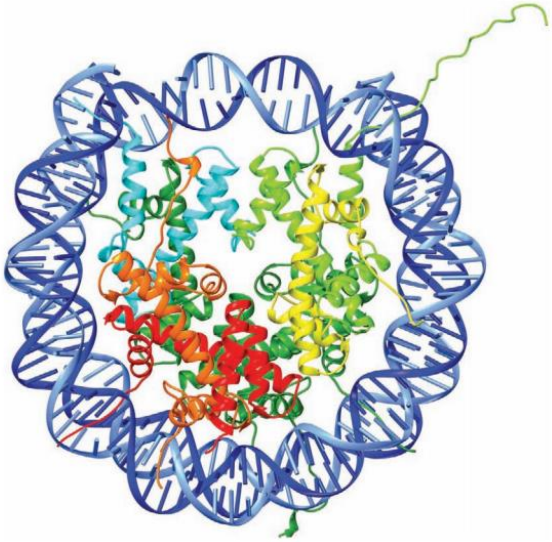
GENERAL CHEMISTRY



Chapter 19

Chemical Thermodynamics

Contents

First Law of Thermodynamics

- You will recall from Chapter 5 that energy cannot be created nor 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.

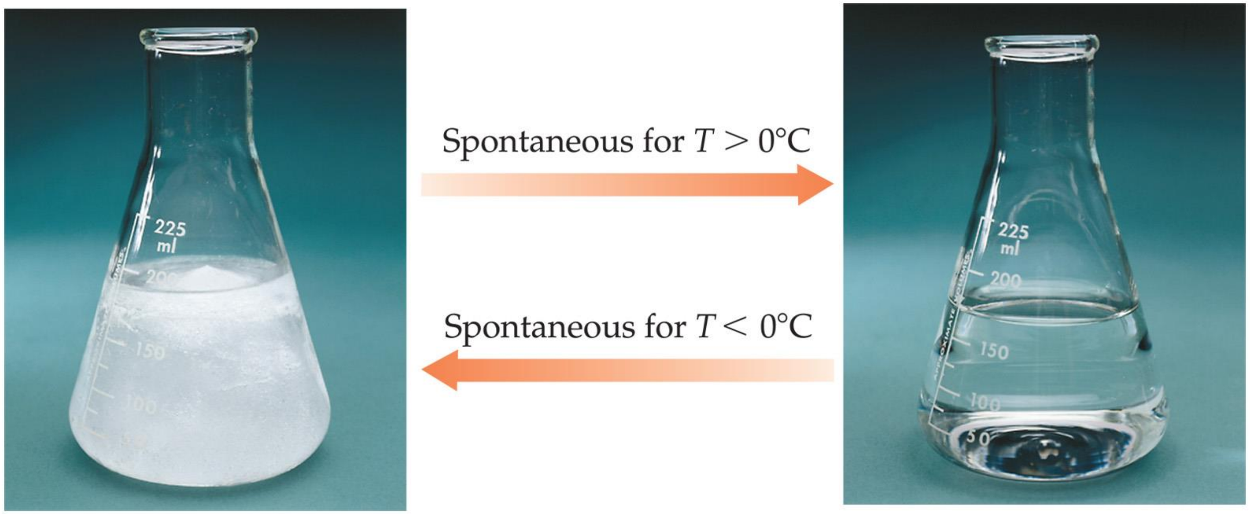
19-1 Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.

- 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.



EXAMPLE

Predict whether the following processes are spontaneous as described, spontaneous in the reverse direction, or in equilibrium:

(a) When a piece of metal heated to 150°C is added to water at 40°C, the water gets hotter.

Spontaneous

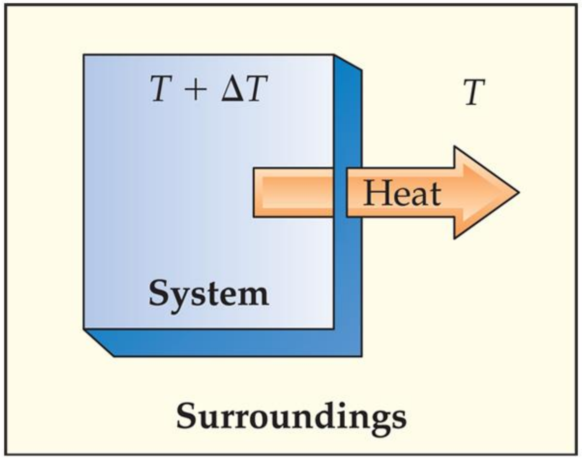
(b) Water at room temperature decomposes into $H_2(g)$ and $O_2(g)$.

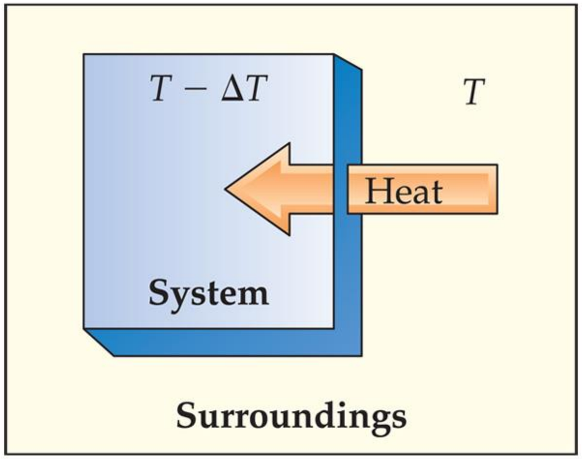
Not spontaneous

(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.

In equilibrium

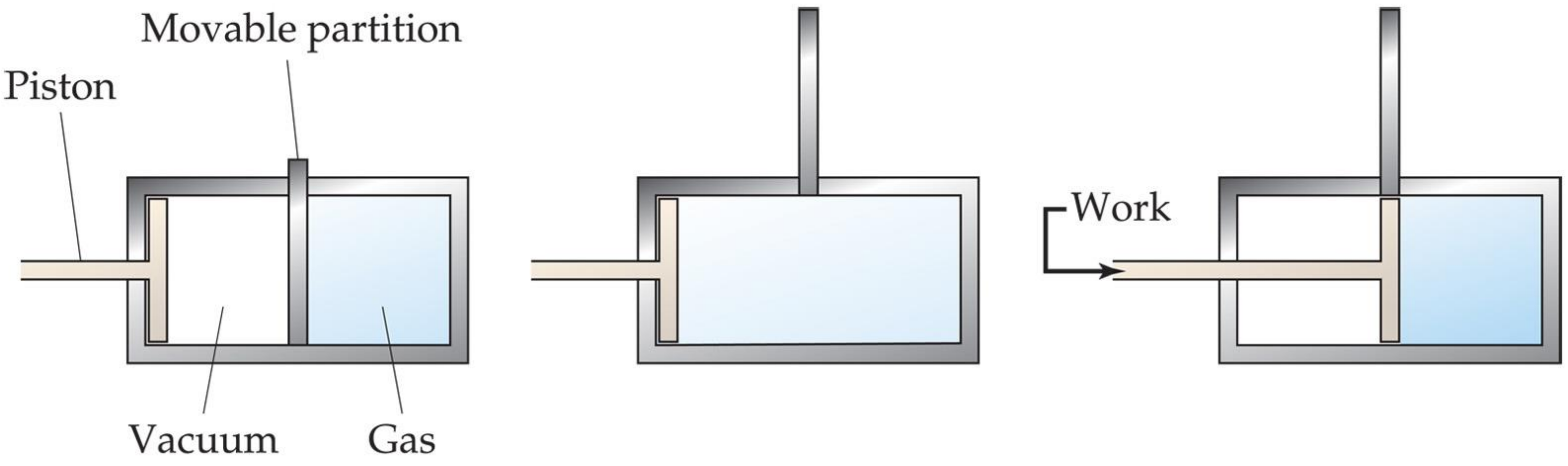
Reversible Processes





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

First Law of Thermodynamics

The First Law of Thermodynamics states that energy cannot be created nor destroyed, but only converted from one form to another

