

Lecture Presentation

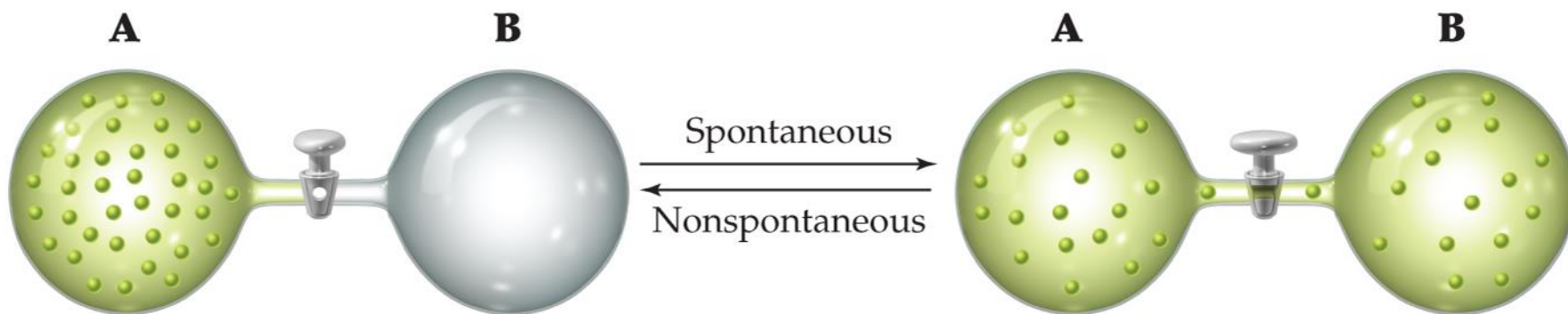
## Chapter 17

# Thermodynamics: Entropy, Free Energy, and Equilibrium

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# Spontaneous Processes

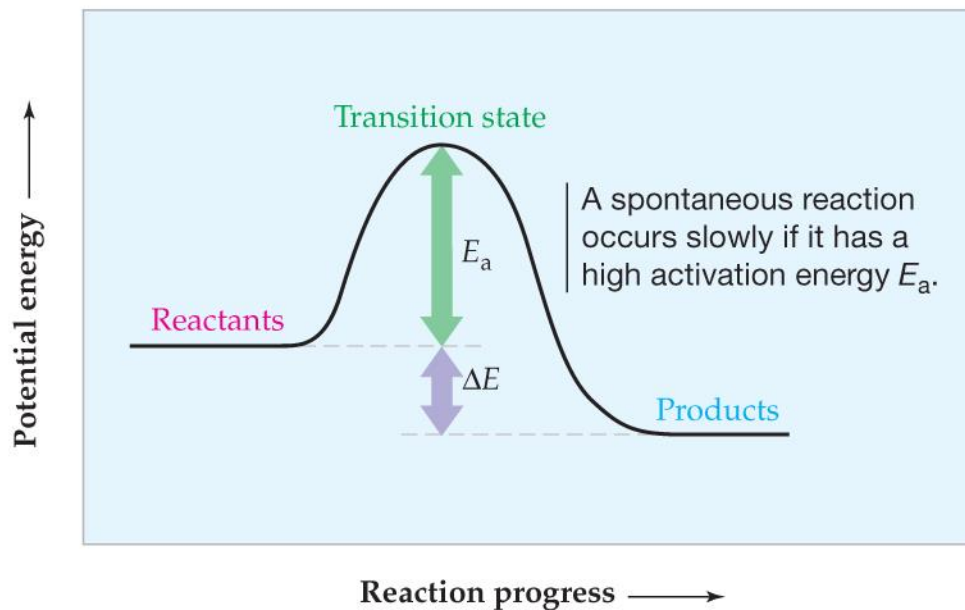
**Spontaneous Process:** A process that, once started, proceeds on its own without a continuous external influence



# Spontaneous Processes



The rusting of these wheel rims is a slow but spontaneous reaction.



# Enthalpy, Entropy, and Spontaneous Processes

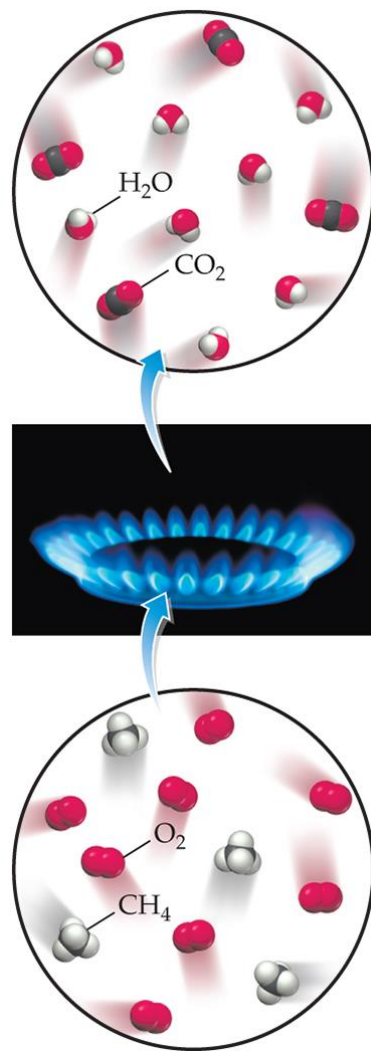
**State Function:** A function or property whose value depends only on the present state, or condition, of the system, not on the path used to arrive at that state

