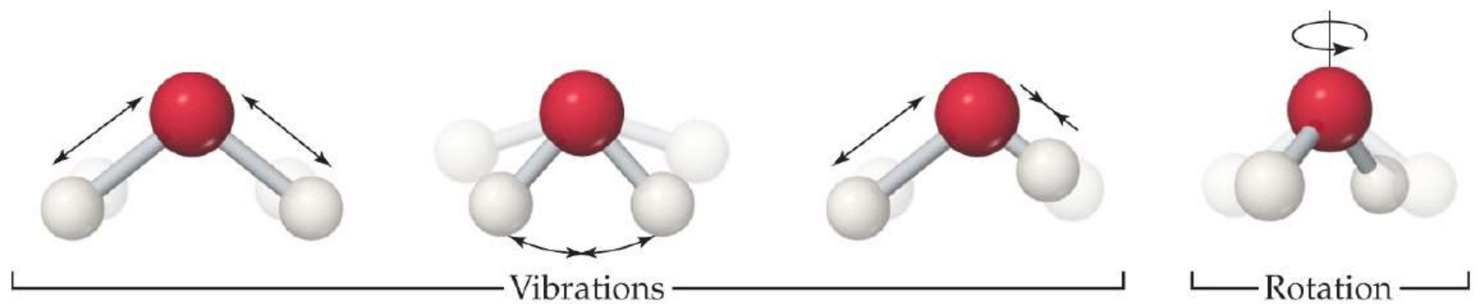
$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$

Effect of Volume and Temperature Change on the System

- If we increase volume, there are more positions possible for the molecules. This results in more microstates, so increased entropy.
- If we increase temperature, the average kinetic energy increases. This results in a greater distribution of molecular speeds. Therefore, there are more possible kinetic energy values, resulting in more microstates, increasing entropy.

Molecular Motions

- 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
- Note: More *atoms* means more microstates (more possible molecular motions).

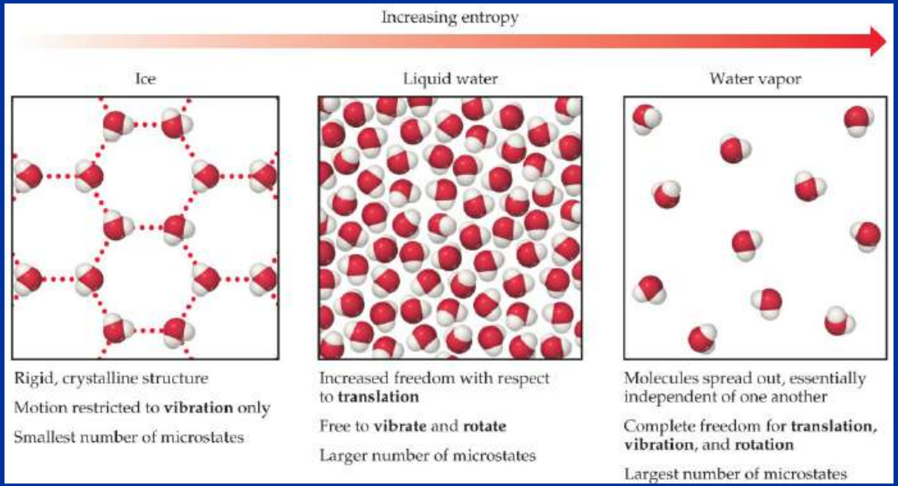


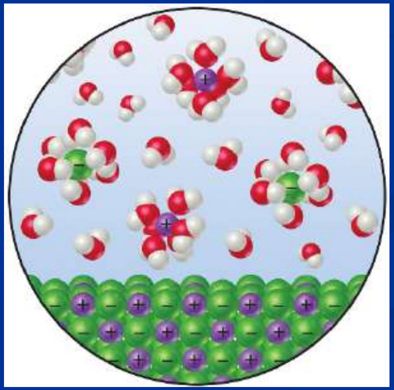
Entropy on the Molecular Scale

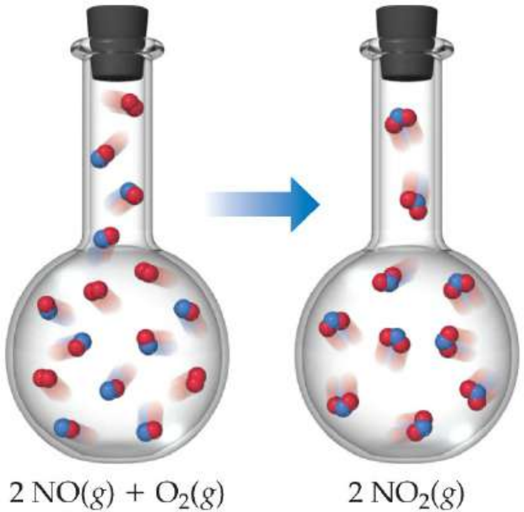
- The number of microstates and, therefore, the entropy tend to increase with increases in
  - temperature.
  - volume.
  - the number of independently moving molecules.

Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- $S(g) > S(l) > S(s)$
- Entropy of a system increases for processes where
  - gases form from either solids or liquids.
  - liquids or solutions form from solids.
  - the number of gas molecules increases during a chemical reaction.





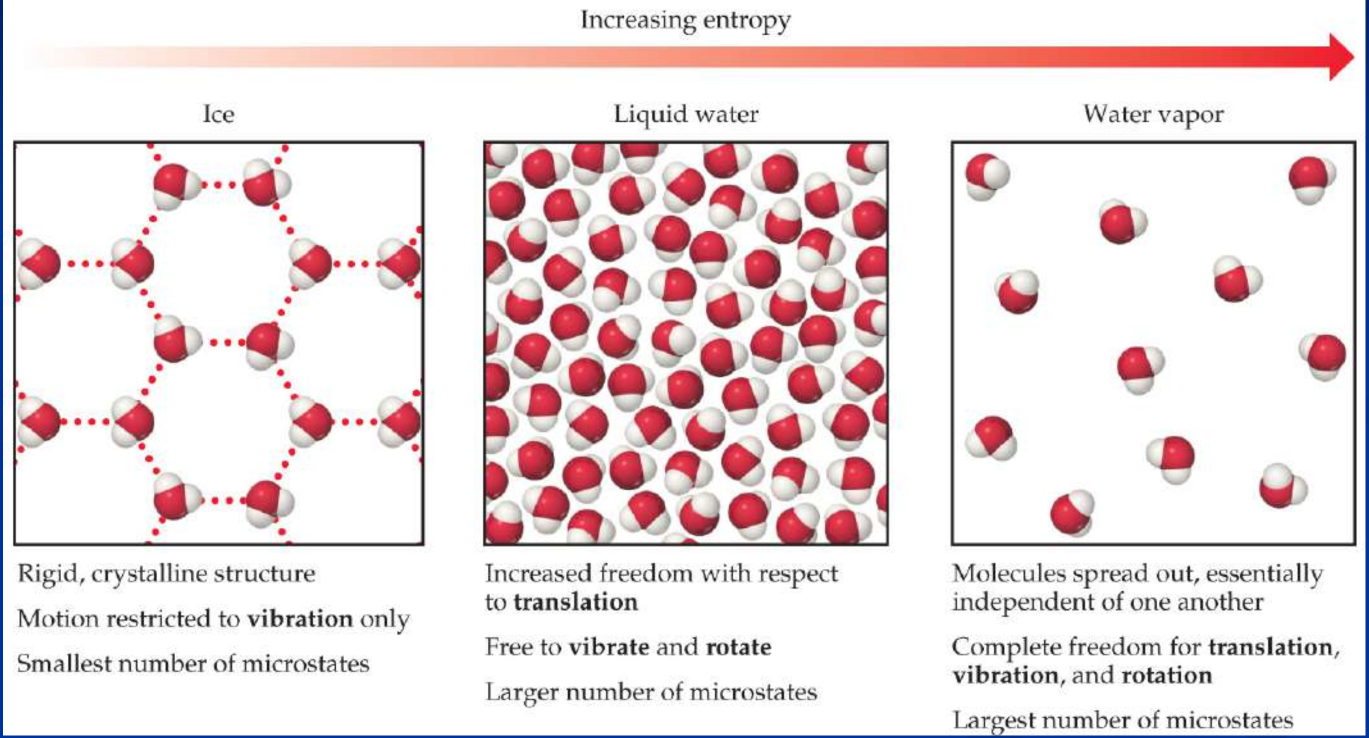


In which phase are water molecules least able to have rotational motion?