System is interior of vault

$\Delta U = \Delta E = q + w$

internal energy

$q = \Delta H$ (enthalpy)

Heat

$w = -P\Delta V$

work

Energy deposited into system
$\Delta E > 0$

Energy withdrawn from system
$\Delta E < 0$

19-2 Entropy and the Second Law of Thermodynamics

- *Entropy* (*S*) is a term coined by Rudolph Clausius in the 19th 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 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

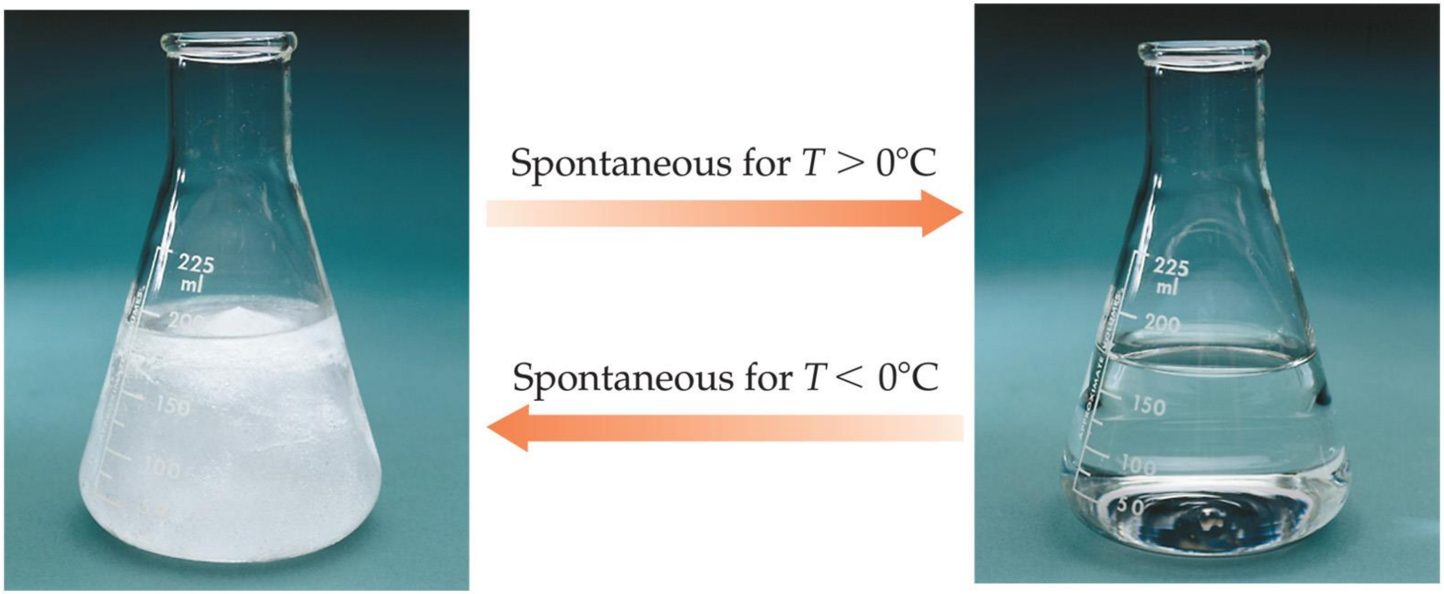
- Like total energy, *E*, and enthalpy, *H*, entropy is a state function.
- Therefore,

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

- 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:

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

ΔS for Phase Change



Spontaneous for $T > 0°C$

Spontaneous for $T < 0°C$

We can melt ice by adding heat to the system from the surroundings: $q = \Delta H_{fusion}$

$$\Delta S_{fusion} = \frac{q_{rev}}{T} = \frac{\Delta H_{fusion}}{T}$$

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.

For **reversible processes**:

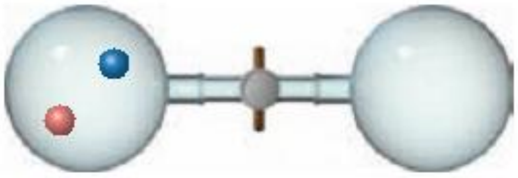
$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For **irreversible processes**:

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

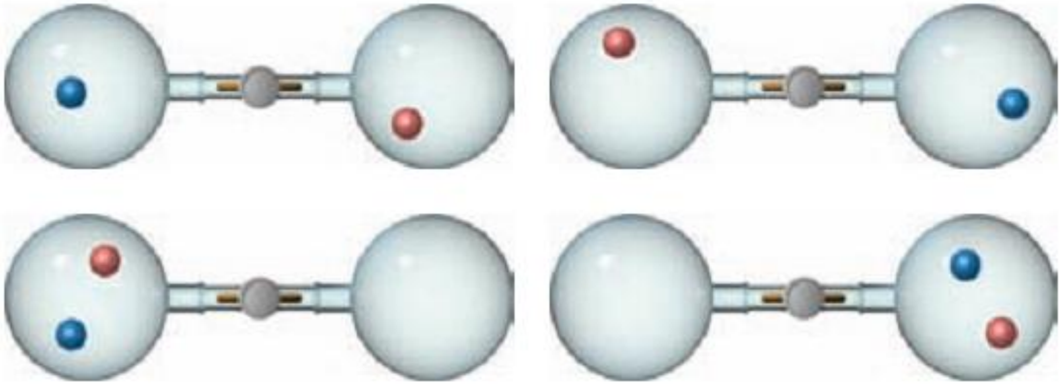
These last truths mean that as a result of all spontaneous processes the entropy of the universe increases.

19-3 The Molecular Interpretation of Entropy and the Third Law of Thermodynamics



(a)

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



(b)

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

- 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.

Boltzmann’s Equation and Microstates

- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time as a microstate of the thermodynamic system.

- 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.

Change in entropy of a process

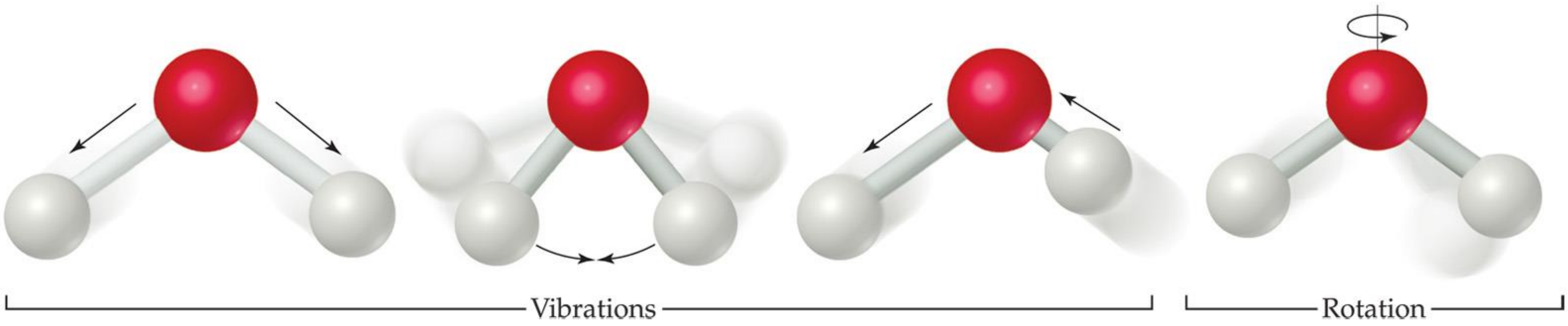
- The change in entropy for a process, then, is

