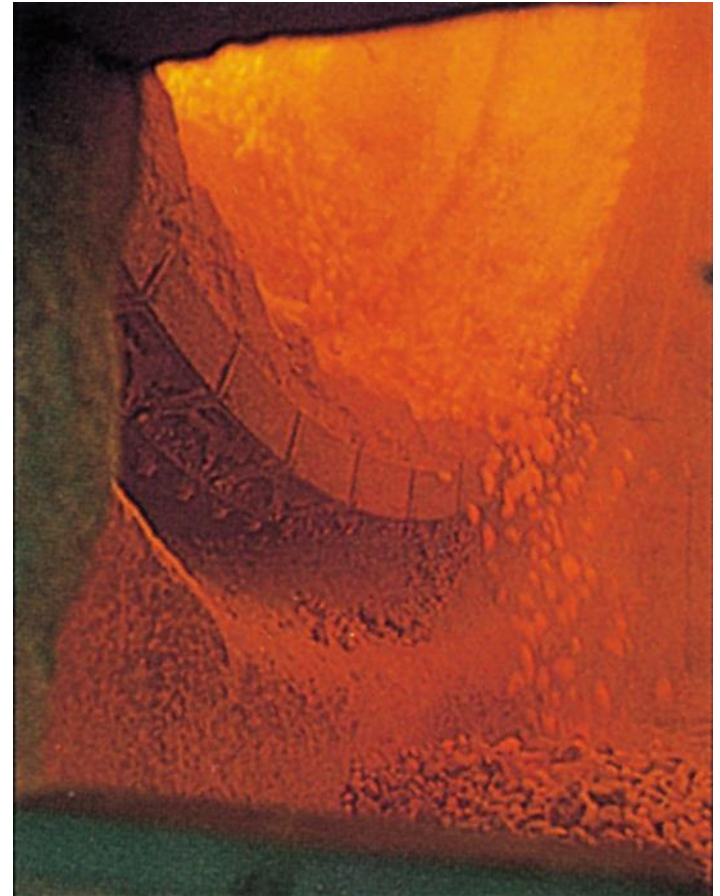


Entropy, Free Energy, and Equilibrium

Chapter 18

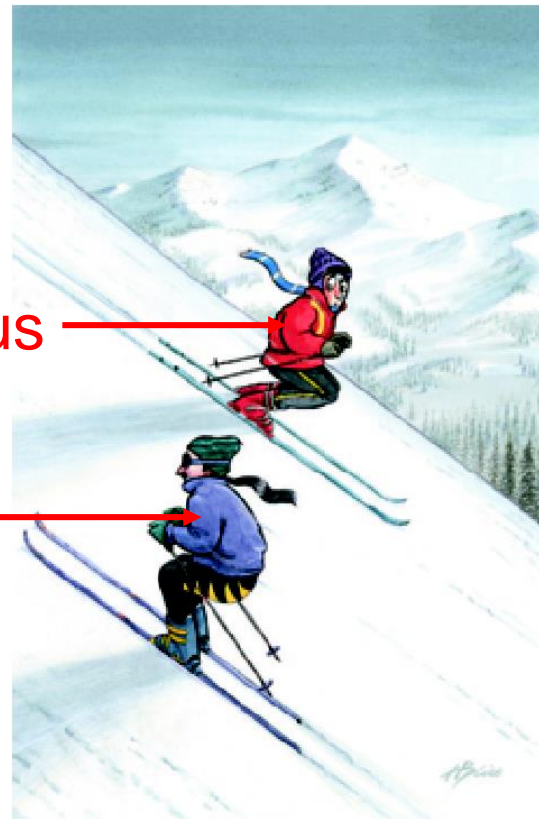


Spontaneous Physical and Chemical Processes

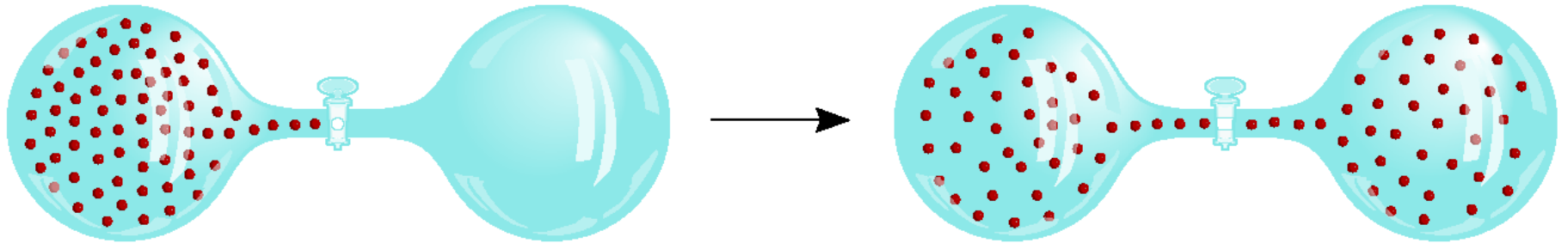
- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0 °C and ice melts above 0 °C
- Heat flows from a hotter object to a colder object
- A gas expands in an evacuated bulb
- Iron exposed to oxygen and water forms rust