a. Vapor

b. Liquid

c. Ice



Rigid, crystalline structure

Motion restricted to **vibration** only

Smallest number of microstates

Increased freedom with respect to **translation**

Free to **vibrate** and **rotate**

Larger number of microstates

Molecules spread out, essentially independent of one another

Complete freedom for **translation**, **vibration**, and **rotation**

Largest number of microstates

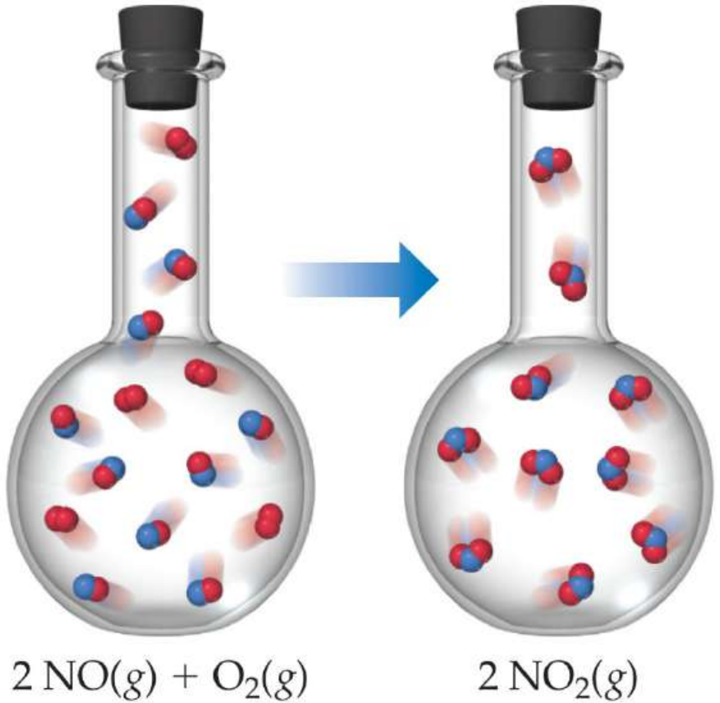
What major factor leads to a decrease in entropy as the reaction shown takes place?

a. Increase in number of molecules during change

b. Decrease in number of molecules during change

c. Change in pressure of system

d. Change in internal energy of system



Sample Exercise 19.3

- Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:
  - A) $H_2O_{(l)} \rightarrow H_2O_{(g)}$
  - B) $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$
  - C) $4\ Fe_{(s)} + 3\ O_{2(g)} \rightarrow 2\ Fe_2O_{3(s)}$
  - D) $N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$

Practice Exercise 1

- Indicate which of the following processes produces an increase or decrease in the entropy of the system:
  - A) $CO_{2(s)} \rightarrow CO_{2(g)}$
  - B) $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$
  - C) $HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$
  - D) $2\ SO_{2(g)} + O_{2(g)} \rightarrow 2\ SO_{3(g)}$

Sample Exercise 19.4

- Choose the sample of matter that has greater entropy in each pair, and explain your choice:
  - A) 1 mol of $NaCl_{(s)}$ of 1 mol of $HCl_{(g)}$ at 25°C
  - B) 2 mol of $HCl_{(g)}$ or 1 mol of $HCl_{(g)}$ at 25°C
  - C) 1 mol of $HCl_{(g)}$ or 1 mol of $Ar_{(g)}$ at 298 K

Practice Exercise 1

Which system has the greatest entropy?