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

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

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

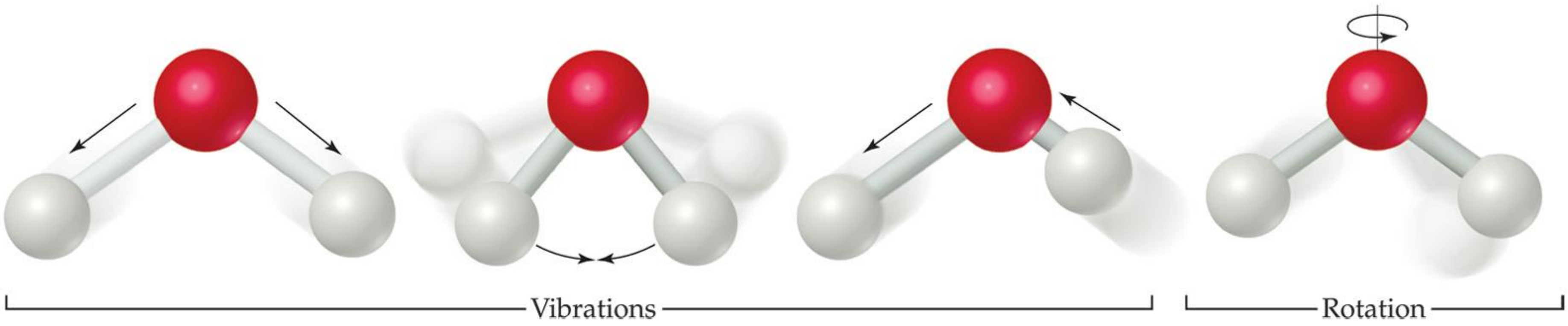
Molecular Motions and Energy



Molecules exhibit several types of motion:

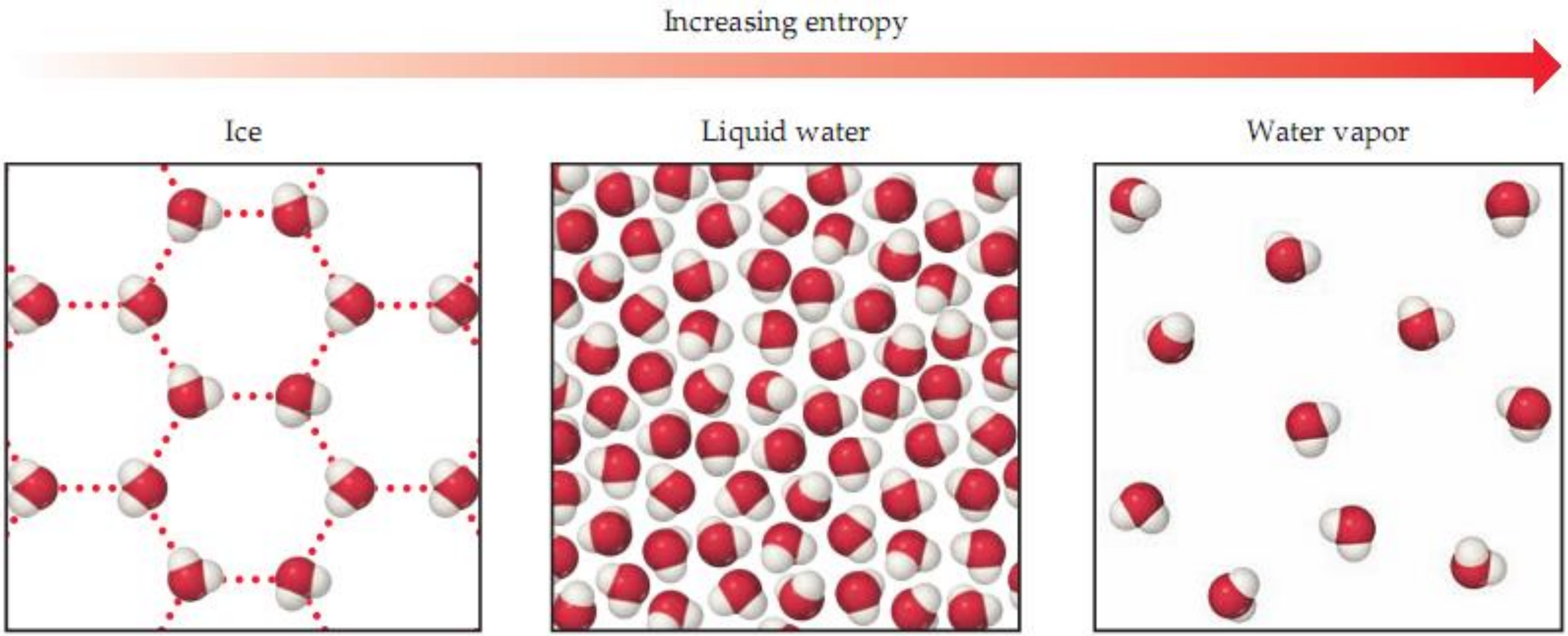
- **Translational**: Movement of the entire molecule from one place to another.
- **Vibrational**: Periodic motion of atoms within a molecule.
- **Rotational**: Rotation of the molecule on about an axis or rotation about σ bonds.

Molecular Motions and Energy



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

Making Qualitative Predictions about ΔS



- Rigid, crystalline structure
- Motion restricted to **vibration** only
- Smallest number of microstates

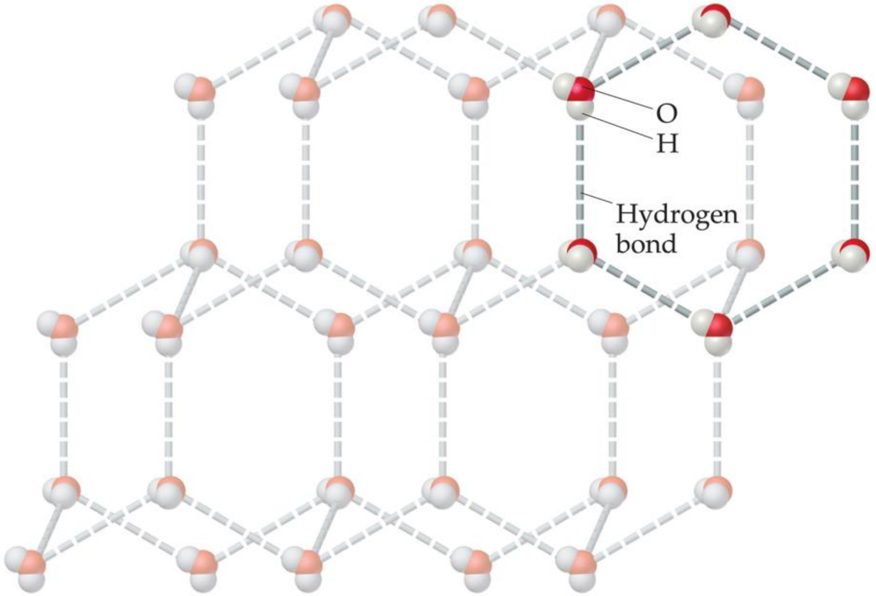
- Increased freedom with respect to **translation**
- Free to **vibrate** and **rotate**
- Larger number of microstates