spontaneous

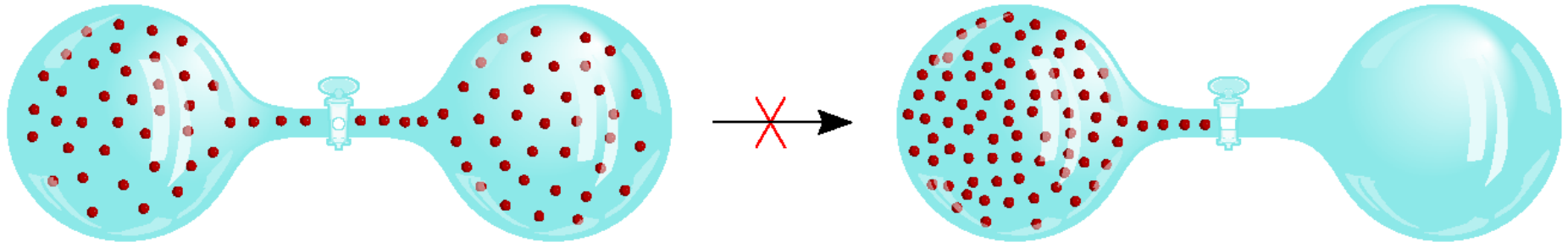
nonspontaneous



spontaneous

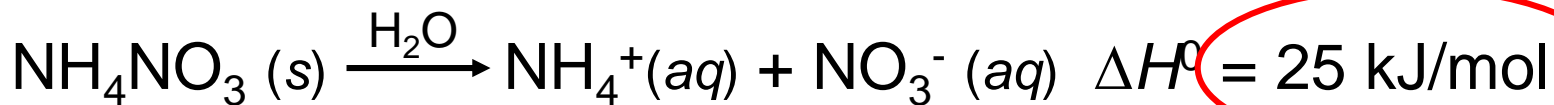
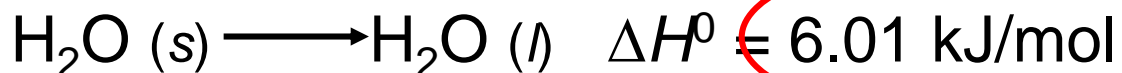
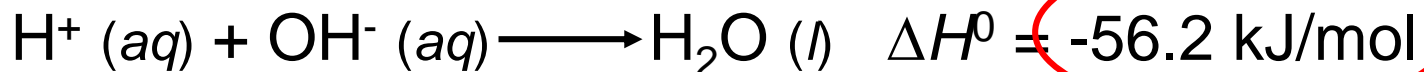
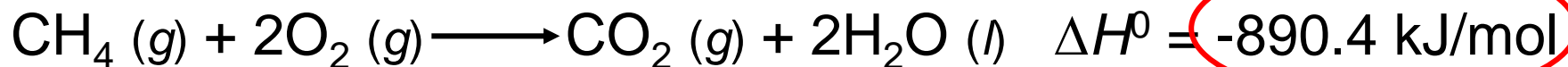


nonspontaneous



Does a decrease in enthalpy mean a reaction proceeds spontaneously?

Spontaneous reactions



Entropy (S) is a measure of the **randomness or disorder** of a system.



$$\Delta S = S_f - S_i$$

If the change from initial to final results in an increase in randomness

$$S_f > S_i \qquad \Delta S > 0$$

For any substance, the solid state is more ordered than the liquid state and the liquid state is more ordered than gas state