(a) 1 mol of $H_2(g)$ at STP

(b) 1 mol of $H_2(g)$ at 100 °C and 0.5 atm

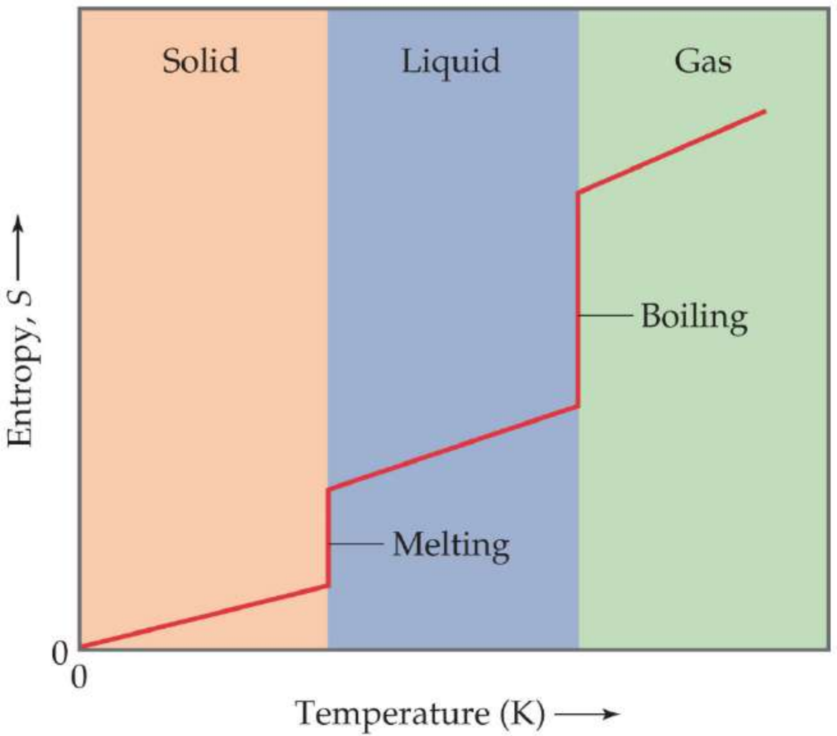
(c) 1 mol of $H_2O(s)$ at 0 °C

(d) 1 mol of $H_2O(l)$ at 25 °C.

Practice Exercise 2

- Choose the substance with the greater entropy:
  - A) 1 mol of $H_{2(g)}$ at STP or 1 mol of $SO_{2(g)}$ at STP
  - B) 1 mol of $N_2O_{4(g)}$ at STP or 2 mol of $NO_{2(g)}$ at STP

Third Law of Thermodynamics



- The entropy of a pure crystalline substance at absolute zero is 0.
- Consider all atoms or molecules in the perfect lattice at 0 K; there will only be *one* microstate.
- $S = k \ln W = k \ln 1 = 0$

Why does the plot show vertical jumps at the melting and boiling points?

a. During melting or boiling at constant temperature, entropy dramatically increases because energy is removed from the system during the change.

b. During melting or boiling at constant temperature, entropy changes significantly because more microstates exist for the final phase compared to the initial phase.

c. During melting or boiling at constant temperature, entropy changes significantly because fewer microstates exist for the final phase compared to the initial phase.

d. During melting or boiling at constant temperature, entropy changes significantly because no change in the number of microstates occurs during the phase change.

19.3 Give It Some Thought

- What is the entropy of a system that has only a single microstate?
- Can an argon atom undergo vibrational motion?
- If you are told the entropy of a certain system is zero, what do you know about the system?

19.4 Entropy Changes in Chemical Reactions

Standard Entropies

- The reference for entropy is 0 K, so the values for elements are *not* 0 J/mol K at 298 K.
- Standard molar enthalpy for gases are generally greater than liquids and solids. (Be careful of size!)
- Standard entropies increase with molar mass.
- Standard entropies increase with number of atoms in a formula.

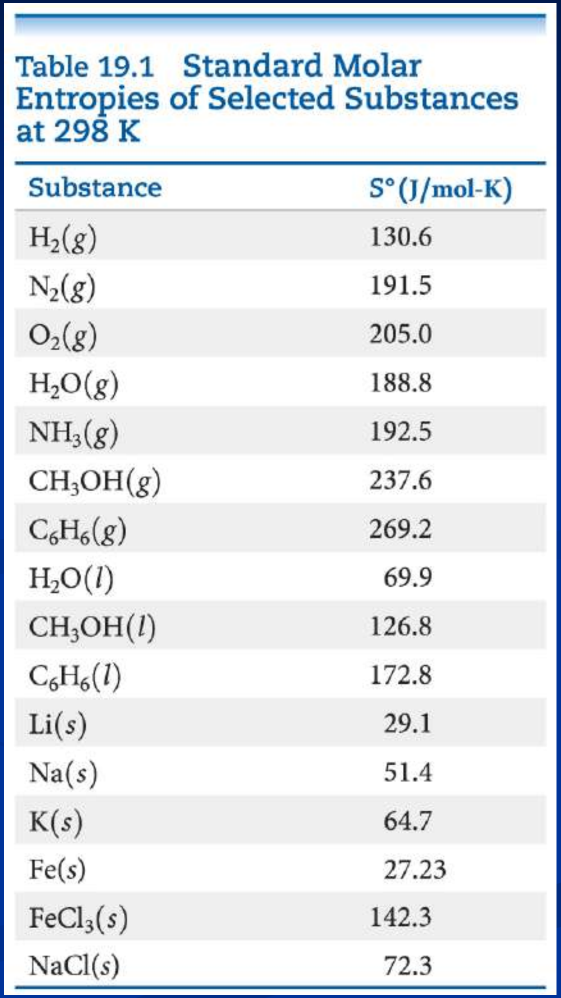


Table 19.1 Standard Molar Entropies of Selected Substances at 298 K

Substance	S° (J/mol-K)
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	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