**Enthalpy Change ( $\Delta H$ ):** The heat change in a reaction or process at constant pressure;

$$\Delta H = \Delta E + P\Delta V$$

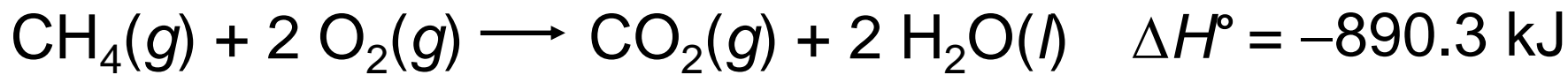
**Entropy ( $S$ ):** The amount of molecular randomness in a system

# Enthalpy, Entropy, and Spontaneous Processes

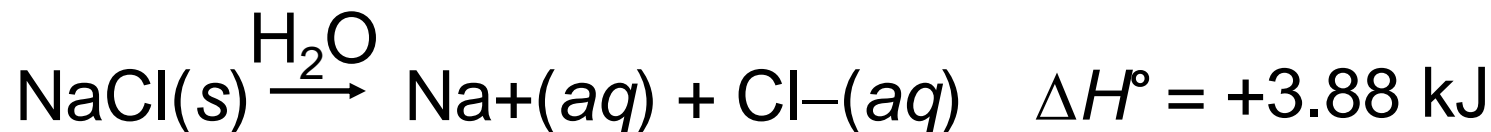


# Enthalpy, Entropy, and Spontaneous Processes

## Exothermic:



## Endothermic:

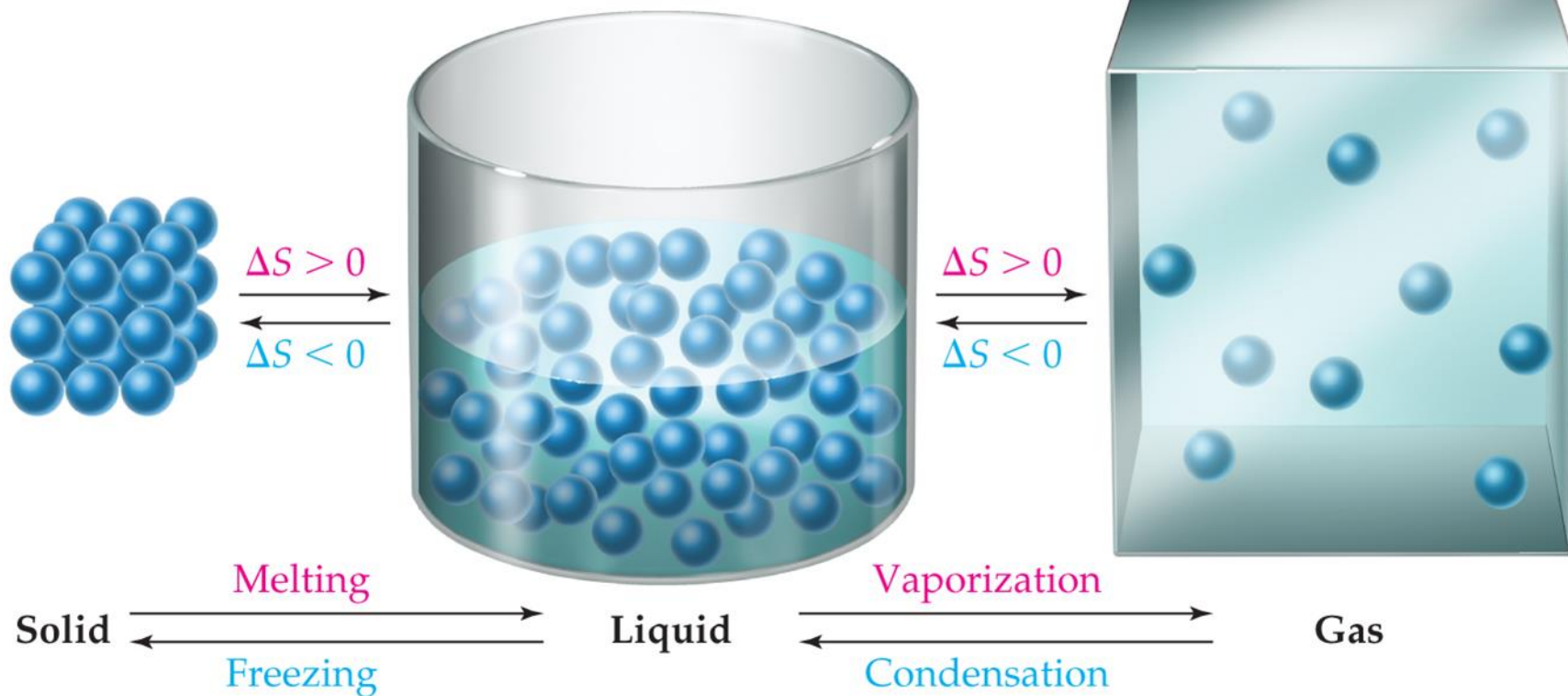


# Enthalpy, Entropy, and Spontaneous Processes

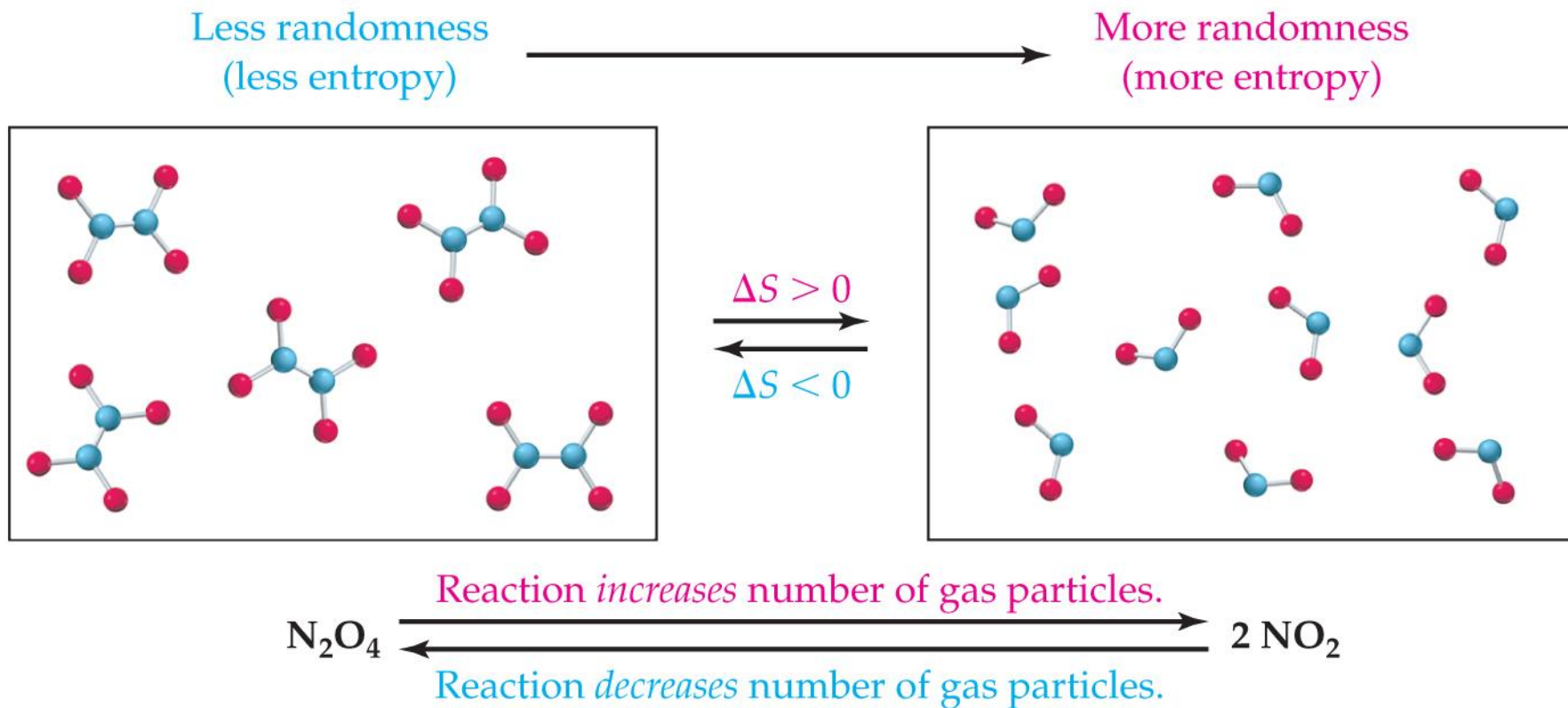
$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Less randomness  
(less entropy)

More randomness  
(more entropy)