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

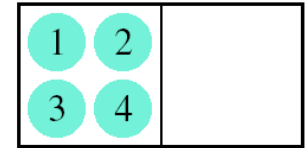


Entropy

Distribution

Microstates

I



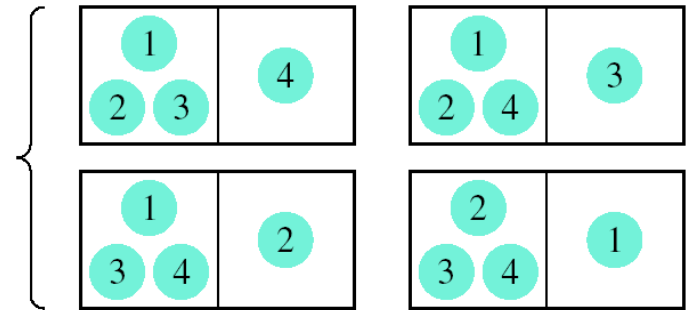
W = number of microstates

$$S = k \ln W$$

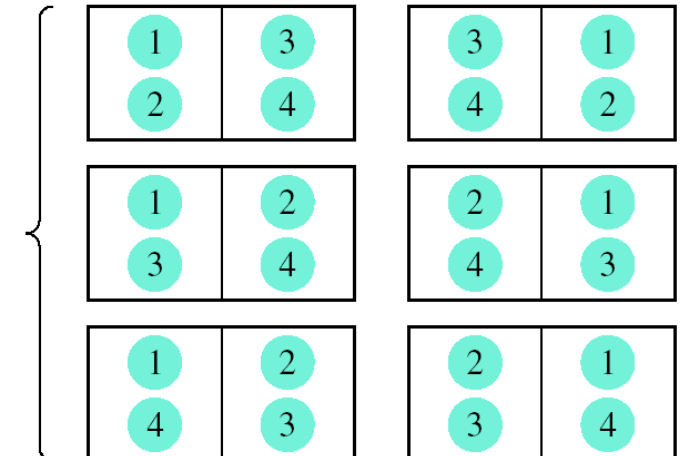
$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln \frac{W_f}{W_i}$$

II



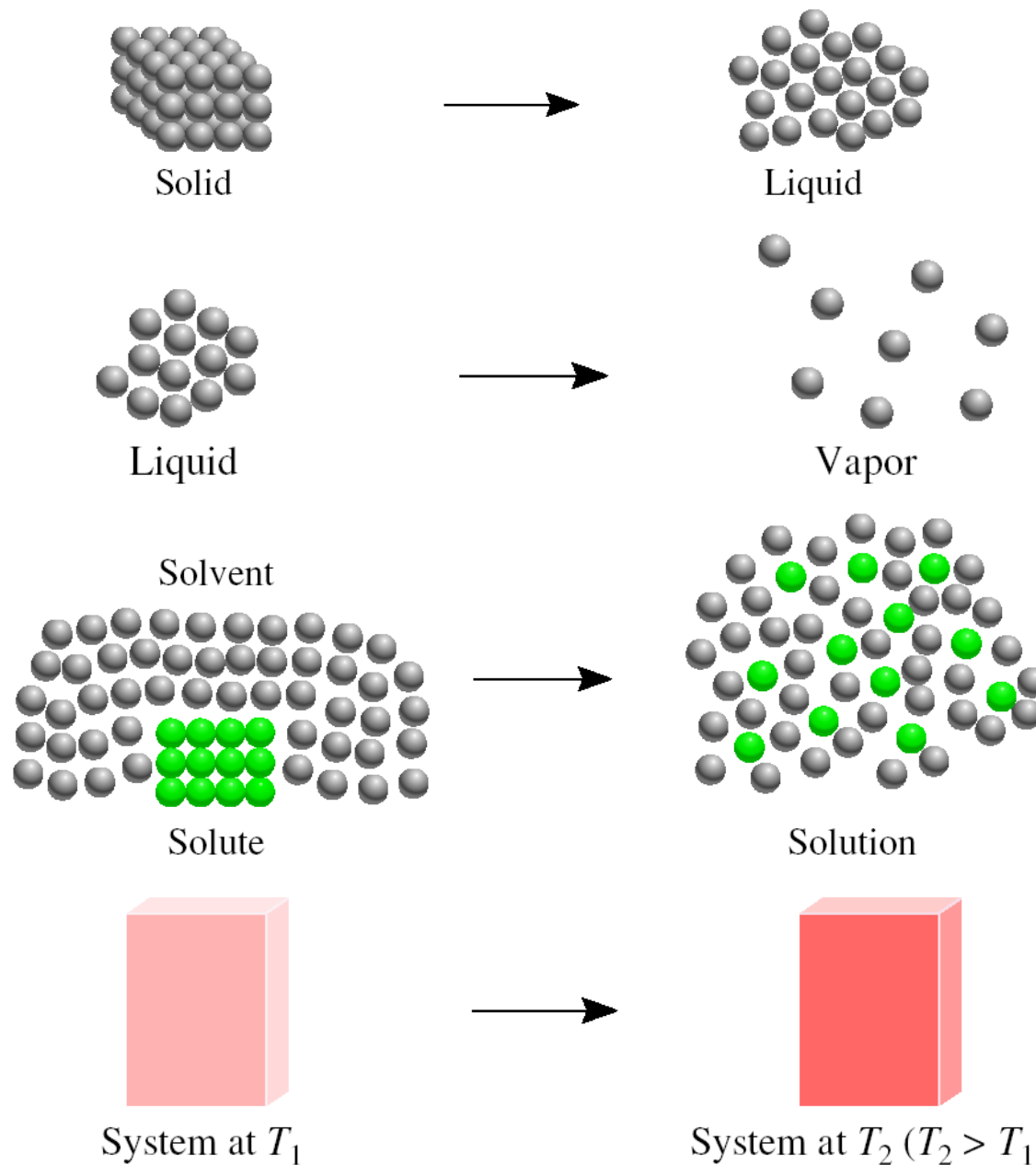
III



$W_f > W_i$ then $\Delta S > 0$

$W_f < W_i$ then $\Delta S < 0$

Processes that lead to an increase in entropy ($\Delta S > 0$)



Example: $\text{Br}_2(\text{l}) \longrightarrow \text{Br}_2(\text{g})$



$$\Delta S > 0$$

Example: $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{g})$



$$\Delta S > 0$$

How does the entropy of a system change for each of the following processes?