Entropy Changes

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

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

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

Sample Exercise 19.5

- Calculate ΔSº for the synthesis of ammonia from $N_{2(g)}$ and $H_{2(g)}$ at 298 K:

$$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$$

Practice Exercise 1

Using the standard molar entropies in Appendix C, calculate the standard entropy change, $\Delta S°$, for the "water-splitting" reaction at 298 K:

$$2\ H_2O(l) \rightarrow 2\ H_2(g) + O^2(g)$$

(a) 326.3 J/K

(b) 265.7 J/K

(c) 163.2 J/K

(d) 88.5 J/K

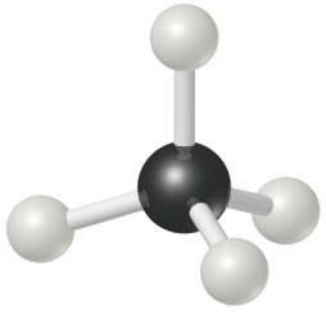
(e) −326.3 J/K.

Practice Exercise 2

Using the standard molar entropies in Appendix C, calculate the standard entropy change, Δ*S*°, for the following reaction at 298 K:

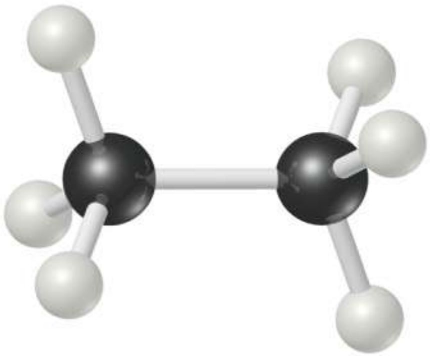
$$Al_2O_3(s) + 3\ H_2(g) \rightarrow 2\ Al(s) + 3\ H_2O(g)$$

What might you expect for the value of S° for butane, C_4H_{10}?



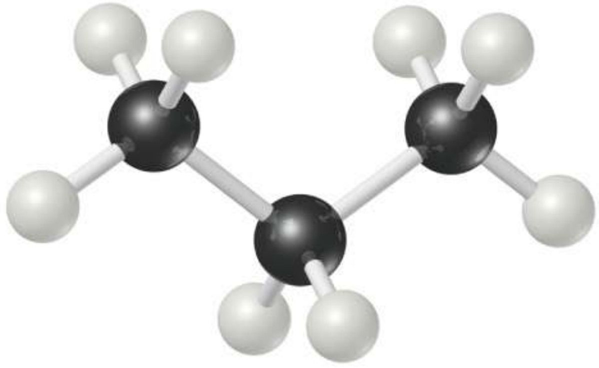
Methane, CH_4

$S° = 186.3$ J/mol-K



Ethane, C_2H_6

$S° = 229.6$ J/mol-K



Propane, C_3H_8

$S° = 270.3$ J/mol-K

a. 270 J/mol-K to 300 J/mole-K

b. 280 J/mol-K to 305 J/mole-K

c. 310 J/mol-K to 315 J/mole-K

d. 320 J/mol-K to 340 J/mole-K

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.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad [\text{at constant P}]$$

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

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

19.4 Give It Some Thought

If a process is exothermic, does the entropy of the surroundings:

(a) always increase

(b) always decrease

(c) sometimes increase and sometimes decrease, depending on the process.