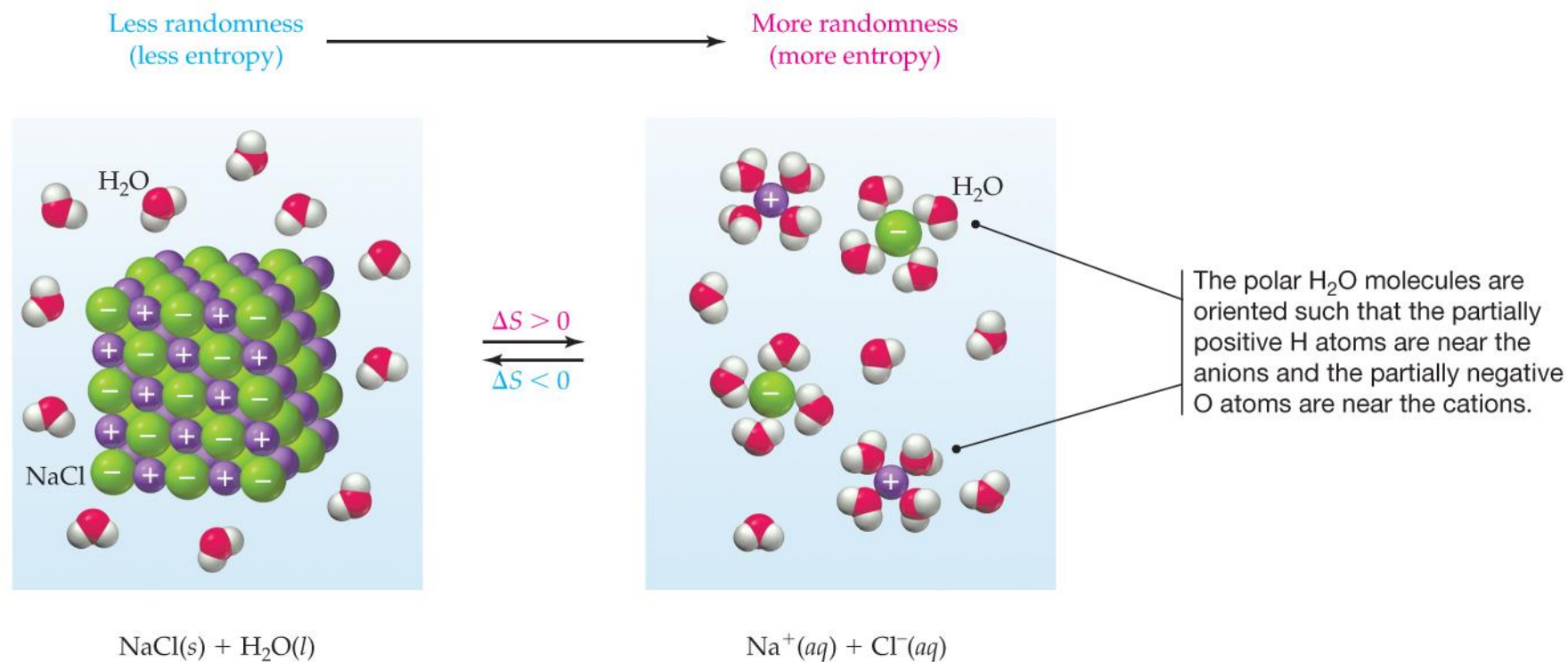


# Enthalpy, Entropy, and Spontaneous Processes





# Enthalpy, Entropy, and Spontaneous Processes



Disruption of the crystal increases the entropy, but the hydration process decreases the entropy. For the dissolution of NaCl, the net effect is an entropy increase.

# Entropy and Probability



# Entropy and Probability

**(a)** The perfectly ordered "heads-up" structure.



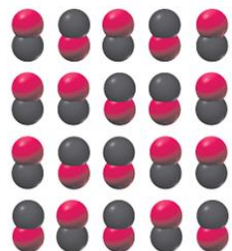
20 "heads"  
0 "tails"

$$S = k \ln W$$

$k$  = Boltzmann's constant.

$$= 1.38 \times 10^{-23} \text{ J/K}$$