- Molecules spread out, essentially independent of one another
- Complete freedom for **translation**, **vibration**, and **rotation**
- Largest number of microstates

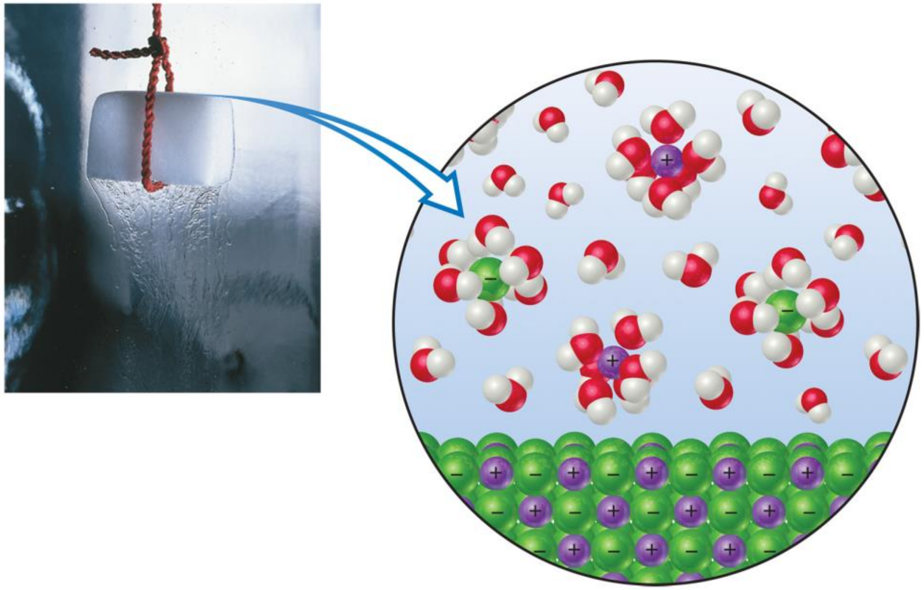
Entropy and Physical States

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

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



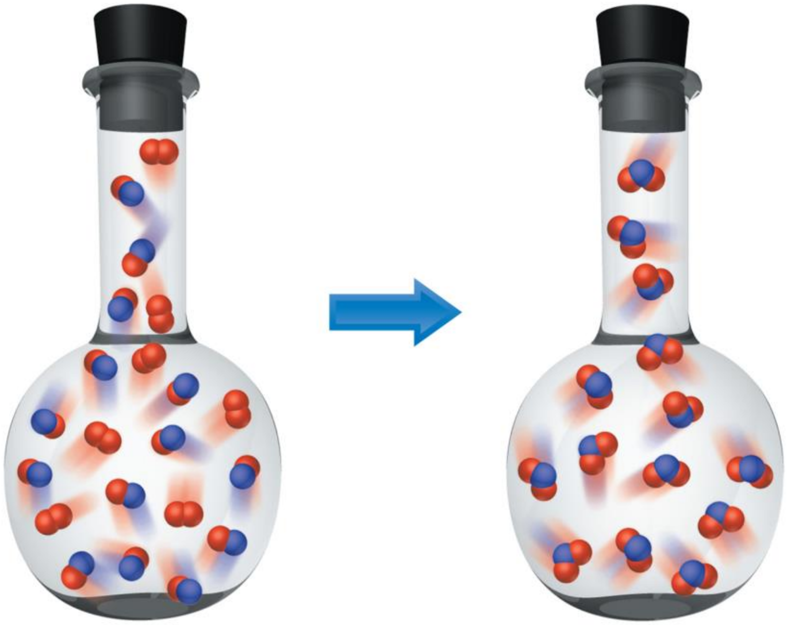
Solutions



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

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.



EXAMPLE

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:

(a) $H_2O\ (l) \rightarrow H_2O\ (g)$

$\Delta S > 0$

(b) $Ag^+\ (aq) + Cl^-\ (aq) \rightarrow AgCl\ (s)$

$\Delta S < 0$

(c) $4\ Fe\ (s) + 3\ O_2\ (g) \rightarrow 2\ Fe_2O_3\ (s)$

$\Delta S < 0$

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

$\Delta S = 0$

EXAMPLE

Choose the sample of matter that has greater entropy in each pair, and explain your choice:

(a) 1 mol of NaCl(*s*) or 1 mol of HCl(*g*) at 25°C,

Gaseous HCl has the higher entropy because gases have more available motions than solids

(b) 2 mol of HCl(*g*) or 1 mol of HCl(*g*) at 25°C,

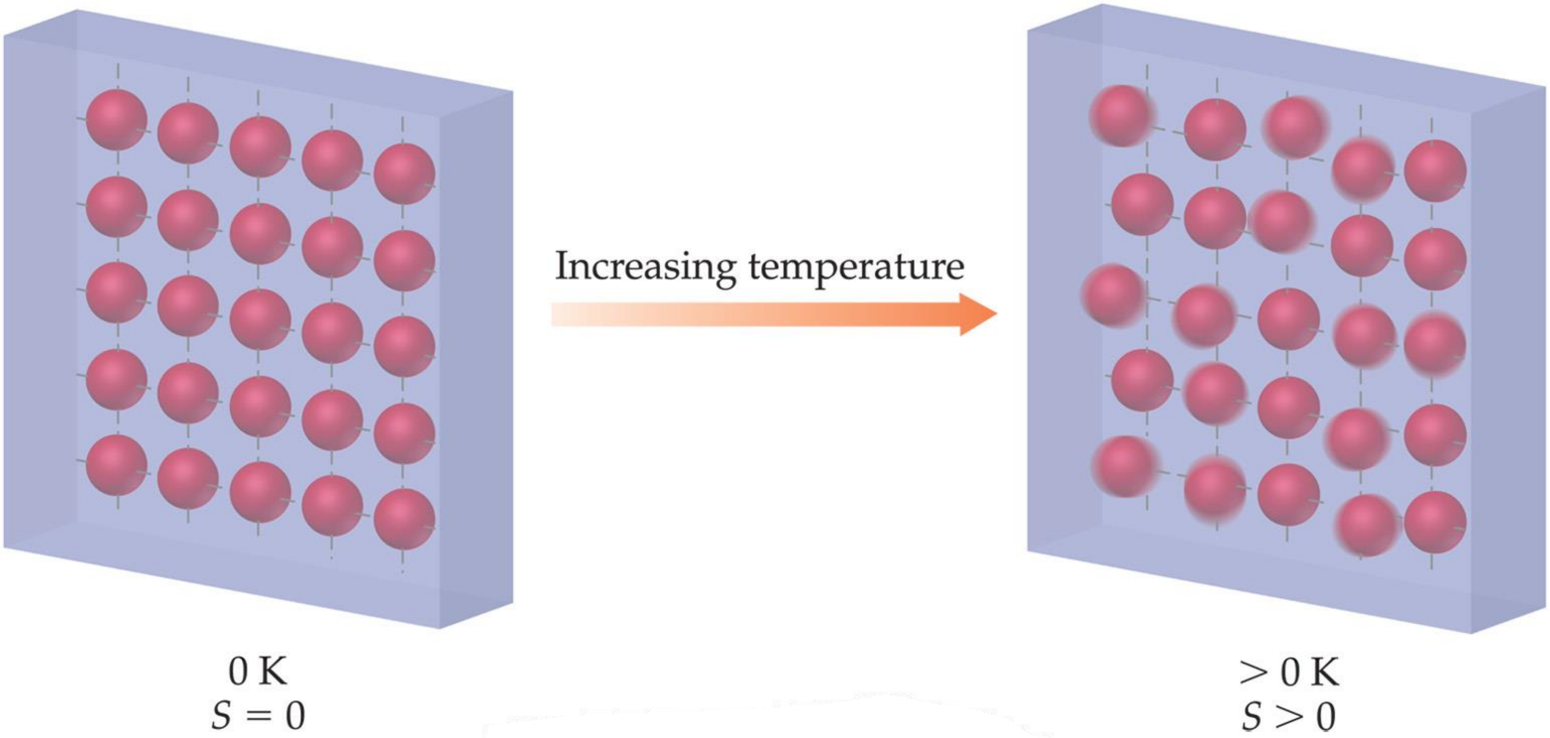
The sample containing 2 mol of HCl has twice the number of molecules as the sample containing 1 mol. Thus, the 2-mol sample has twice the number of microstates and twice the entropy

(c) 1 mol of HCl(*g*) or 1 mol of Ar(*g*) at 298 K.