(a) Condensing water vapor

Randomness decreases

Entropy decreases ($\Delta S < 0$)

(b) Forming sucrose crystals from a supersaturated solution

Randomness decreases

Entropy decreases ($\Delta S < 0$)

(c) Heating hydrogen gas from 60°C to 80°C

Randomness increases

Entropy increases ($\Delta S > 0$)

(d) Subliming dry ice

Randomness increases

Entropy increases ($\Delta S > 0$)

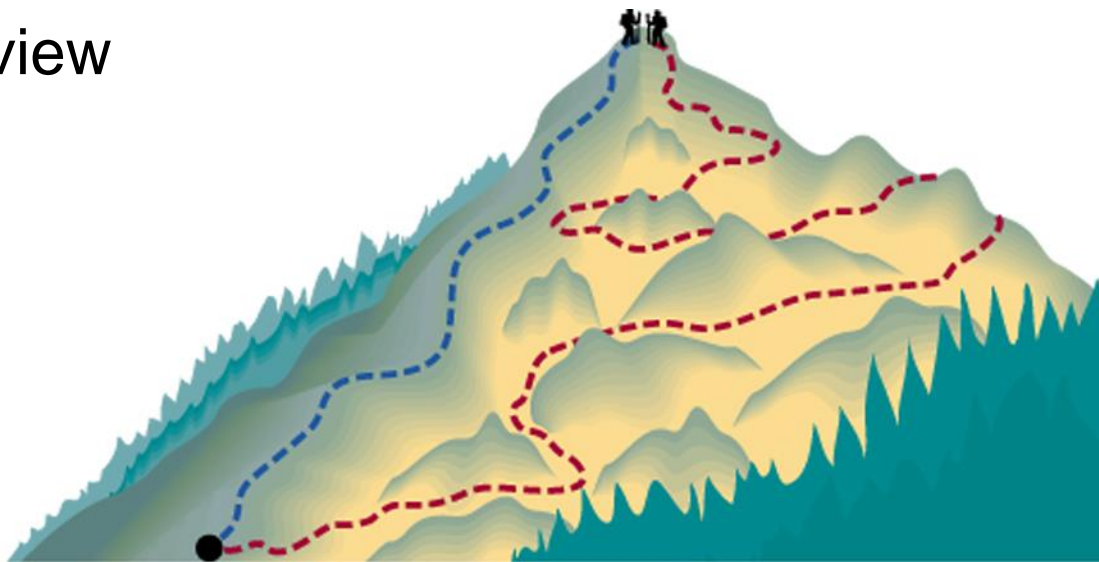
Entropy

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

Examples:

energy, enthalpy, pressure, volume, temperature, **entropy**

Review



Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

TABLE 18.1**Standard Entropy Values
(S°) for Some Substances
at 25°C**

Substance	S° (J/K · mol)
$\text{H}_2\text{O}(l)$	69.9
$\text{H}_2\text{O}(g)$	188.7
$\text{Br}_2(l)$	152.3
$\text{Br}_2(g)$	245.3
$\text{I}_2(s)$	116.7
$\text{I}_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
$\text{He}(g)$	126.1
$\text{Ne}(g)$	146.2

First Law of Thermodynamics

Energy can be converted from one form to another but energy cannot be created or destroyed.

Second Law of Thermodynamics

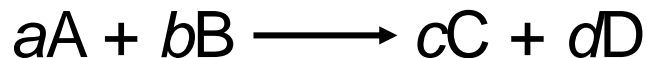
The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

Entropy Changes in the System (ΔS_{sys})

The **standard entropy of reaction** (ΔS_{rxn}^0) is the entropy change for a reaction carried out at 1 atm and 25°C.



$$\Delta S_{\text{rxn}}^0 = [cS^0(\text{C}) + dS^0(\text{D})] - [aS^0(\text{A}) + bS^0(\text{B})]$$

$$\Delta S_{\text{rxn}}^0 = \Sigma nS^0(\text{products}) - \Sigma mS^0(\text{reactants})$$

What is the standard entropy change for the following reaction at 25°C? $2\text{CO} (g) + \text{O}_2 (g) \longrightarrow 2\text{CO}_2 (g)$

$$S^0(\text{CO}) = 197.9 \text{ J/K}\cdot\text{mol} \quad S^0(\text{CO}_2) = 213.6 \text{ J/K}\cdot\text{mol}$$

$$S^0(\text{O}_2) = 205.0 \text{ J/K}\cdot\text{mol}$$

$$\Delta S_{\text{rxn}}^0 = 2 \times S^0(\text{CO}_2) - [2 \times S^0(\text{CO}) + S^0(\text{O}_2)]$$

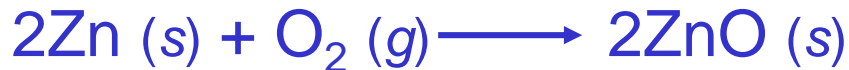
$$\Delta S_{\text{rxn}}^0 = 427.2 - [395.8 + 205.0] = -173.6 \text{ J/K}\cdot\text{mol}$$