**(b)** The molecules arranged randomly in one of the  $2^{20}$  ways in which a disordered structure can be obtained.

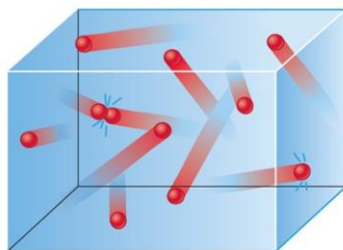


9 "heads"  
11 "tails"

$W$  = The number of ways that the state can be achieved.

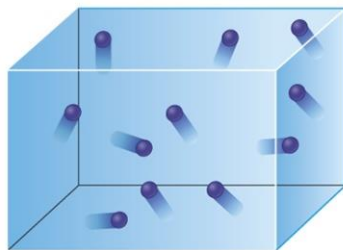
# Entropy and Temperature

**Third Law of Thermodynamics:** The entropy of a perfectly ordered crystalline substance at 0 K is zero.



**Higher temperature:**

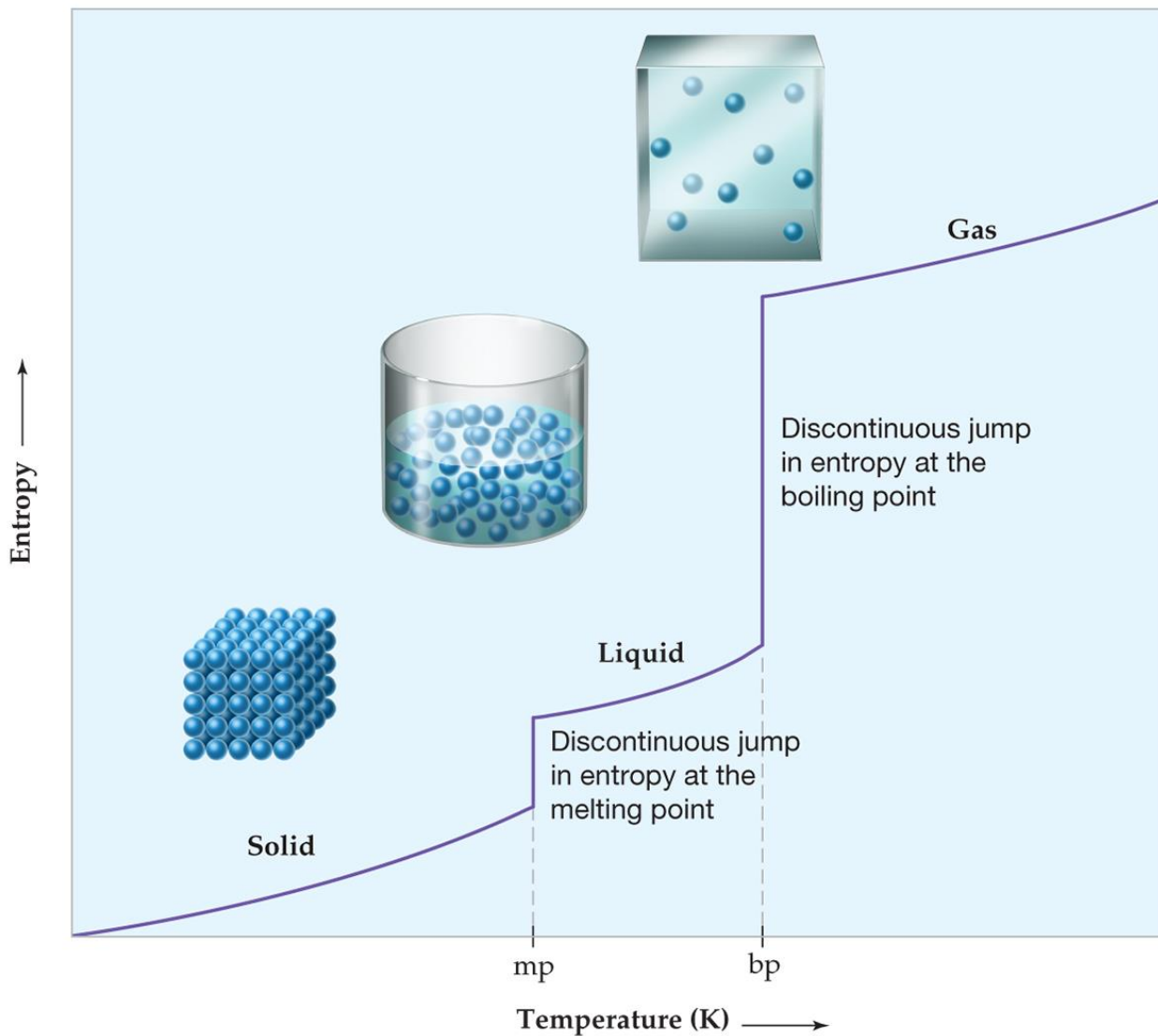
- Greater molecular speeds
- Broader distribution of individual kinetic energies
- More randomness
- Higher entropy