19.5 Gibbs Free Energy

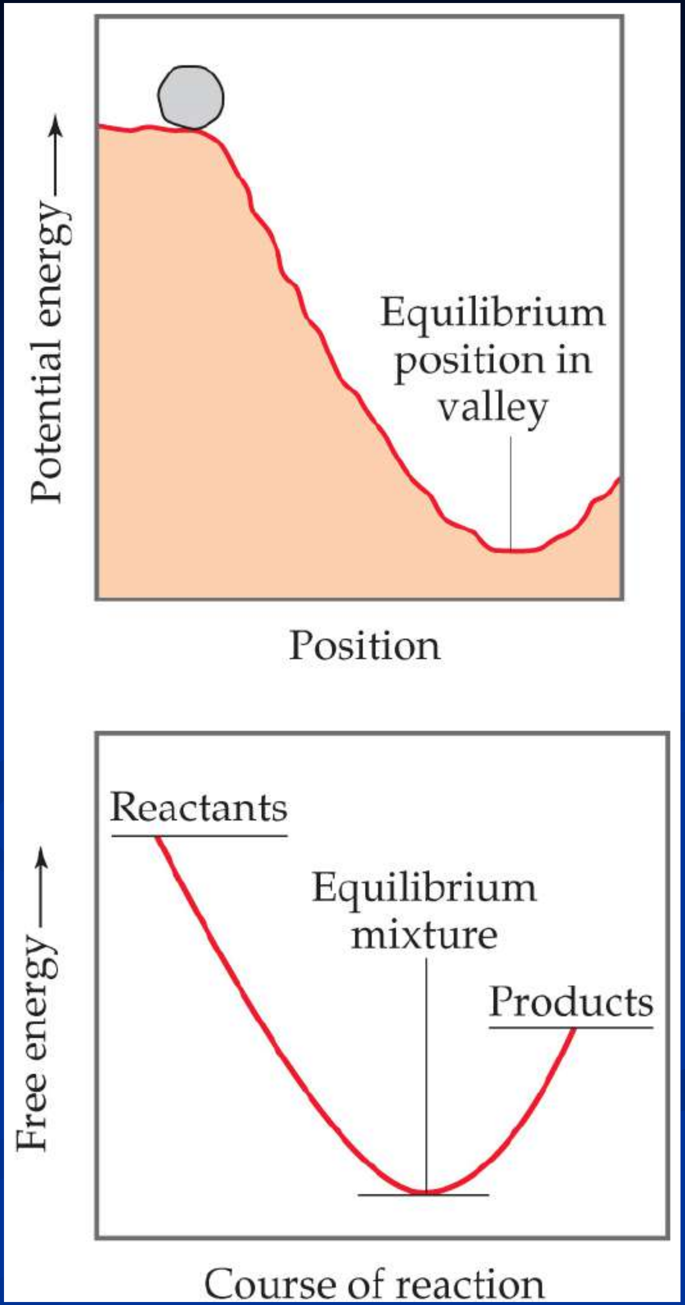
Total Entropy and Spontaneity

- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- Substitute for the entropy of the surroundings:
  - $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T$
- Multiply by $-T$:
  - $-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$
- Rearrange:
  - $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$
- Call $\boldsymbol{-T\Delta S_{\text{universe}}}$ the **Gibbs Free Energy (ΔG)**:
  - $\boldsymbol{\Delta G = \Delta H - T\Delta S}$

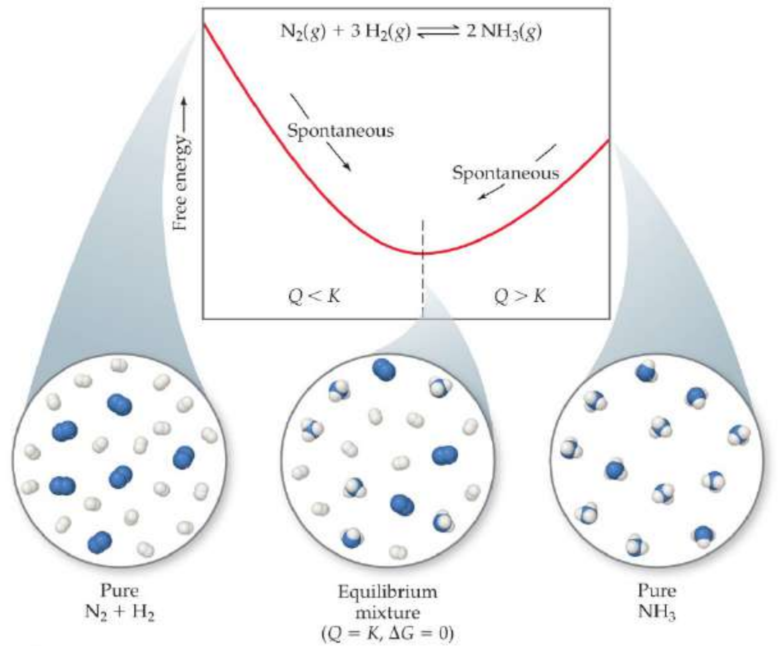
Are the processes that move a system toward equilibrium spontaneous or nonspontaneous?