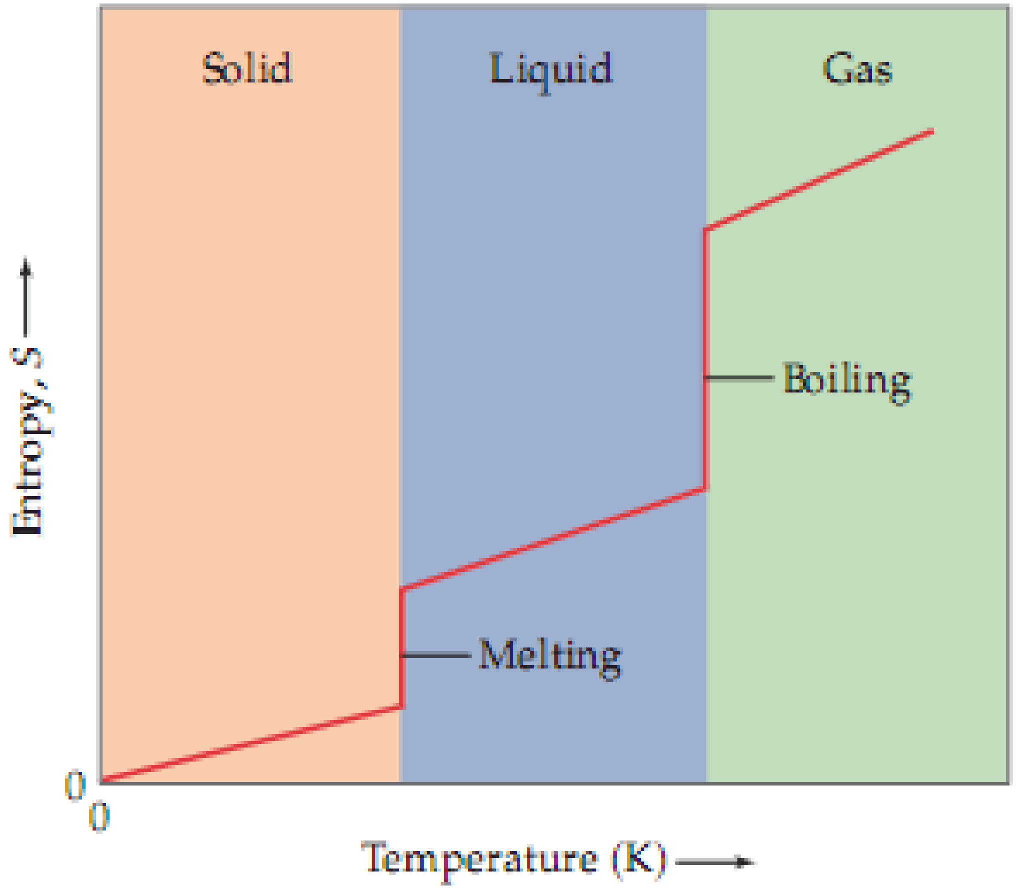
The HCl sample has the higher entropy because the HCl molecule is capable of storing energy in more ways than is Ar. HCl molecules can rotate and vibrate; Ar atoms cannot.

19-4 Entropy Changes in Chemical Reactions

Third Law of Thermodynamics: The entropy of a pure crystalline substance at absolute zero is 0.



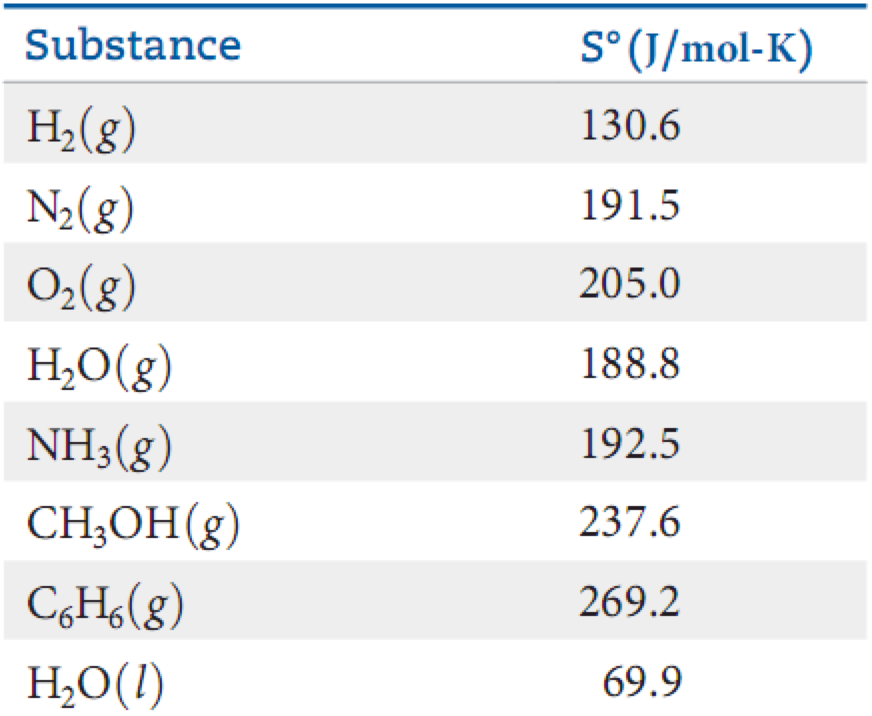
Entropy increases as the temperature of the crystal is increased



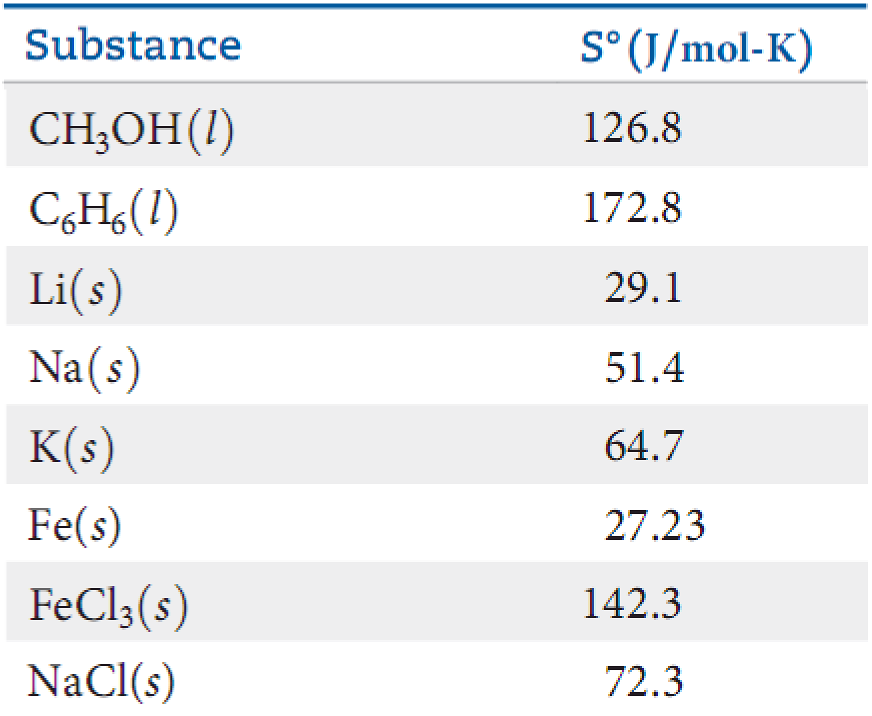
The standard molar entropies of *gases are greater than those of liquids and solids*