Entropy Changes in the System (ΔS_{sys})

When gases are produced (or consumed)

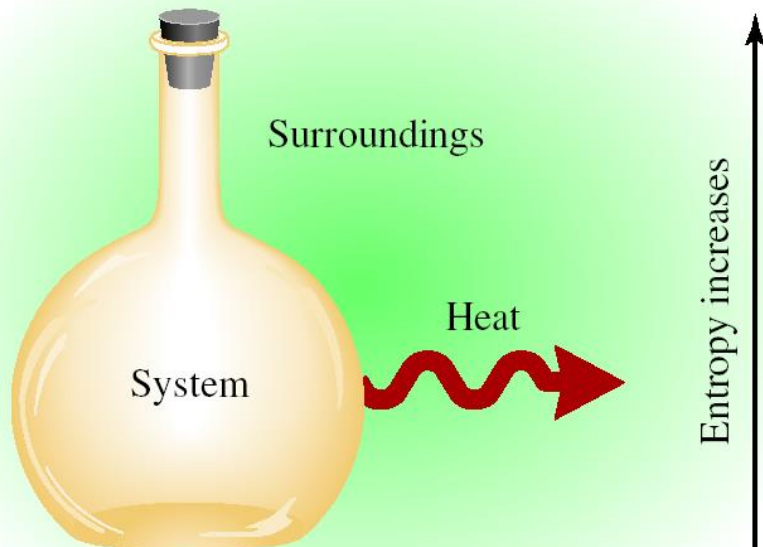
- If a reaction produces more gas molecules than it consumes, $\Delta S^0 > 0$.
- If the total number of gas molecules diminishes, $\Delta S^0 < 0$.
- If there is no net change in the total number of gas molecules, then ΔS^0 may be positive or negative BUT ΔS^0 will be a small number.

What is the sign of the entropy change for the following reaction?



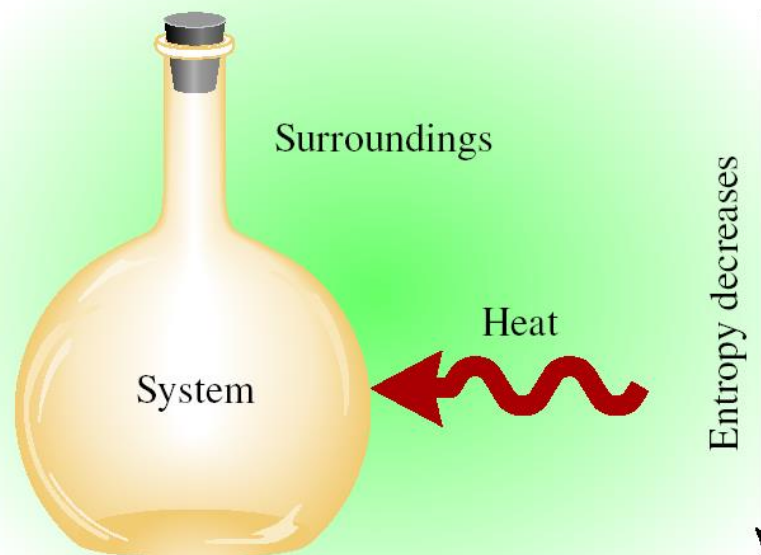
The total number of gas molecules goes down, ΔS is negative.

Entropy Changes in the Surroundings (ΔS_{surr})