a. Spontaneous

b. Nonspontaneous

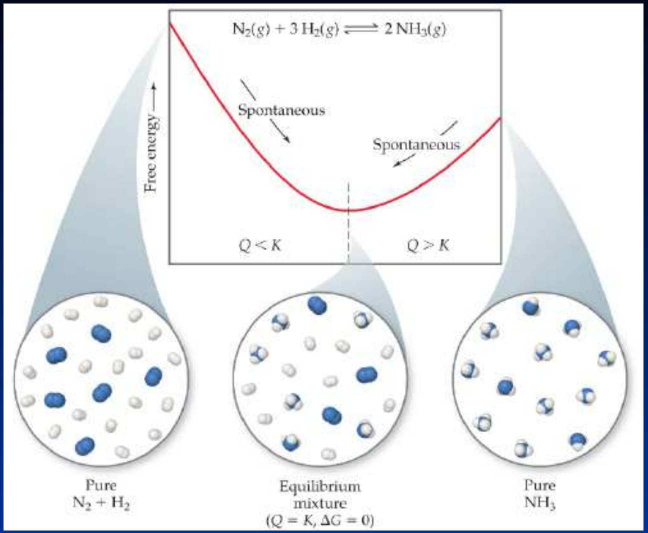


Gibbs Free Energy



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.

Why are the spontaneous processes shown sometimes said to be “downhill” in free energy?



a. The “downhill” in free energy leads to a transition state.

b. An equilibrium is always achieved when both enthalpy and entropy decrease in magnitude, that is “downhill.”

c. Free-energy difference between a product and a reactant is always negative, that is “downhill.”

d. An equilibrium reaches a state of minimum free energy, which is lower than the free energies of the reactants and products, in a “downhill” direction.

Sample Exercise 19.6 Calculating Free-Energy Change from ΔH°, T, ΔS°

Calculate the standard free energy change for the formation of NO(*g*) from $N_2(g)$ and $O_2(g)$ at 298 K:

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$

given that $\Delta H^\circ = 180.7$ kJ and $\Delta S^\circ = 24.7$ J/K. Is the reaction spontaneous under these circumstances?

Practice Exercise 1

Which of these statements is true?

(a) All spontaneous reactions have a negative enthalpy change

(b) All spontaneous reactions have a positive entropy change

(c) All spontaneous reactions have a positive free-energy change

(d) All spontaneous reactions have a negative free-energy change

(e) All spontaneous reactions have a negative entropy change.

Practice Exercise 2

Calculate $\Delta G°$ for a reaction for which $\Delta H° = 24.6$ kJ and $\Delta S° = 132$ J / K at 298 K. Is the reaction spontaneous under these conditions?

Standard Free Energy Changes

Analogous to standard enthalpies of formation are standard free energies of formation, $\Delta G_f°$:

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

where n and m are the stoichiometric coefficients.

Sample Exercise 19.7 Calculating Standard Free Energy Change from Free Energies of Formation

(a) Use data from Appendix C to calculate the standard free-energy change for the following reaction at
298 K:
$P_4(g) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g)$

(b) What is ΔG° for the reverse of the above reaction?

Practice Exercise 1

The following chemical equations describe the same chemical reaction. How do the free energies of these two chemical equations compare?

(1) $2\ H_2O(l) \longrightarrow \quad 2\ H_2(g) + O_2(g)$

(2) $H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}\ O_2(g)$

(a) $\Delta G°_1 = \Delta G°_2$

(b) $\Delta G°_1 = 2\ \Delta G°_2$

(c) $2\Delta G°_1 = \Delta G°_2$

(d) None of the above.

Practice Exercise 2

By using data from Appendix C, calculate ΔG° at 298 K for the combustion of methane:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$.

Sample Exercise 19.8

- In section 5.7 we used Hess's law to calculate ΔHº for the combustion of propane gas at 298K: $C_3H_{8(g)} + 5\ O_{2(g)} \rightarrow 3\ CO_{2(g)} + 4\ H_2O_{(l)}$ ΔHº = -2220 kJ
  - A) Without using the data from Appendix C, predict whether ΔGº for this reaction is more negative or less negative than ΔHº.
  - B) Use the date from Appendix C to calculate the standard free-energy change for the reaction at 298 K. Is your prediction correct?