The standard molar entropies of *liquids are greater than those of solids*

Standard Molar Entropies



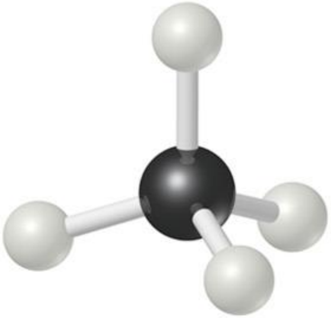
Substance	**S° (J/mol-K)**
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9



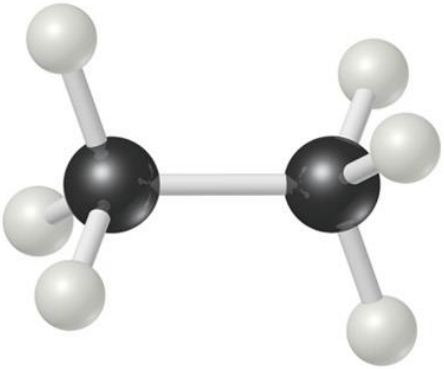
Substance	**S° (J/mol-K)**
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Standard entropies tend to *increase with increasing molar mass.*

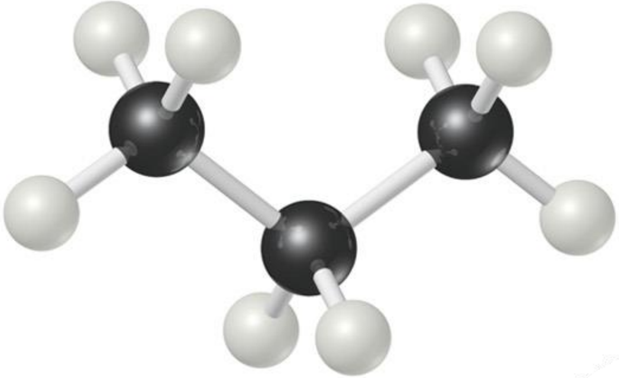
Standard Molar Entropies



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

Larger and more complex molecules have greater entropies.

The entropy change in a chemical reaction

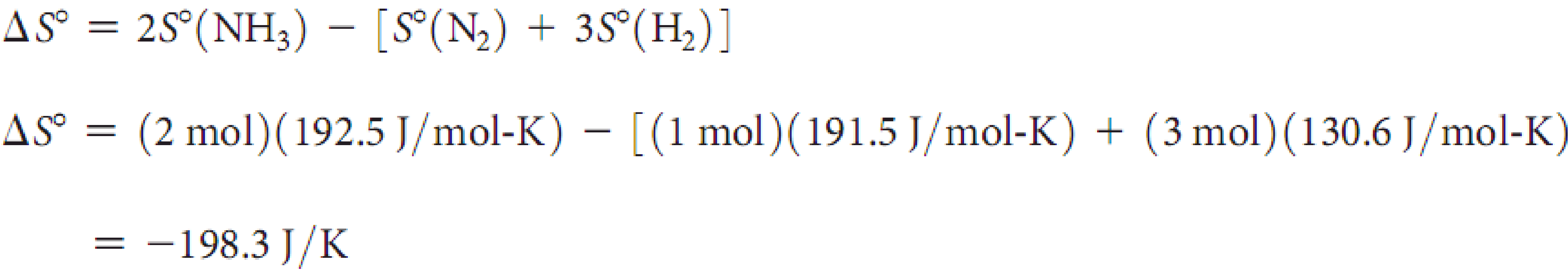
$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

The coefficients *n* and *m* are the coefficients in the balanced chemical reaction

EXAMPLE

Calculate the change in the standard entropy of the system, ΔS°, for the synthesis of ammonia from N_2 (g) and H_2 (g) at 298 K.

$$3\ N_2\ (g) + H_2\ (g) \rightarrow 2\ NH_3\ (g)$$



$$\Delta S^\circ = 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)]$$

$$\Delta S^\circ = (2\ \text{mol})(192.5\ \text{J/mol-K}) - [(1\ \text{mol})(191.5\ \text{J/mol-K}) + (3\ \text{mol})(130.6\ \text{J/mol-K})$$

$$= -198.3\ \text{J/K}$$

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.

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

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

- For spontaneous processes:

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

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

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

19-5 Gibbs Free Energy

- We have

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

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

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

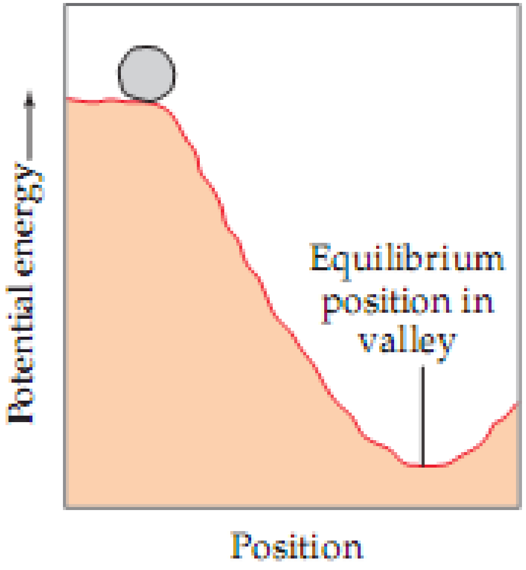
- When $\Delta S_{\text{universe}}$ is positive, ΔG is negative.
- Therefore, when ΔG is negative, a process is spontaneous.

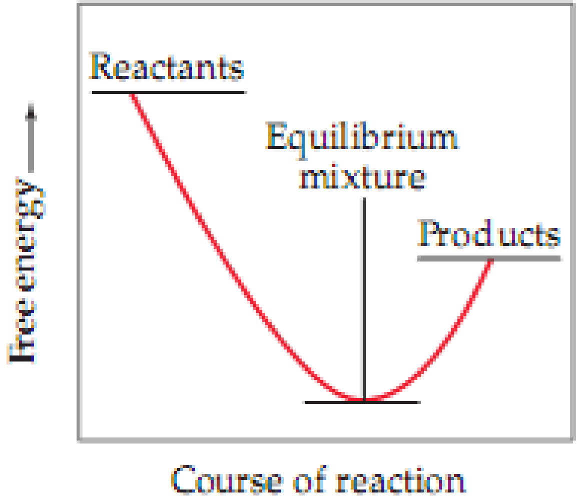
The spontaneity of a reaction

If both T and P are constant

1. If $\Delta G < 0$, the forward reaction is spontaneous.
2. If $\Delta G = 0$, the system is at equilibrium.
3. If $\Delta G > 0$, the reaction is spontaneous in the reverse direction.