Exothermic Process

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

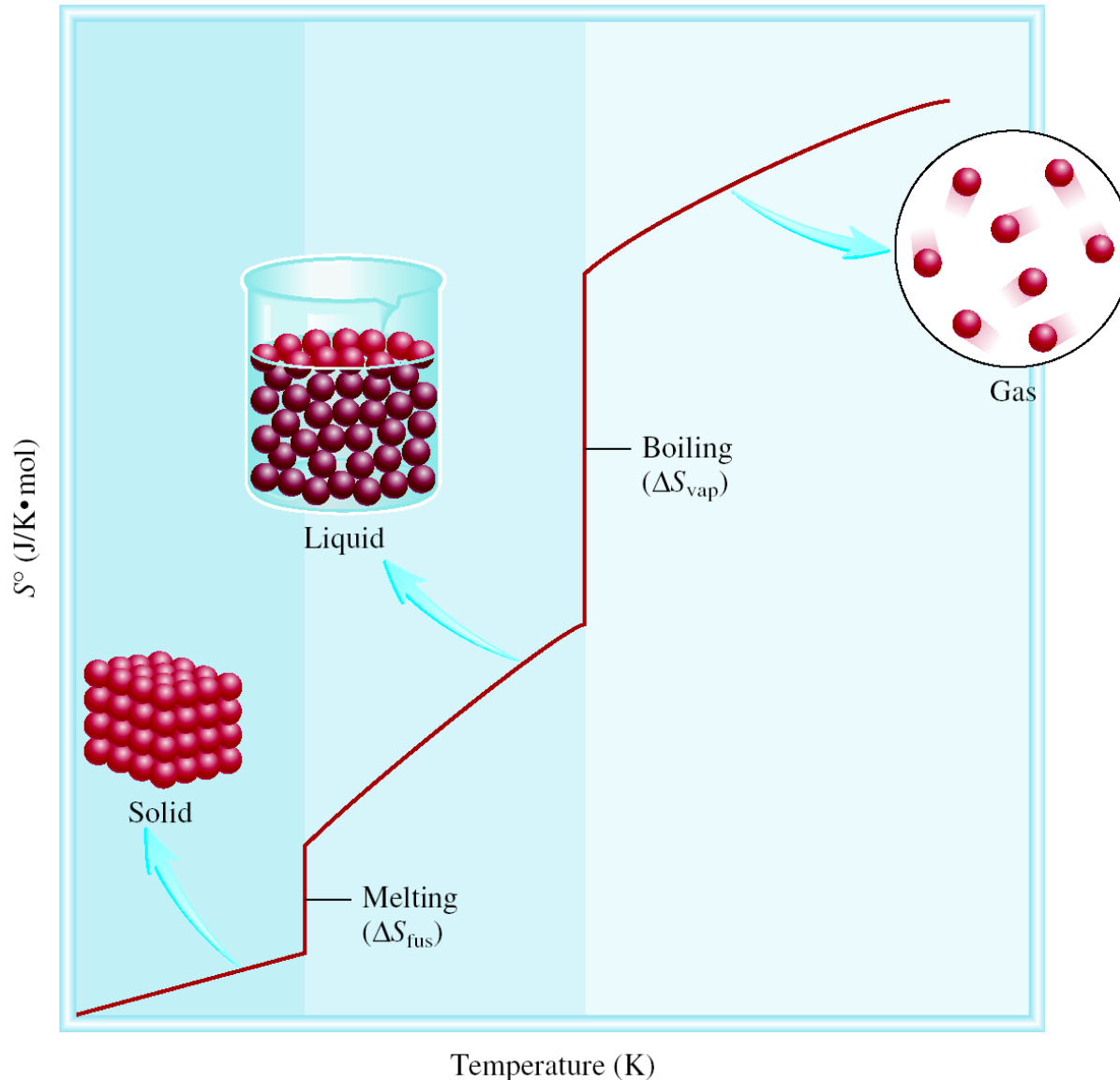


Endothermic Process

$$\Delta S_{\text{surr}} < 0$$

Third Law of Thermodynamics

The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.



$$S = k \ln W$$

$$W = 1$$

$$S = 0$$

Gibbs Free Energy

Spontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

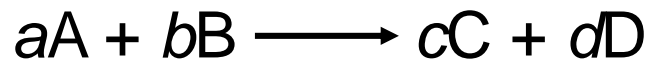
For a constant temperature and
constant pressure process:

***Gibbs free
energy (G)***

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

- $\Delta G < 0$ The reaction is spontaneous in the forward direction.
- $\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.
- $\Delta G = 0$ The reaction is at equilibrium.

The ***standard free-energy of reaction*** (ΔG_{rxn}^0) is the free-energy change for a reaction when it occurs under standard-state conditions.



$$\Delta G_{\text{rxn}}^0 = [c\Delta G_{\text{f}}^0(\text{C}) + d\Delta G_{\text{f}}^0(\text{D})] - [a\Delta G_{\text{f}}^0(\text{A}) + b\Delta G_{\text{f}}^0(\text{B})]$$

$$\Delta G_{\text{rxn}}^0 = \Sigma n\Delta G_{\text{f}}^0(\text{products}) - \Sigma m\Delta G_{\text{f}}^0(\text{reactants})$$

Standard free energy of formation (ΔG_{f}^0) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

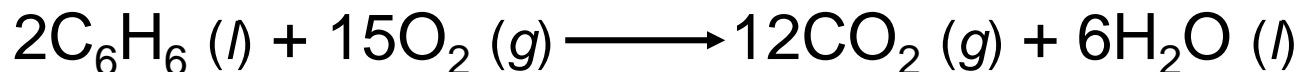
ΔG_{f}^0 of any element in its stable form is zero.

TABLE 18.2**Conventions for Standard States**

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G_f^\circ = 0$
Solution	1 molar concentration

*The most stable allotropic form at 25°C and 1 atm.