Practice Exercise 1

If a reaction is exothermic and its entropy change is positive, which statement is true?

(a) The reaction is spontaneous at all temperatures

(b) The reaction is nonspontaneous at all temperatures

(c) The reaction is spontaneous only at higher temperatures

(d) The reaction is spontaneous only at lower temperatures.

Practice Exercise 2

Consider the combustion of propane to form $CO_2(g)$ and $H_2O(g)$ at 298 K: $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$. Would you expect ΔG° to be more negative or less negative than ΔH° ?

19.6 Free Energy and Temperature

Free Energy Changes

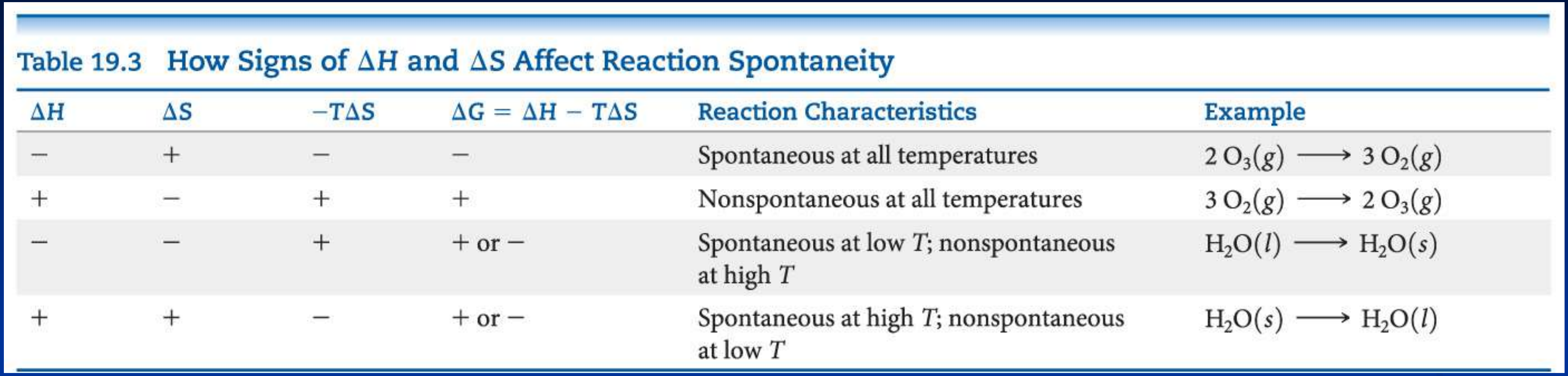


Table 19.3 How Signs of ΔH and ΔS Affect Reaction Spontaneity

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	$H_2O(s) \longrightarrow H_2O(l)$

- How does ΔG change with temperature?
- $\Delta G = \Delta H - T\Delta S$
- Since reactions are spontaneous if $\Delta G < 0$, the sign of enthalpy and entropy and the magnitude of the temperature matters to spontaneity.

Free Energy and Temperature

- Another useful equation – since $\Delta G = 0$ when a system is at equilibrium, the equation can be rearranged to solve for the temperature of the reaction at equilibrium.
- $$T = \frac{\Delta H^o}{\Delta S^o}$$

19.6 Give It Some Thought

The normal boiling point of benzene is 80°C. At 100°C and 1 atm, which term is greater for the vaporization of benzene, ΔH or $T\Delta S$?

Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity

The Haber process for the production of ammonia involves the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Assume that ΔH° and ΔS° for this reaction do not change with temperature. **(a)** Predict the direction in which ΔG° for this reaction changes with increasing temperature. **(b)** Calculate the values ΔG° of for the reaction at 25 ° C and 500 ° C.

Practice Exercise 1

What is the temperature above which the Haber ammonia process becomes nonspontaneous?

(a) 25 °C

(b) 47 °C

(c) 61 °C

(d) 193 °C

(e) 500 °C.

Practice Exercise 2

(a) Using standard enthalpies of formation and standard entropies in Appendix C, calculate ΔH° and ΔS° at 298 K for the following reaction: $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$.

(b) Using the values obtained in part (a), estimate ΔG° at 400 K.