In any spontaneous process carried out at constant temperature and pressure, the free energy always decreases

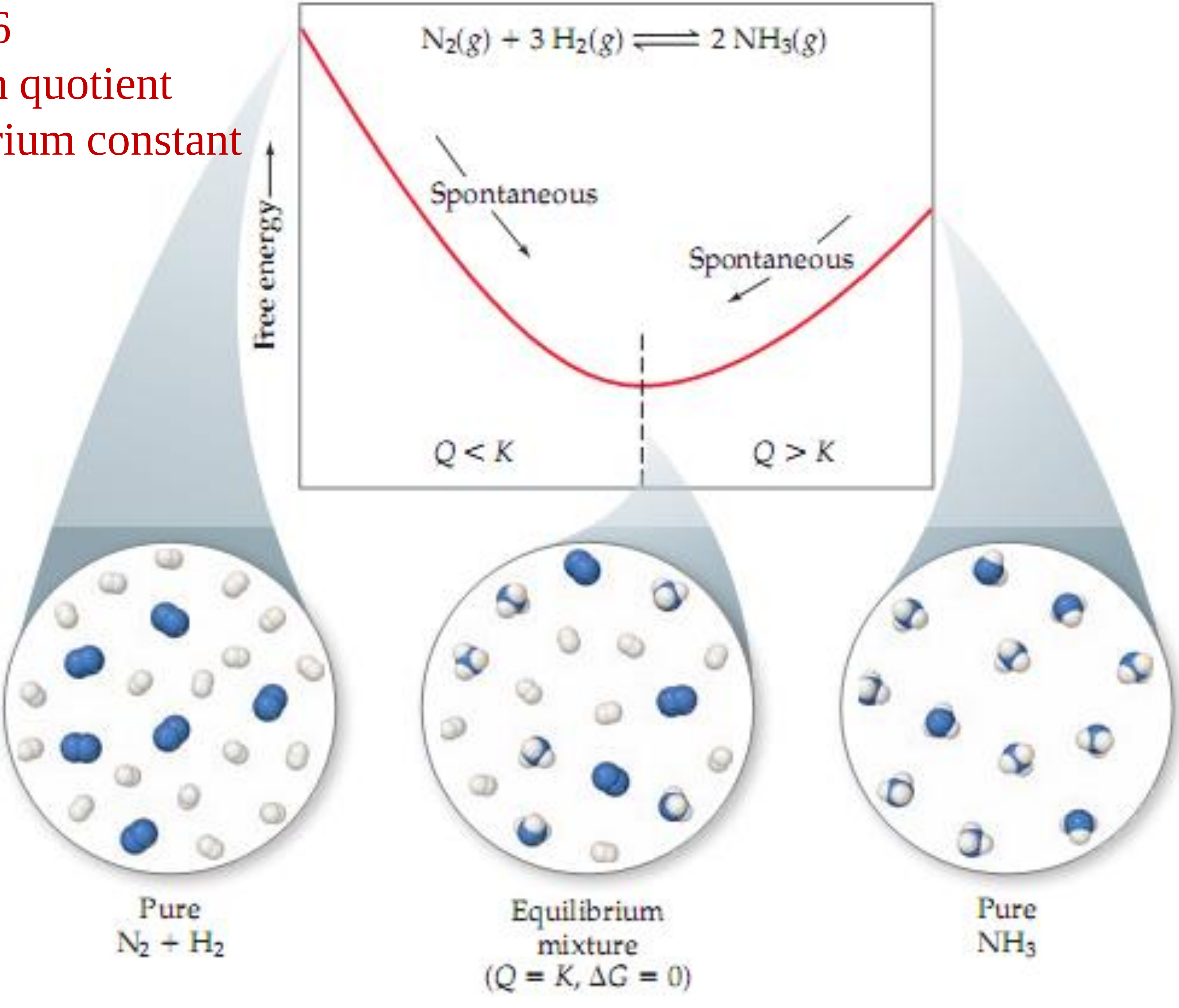




Recall 15.6

Q: reaction quotient

K: equilibrium constant



Standard Free Energy Changes

Analogous to standard enthalpies of formation are standard free energies of formation, ΔG°_f

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

where n and m are the stoichiometric coefficients.

EXAMPLE

(a) Calculate the standard free-energy change for the following reaction at 298 K:

$$P_4\ (g) + 6Cl_2\ (g) \rightarrow 4\ PCl_3\ (g)$$

(b) What is $\Delta G°$ for the reverse of the above reaction?

Cl_2 is in its standard state, $\Delta G°_{f,\ Cl2} = 0$.

$\Delta G°_{f,\ P4} = 24.4$ kJ/mol, $\Delta G°_{f,\ PCl3} = -269.6$ kJ/mol

(a)

$$\begin{aligned}\Delta G°_{rxn} &= 4\Delta G°_f[PCl_3(g)] - \Delta G°_f[P_4(g)] - 6\Delta G°_f[Cl_2(g)]\\ &= 4\text{mol}(-269.6\ \text{kJ/mol}) - (24.4\ \text{kJ/mol}) - 0\\ &= -1102.8\ \text{kJ}\end{aligned}$$

(b)

$$4\,PCl_3(g) \longrightarrow P_4(g) + 6\,Cl_2(g) \qquad \Delta G° = +1102.8\ \text{kJ}$$

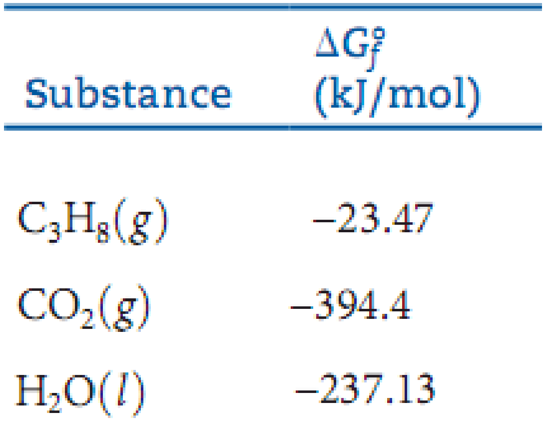
EXAMPLE

(a) Without using the table, predict whether $\Delta G°$ for the following reaction is more negative or less negative than $\Delta H°$.

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H° = -2220\text{ kJ}$$

$\Delta G°$ is *less negative* than $\Delta H°$.

(b) Calculate the standard free-energy change for the reaction at 298 K. Is your prediction from part (a) correct?



Substance	$\Delta G_f°$ (kJ/mol)
$C_3H_8(g)$	–23.47
$CO_2(g)$	–394.4
$H_2O(l)$	–237.13

$$\begin{aligned}\Delta G° &= 3\Delta G_f°[CO_2(g)] + 4\Delta G_f°[H_2O(l)] - \Delta G_f°[C_3H_8(g)] - 5\Delta G_f°[O_2(g)]\\ &= 3\text{ mol}(-394.4\text{ kJ/mol}) + 4\text{ mol}(-237.13\text{ kJ/mol}) -\\ &\qquad 1\text{ mol}(-23.47\text{ kJ/mol}) - 5\text{ mol }(0\text{ kJ/mol}) = -2108\text{ kJ}\end{aligned}$$

19.6 Free energy and Temperature

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:
  - $\Delta H°$— the enthalpy term
  - $T\Delta S°$ — the entropy term
- The temperature dependence of free energy, then comes from the entropy term.