What is the standard free-energy change for the following reaction at 25 °C?



$$\Delta G_{\text{rxn}}^0 = \Sigma n\Delta G_{\text{f}}^0 (\text{products}) - \Sigma m\Delta G_{\text{f}}^0 (\text{reactants})$$

$$\Delta G_{\text{rxn}}^0 = [12\Delta G_{\text{f}}^0 (\text{CO}_2) + 6\Delta G_{\text{f}}^0 (\text{H}_2\text{O})] - [2\Delta G_{\text{f}}^0 (\text{C}_6\text{H}_6)]$$

$$\Delta G_{\text{rxn}}^0 = [12 \times -394.4 + 6 \times -237.2] - [2 \times 124.5] = -6405 \text{ kJ/mol}$$

Is the reaction spontaneous at 25 °C?

$$\Delta G^0 = -6405 \text{ kJ/mol} < 0$$

spontaneous

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

TABLE 18.3 Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

Temperature and Spontaneity of Chemical Reactions



$$\Delta H^0 = 177.8 \text{ kJ/mol}$$

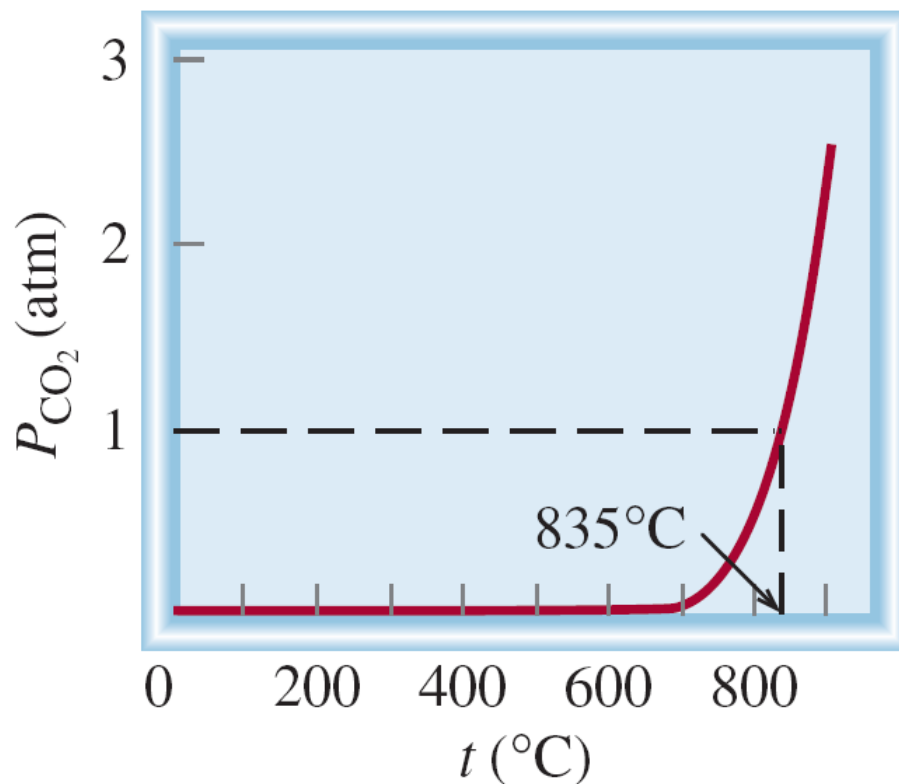
$$\Delta S^0 = 160.5 \text{ J/K}\cdot\text{mol}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\text{At } 25^\circ\text{C}, \Delta G^0 = 130.0 \text{ kJ/mol}$$

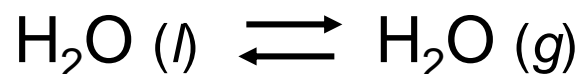
$$\Delta G^0 = 0 \text{ at } 835^\circ\text{C}$$

Equilibrium Pressure of CO_2



Gibbs Free Energy and Phase Transitions

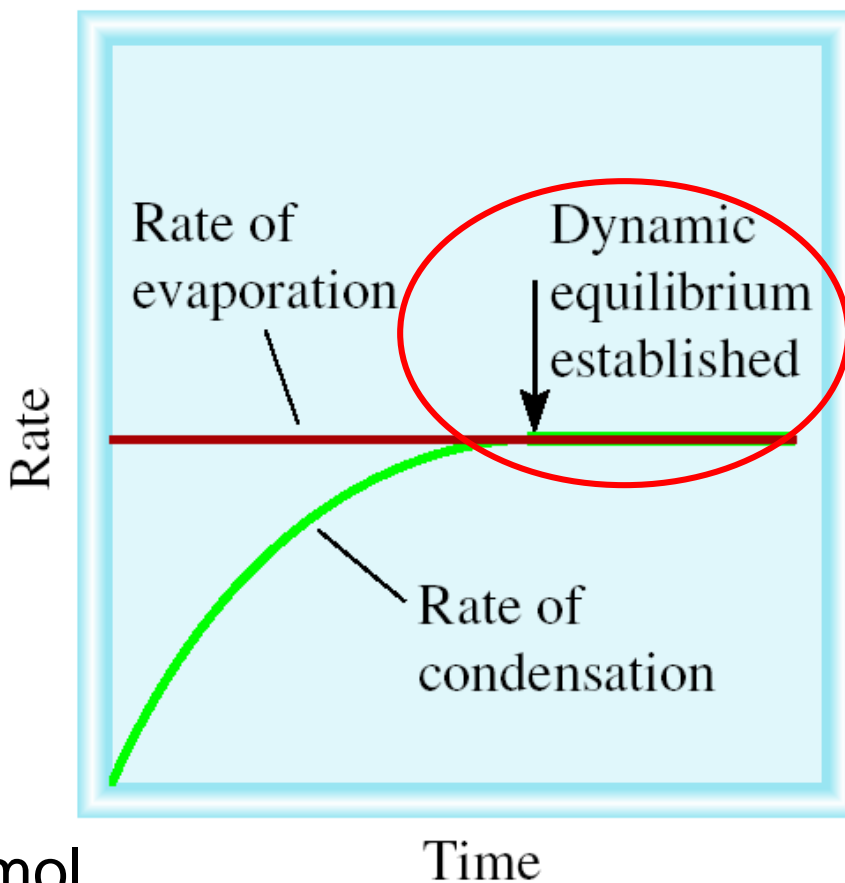
$$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$$