**Lower temperature:**

- Lesser molecular speeds
- Narrower distribution of individual kinetic energies
- Less randomness
- Lower entropy

# Entropy and Temperature



# Standard Molar Entropies and Standard Entropies of Reaction

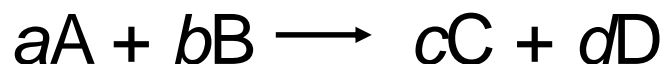
**Standard Molar Entropy ( $S^\circ$ ):** The entropy of 1 mole of a pure substance at 1 atm pressure and a specified temperature.

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

Substance	Formula	$S^\circ$ [J/(K · mol)]	Substance	Formula	$S^\circ$ [J/(K · mol)]
<b>Gases</b>			<b>Liquids</b>		
Acetylene	C <sub>2</sub> H <sub>2</sub>	200.8	Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	160
Ammonia	NH <sub>3</sub>	192.3	Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	161
Carbon dioxide	CO <sub>2</sub>	213.6	Methanol	CH <sub>3</sub> OH	127
Carbon monoxide	CO	197.6	Water	H <sub>2</sub> O	69.9
Ethylene	C <sub>2</sub> H <sub>4</sub>	219.5	<b>Solids</b>		
Hydrogen	H <sub>2</sub>	130.6	Calcium carbonate	CaCO <sub>3</sub>	91.7
Methane	CH <sub>4</sub>	186.2	Calcium oxide	CaO	38.1
Nitrogen	N <sub>2</sub>	191.5	Diamond	C	2.4
Nitrogen dioxide	NO <sub>2</sub>	240.0	Graphite	C	5.7
Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	304.3	Iron	Fe	27.3
Oxygen	O <sub>2</sub>	205.0	Iron(III) oxide	Fe <sub>2</sub> O <sub>3</sub>	87.4

# Standard Molar Entropies and Standard Entropies of Reaction

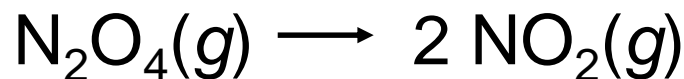
$$\Delta S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$$



$$\Delta S^\circ = \underbrace{[cS^\circ(\text{C}) + dS^\circ(\text{D})]}_{\text{Products}} - \underbrace{[aS^\circ(\text{A}) + bS^\circ(\text{B})]}_{\text{Reactants}}$$

# Standard Molar Entropies and Standard Entropies of Reaction

Using standard entropies, calculate the standard entropy change for the decomposition of  $\text{N}_2\text{O}_4$ .



$$\Delta S^\circ = 2 S^\circ(\text{NO}_2(g)) - S^\circ(\text{N}_2\text{O}_4(g))$$

$$\Delta S^\circ = (2 \text{ mol}) \left( 240.0 \frac{\text{J}}{\text{K mol}} \right) - (1 \text{ mol}) \left( 304.3 \frac{\text{J}}{\text{K mol}} \right)$$

$$\Delta S^\circ = \boxed{175.7 \text{ J/K}}$$



# Entropy and the Second Law of Thermodynamics

**First Law of Thermodynamics:** In any process, spontaneous or nonspontaneous, the total energy of a system and its surroundings is constant.

**Second Law of Thermodynamics:** In any *spontaneous* process, the total entropy of a system and its surroundings always increases.

# Entropy and the Second Law of Thermodynamics

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

or

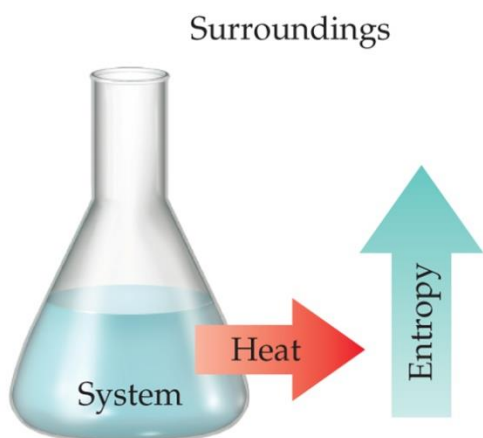
$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

**$\Delta S_{\text{total}} > 0$**  The reaction is spontaneous.

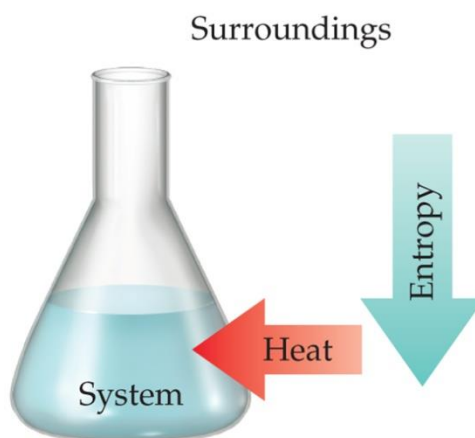
**$\Delta S_{\text{total}} < 0$**  The reaction is nonspontaneous.