Free Energy and Temperature

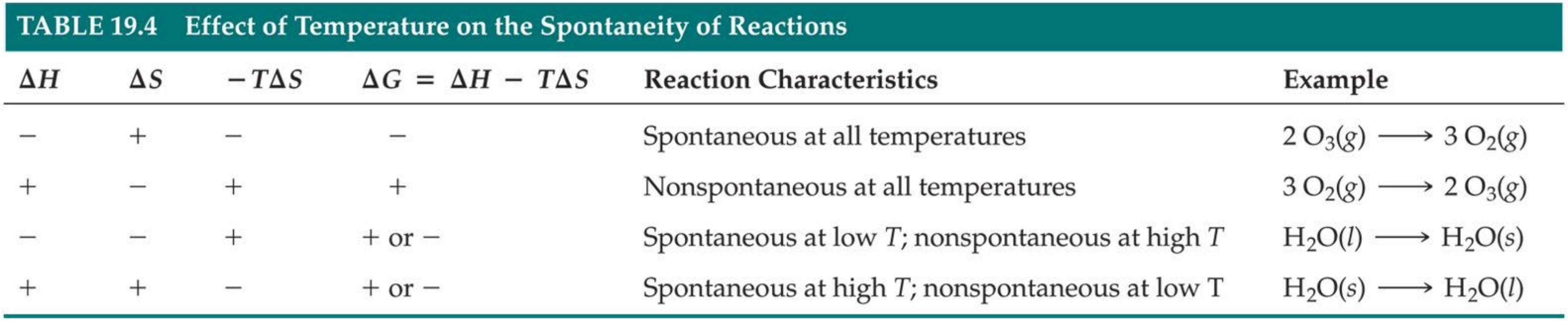


TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

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

EXAMPLE

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 $\Delta H°$ and $\Delta S°$ for this reaction do not change with temperature.

(a) Predict the direction in which $\Delta G°$ for this reaction changes with increasing temperature.

(b) Calculate the values of $\Delta G°$ for the reaction at 25°C and 500°C if $\Delta H° = –92.38$ kJ and $\Delta S° = –198.4$ J/K

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

Since a decrease in the number of gas molecules to lead to a decrease in the entropy of the system, $\Delta S°$ is expected to be negative.
$–T\Delta S°$ is positive and grows larger with increasing temperature.
As a result, $\Delta G°$ becomes less negative (or more positive) with increasing temperature. Thus, the driving force for the production of NH_3 becomes smaller with increasing temperature.

$$\Delta G^\circ = -92.38\ \text{kJ} - (298\ \text{K})(-198.4\ \text{J/K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -92.38\ \text{kJ} + 59.1\ \text{kJ} = -33.3\ \text{kJ}$$

At $T = 500 + 273 = 773$ K we have

$$\Delta G^\circ = -92.38\ \text{kJ} - (773\ \text{K})\left(-198.4\frac{\text{J}}{\text{K}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -92.38\ \text{kJ} + 153\ \text{kJ} = 61\ \text{kJ}$$

Comment: Increasing the temperature from 298 K to 773 K changes ΔG° from –33.3 kJ to +61 kJ. Of course, the result at 773 K depends on the assumption that ΔH° and ΔS° do not change with temperature. In fact, these values do change slightly with temperature. Nevertheless, the result at 773 K should be a reasonable approximation. Thus, when the mixture of three gases, each at a partial pressure of 1 atm, is heated to 773 K, some of the $NH_3(g)$ spontaneously decomposes into $N_2(g)$ and $H_2(g)$.

19.7 Free energy and the equilibrium Constant

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.)

EXAMPLE

The *normal boiling point* is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of 1 atm.

(a) Write the chemical equation that defines the normal boiling point of liquid carbon tetrachloride, $CCl_4(l)$.

(b) What is the value of $\Delta G°$ for the equilibrium in part (a)?

(c) Estimate the normal boiling point of CCl_4. The standard enthalpy of formation of CCl_4 in its liquid and gaseous forms are -139.3 kJ/mol and -106.7 kJ/mol, respectively. The standard entropy of formation of CCl_4 in its liquid and gaseous forms are 214.4 kJ/mol.K and 309.4 kJ/mol.K

(a) $$CCl_4(l) \rightleftharpoons CCl_4\,(g, 1\text{ atm})$$

(b) At equilibrium $\Delta G = 0$.

In any normal boiling-point equilibrium both the liquid and the vapor are in their standard states.

Thus, $Q = 1$, $\ln Q = 0$, and $\Delta G = \Delta G°$ for this process.

Thus, we conclude that $\Delta G° = 0$

$$\Delta G^\circ = \Delta H^\circ - T_b \Delta S^\circ = 0$$

$$T_b = \Delta H^\circ / \Delta S^\circ$$

$$\Delta H^\circ = (1\text{ mol})(-106.7\text{ kJ/mol}) - (1\text{ mol})(-139.3\text{ kJ/mol}) = +32.6\text{ kJ}$$

$$\Delta S^\circ = (1\text{ mol})(309.4\text{ J/mol-K}) - (1\text{ mol})(214.4\text{ J/mol-K}) = +95.0\text{ J/K}$$

$$T_b = \frac{\Delta H^\circ}{\Delta S^\circ} = \left(\frac{32.6\text{ kJ}}{95.0\text{ J/K}}\right)\left(\frac{1000\text{ J}}{1\text{ kJ}}\right) = 343\text{ K} = 70^\circ\text{C}$$

EXAMPLE

Calculate ΔG at 298 K for a reaction mixture that consists of 1.0 atm N_2, 3.0 atm H_2, and 0.50 atm NH_3. $\Delta G° = –33.3$ kJ/mol

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

$$\Delta G = \Delta G° + RT \ln Q$$

$$Q = \frac{{P_{NH_3}}^2}{P_{N_2}{P_{H_2}}^3} = \frac{(0.50)^2}{(1.0)(3.0)^3} = 9.3 \times 10^{-3}$$

$$\begin{aligned}\Delta G &= \Delta G° + RT \ln Q \\ &= (-33.3\ \text{kJ/mol}) + (8.314\ \text{J/mol-K})(298\ \text{K})(1\ \text{kJ}/1000\ \text{J}) \ln(9.3 \times 10^{-3}) \\ &= (-33.3\ \text{kJ/mol}) + (-11.6\ \text{kJ/mol}) = -44.9\ \text{kJ/mol}\end{aligned}$$

Comment: We see that ΔG becomes more negative, changing from –33.3 kJ/mol to –44.9 kJ/mol as the pressures of N_2, H_2, and NH_3 are changed from 1.0 atm each (standard conditions, $\Delta G°$) to 1.0 atm, 3.0 atm, and 0.50 atm, respectively. The larger negative value for ΔG indicates a larger “driving force” to produce NH_3. We would have made the same prediction on the basis of Le Châtelier’s principle

Free Energy and Equilibrium

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

$$0 = \Delta G° + RT \ln K$$

- Rearranging, this becomes

$$\Delta G° = -RT \ln K$$

or,

$$K = e^{-\Delta G°/RT}$$

EXAMPLE

Use standard free energies of formation to calculate the equilibrium constant, *K*, at 25°C for the reaction involved in the Haber process:

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

The standard free-energy change for this reaction is $\Delta G° = -33.3$ kJ/mol

$$K = e^{-\Delta G°/RT} = e^{13.4} = 7 \times 10^5$$

$$\frac{-\Delta G°}{RT} = \frac{-(-33{,}300\ \mathrm{J/mol})}{(8.314\ \mathrm{J/mol\text{-}K})(298\ \mathrm{K})} = 13.4$$

$$K = e^{-\Delta G°/RT} = e^{13.4} = 7 \times 10^5$$

Comment: This is a large equilibrium constant, which indicates that the product, NH_3, is greatly favored in the equilibrium mixture at 25°C.