**$\Delta S_{\text{total}} = 0$**  The reaction mixture is at equilibrium.

# Entropy and the Second Law of Thermodynamics



**(a)** When an exothermic reaction occurs in the system ( $\Delta H < 0$ ), the surroundings gains heat and its entropy increases ( $\Delta S_{\text{surr}} > 0$ ).



**(b)** When an endothermic reaction occurs in the system ( $\Delta H > 0$ ), the surroundings loses heat and its entropy decreases ( $\Delta S_{\text{surr}} < 0$ ).

$$\Delta S_{\text{surr}} \propto -\Delta H$$

$$\Delta S_{\text{surr}} \propto \frac{1}{T}$$

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

# Free Energy

**Free Energy:  $G = H - TS$**

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

Using:  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

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

$$\Delta S = \Delta S_{\text{sys}}$$

$$\Delta G = \Delta H - T\Delta S = -T\Delta S_{\text{total}}$$

# Free Energy

Using the second law and  $\Delta G = \Delta H - T\Delta S = -T\Delta S_{\text{total}}$

**$\Delta G < 0$**       The reaction is spontaneous.

**$\Delta G > 0$**       The reaction is nonspontaneous.

**$\Delta G = 0$**       The reaction mixture is at equilibrium.

# Free Energy

**TABLE 17.2** Signs of Enthalpy, Entropy, and Free-Energy Changes and Reaction Spontaneity for a Reaction at Constant Temperature and Pressure

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity	Example
-	+	-	Spontaneous at all temperatures	$2 \text{NO}_2(g) \longrightarrow \text{N}_2(g) + 2 \text{O}_2(g)$
+	-	+	Nonspontaneous at all temperatures	$3 \text{O}_2(g) \longrightarrow 2 \text{O}_3(g)$
-	-	- or +	Spontaneous at low temperatures where $\Delta H$ outweighs $T\Delta S$ Nonspontaneous at high temperatures where $T\Delta S$ outweighs $\Delta H$	$\text{N}_2(g) + 3 \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$
+	+	- or +	Spontaneous at high temperatures where $T\Delta S$ outweighs $\Delta H$ Nonspontaneous at low temperatures where $\Delta H$ outweighs $T\Delta S$	$2 \text{HgO}(s) \longrightarrow 2 \text{Hg}(l) + \text{O}_2(g)$

# Standard Free-Energy Changes for Reactions

**Thermodynamic Standard State:** Most stable form of a substance at 1 atm pressure and at a specified temperature, usually 25 °C; 1 M concentration for all substances in solution

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

# Standard Free-Energy Changes for Reactions

Calculate the standard free-energy change at 25 °C for the Haber synthesis of ammonia using the given values for the standard enthalpy and standard entropy changes:



$$\Delta S^\circ = -198.7 \text{ J/K}$$

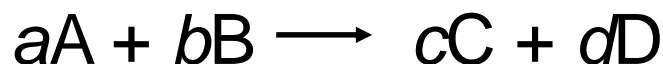
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -92.2 \text{ kJ} - \left( 298 \text{ K} \times \frac{-198.7 \text{ J}}{\text{K}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \right) = \boxed{-33.0 \text{ kJ}}$$



# Standard Free Energies of Formation

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



$$\Delta G^\circ = \underbrace{[c\Delta G^\circ_f (C) + d\Delta G^\circ_f (D)]}_{\text{Products}} - \underbrace{[a\Delta G^\circ_f (A) + b\Delta G^\circ_f (B)]}_{\text{Reactants}}$$

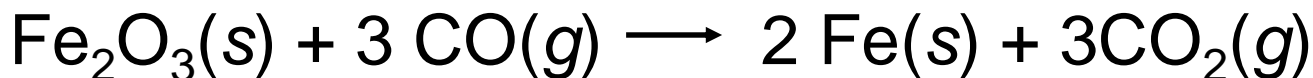
# Standard Free Energies of Formation

**TABLE 17.3** Standard Free Energies of Formation for Some Common Substances at 25 °C

Substance	Formula	$\Delta G_f^\circ$ [kJ/mol]	Substance	Formula	$\Delta G_f^\circ$ [kJ/mol]
<b>Gases</b>			<b>Liquids</b>		
Acetylene	C <sub>2</sub> H <sub>2</sub>	209.9	Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	-390
Ammonia	NH <sub>3</sub>	-16.5	Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	-174.9
Carbon dioxide	CO <sub>2</sub>	-394.4	Methanol	CH <sub>3</sub> OH	-166.6
Carbon monoxide	CO	-137.2	Water	H <sub>2</sub> O	-237.2
Ethylene	C <sub>2</sub> H <sub>4</sub>	68.1	<b>Solids</b>		
Hydrogen	H <sub>2</sub>	0	Calcium carbonate	CaCO <sub>3</sub>	-1129.1
Methane	CH <sub>4</sub>	-50.8	Calcium oxide	CaO	-603.3
Nitrogen	N <sub>2</sub>	0	Diamond	C	2.9
Nitrogen dioxide	NO <sub>2</sub>	51.3	Graphite	C	0
Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	99.8	Iron(III) oxide	Fe <sub>2</sub> O <sub>3</sub>	-742.2

# Standard Free Energies of Formation

Using table values, calculate the standard free-energy change at 25 °C for the reduction of iron(III) oxide with carbon monoxide:



$$\Delta G^\circ = [2 \Delta G^\circ_f (\text{Fe}(\text{s})) + 3 \Delta G^\circ_f (\text{CO}_2(\text{g}))]$$

$$- [1 \Delta G^\circ_f (\text{Fe}_2\text{O}_3(\text{s})) + 3 \Delta G^\circ_f (\text{CO}(\text{g}))]$$

$$\Delta G^\circ = [(2 \text{ mol})(0 \text{ kJ/mol}) + (3 \text{ mol})(-394.4 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(-742.2 \text{ kJ/mol}) + (3 \text{ mol})(-137.2 \text{ kJ/mol})]$$

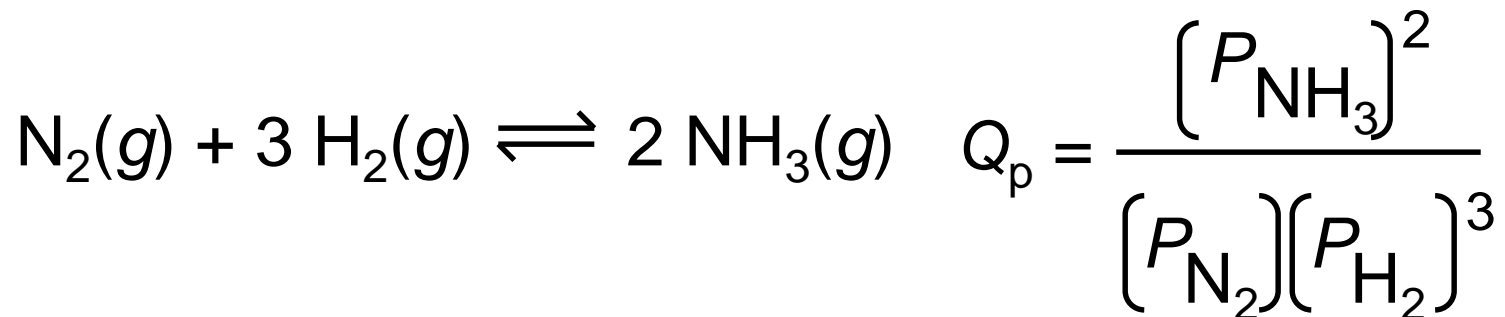
$$\Delta G^\circ = \boxed{-29.4 \text{ kJ}}$$

# Free Energy Changes and the Reaction Mixture

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

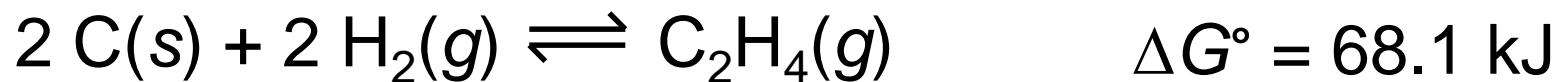
$\Delta G$  = Free-energy change under nonstandard conditions.

For the Haber synthesis of ammonia:



# Free Energy Changes and the Reaction Mixture

Calculate  $\Delta G$  for the formation of ethylene ( $\text{C}_2\text{H}_4$ ) from carbon and hydrogen at 25 °C when the partial pressures are 100 atm  $\text{H}_2$  and 0.10 atm  $\text{C}_2\text{H}_4$ .



**Use:**

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

$$Q_p = \frac{P_{\text{C}_2\text{H}_4}}{(P_{\text{H}_2})^2}$$

# Free Energy Changes and the Reaction Mixture

**Calculate ln Q:**

$$\ln \left( \frac{0.10}{1002} \right) = -11.51$$

**Calculate ΔG:**

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

$$= 68.1 \text{ kJ/mol} + \left( 8.314 \frac{\text{J}}{\text{K mol}} \right) (298 \text{ K})(-11.51) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

$$\Delta G = \boxed{39.6 \text{ kJ/mol}}$$

# Free Energy and Chemical Equilibrium

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

- **When the reaction mixture is mostly reactants:**

$$Q \ll 1 \qquad RT \ln Q \ll 0 \qquad \Delta G < 0$$

The total free energy decreases as the reaction proceeds spontaneously in the *forward* direction.

- **When the reaction mixture is mostly products:**

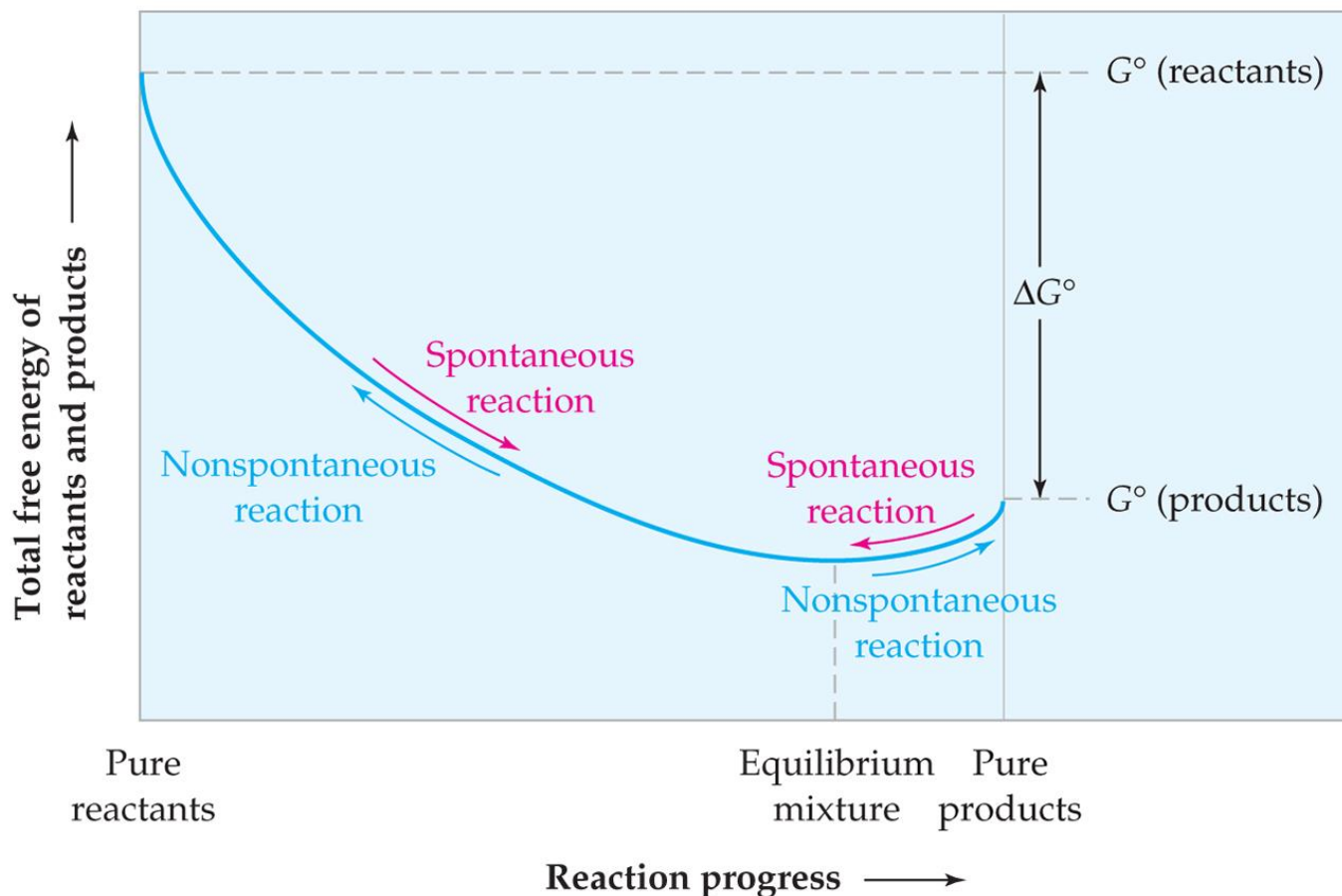
$$Q \gg 1 \qquad RT \ln Q \gg 0 \qquad \Delta G > 0$$

The total free energy decreases as the reaction proceeds spontaneously in the *reverse* direction.

# Free Energy and Chemical Equilibrium

Beginning with pure reactants, the free energy decreases ( $\Delta G < 0$ ) as the system moves toward equilibrium.

Beginning with pure products, the free energy also decreases ( $\Delta G < 0$ ) as the system moves toward equilibrium.





# Free Energy and Chemical Equilibrium

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

At equilibrium,  $\Delta G = 0$  and  $Q = K$ .

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

**TABLE 17.4** Relationship Between the Standard Free-Energy Change and the Equilibrium Constant for a Reaction:  $\Delta G^\circ = -RT \ln K$

$\Delta G^\circ$	$\ln K$	$K$	Comment
$\Delta G^\circ < 0$	$\ln K > 0$	$K > 1$	The equilibrium mixture is mainly products.
$\Delta G^\circ > 0$	$\ln K < 0$	$K < 1$	The equilibrium mixture is mainly reactants.
$\Delta G^\circ = 0$	$\ln K = 0$	$K = 1$	The equilibrium mixture contains comparable amounts of reactants and products.

# Free Energy and Chemical Equilibrium

Calculate  $K_p$  at 25 °C for the following reaction:



**Calculate  $\Delta G^\circ$ :**

$$\begin{aligned}\Delta G^\circ &= [\Delta G^\circ_f (\text{CaO}(\text{s})) + \Delta G^\circ_f (\text{CO}_2(\text{g}))] - [\Delta G^\circ_f (\text{CaCO}_3(\text{s}))] \\ &= [(1 \text{ mol})(-603.3 \text{ kJ/mol}) + (1 \text{ mol})(-394.4 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol})(-1129.1 \text{ kJ/mol})]\end{aligned}$$

$$\Delta G^\circ = +131.4 \text{ kJ/mol}$$

# Free Energy and Chemical Equilibrium

**Calculate  $\ln K$ :**

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

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-131.4 \text{ kJ/mol}}{\left(8.314 \frac{\text{J}}{\text{K mol}}\right) (298 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)}$$

$$\ln K = -53.04$$

**Calculate  $K$ :**

$$K = e^{-53.04} = \boxed{9.2 \times 10^{-24}}$$