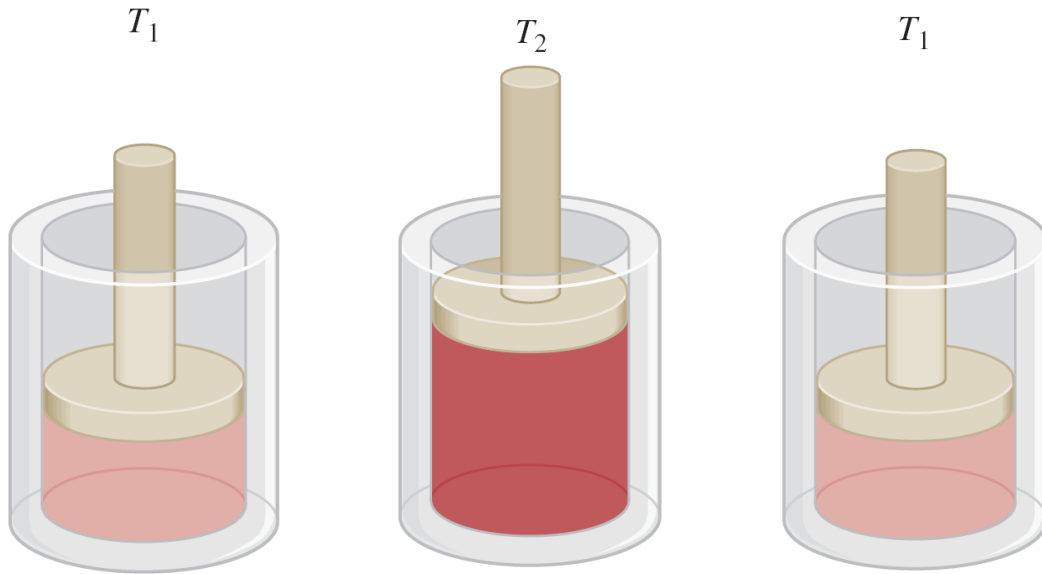
$$\Delta S = \frac{\Delta H}{T} = \frac{40.79 \text{ kJ/mol}}{373 \text{ K}}$$

$$= 1.09 \times 10^{-1} \text{ kJ/K}\cdot\text{mol}$$

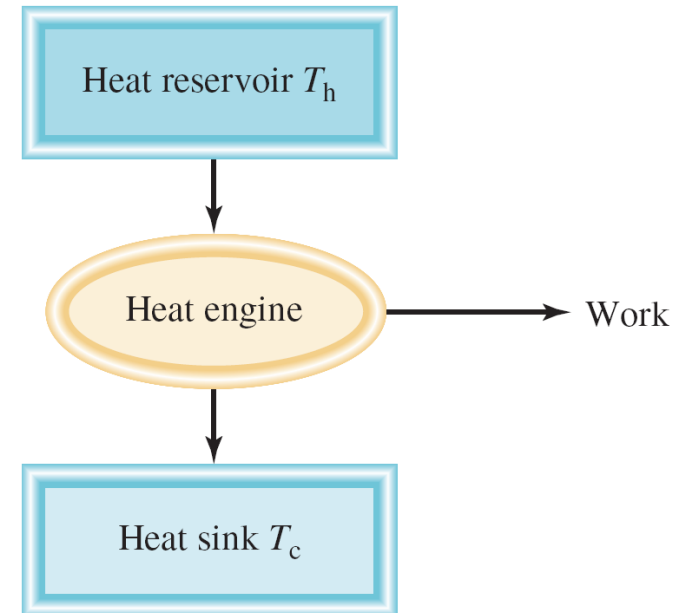
$$= 109 \text{ J/K}\cdot\text{mol}$$



Chemistry In Action: The Efficiency of Heat Engines



$$\text{Efficiency} = \frac{T_h - T_c}{T_h} \times 100\%$$



Gibbs Free Energy and Chemical Equilibrium

$$\Delta G = \Delta G^0 + RT \ln Q$$

R is the gas constant (8.314 J/K·mol)

T is the absolute temperature (K)

Q is the reaction quotient

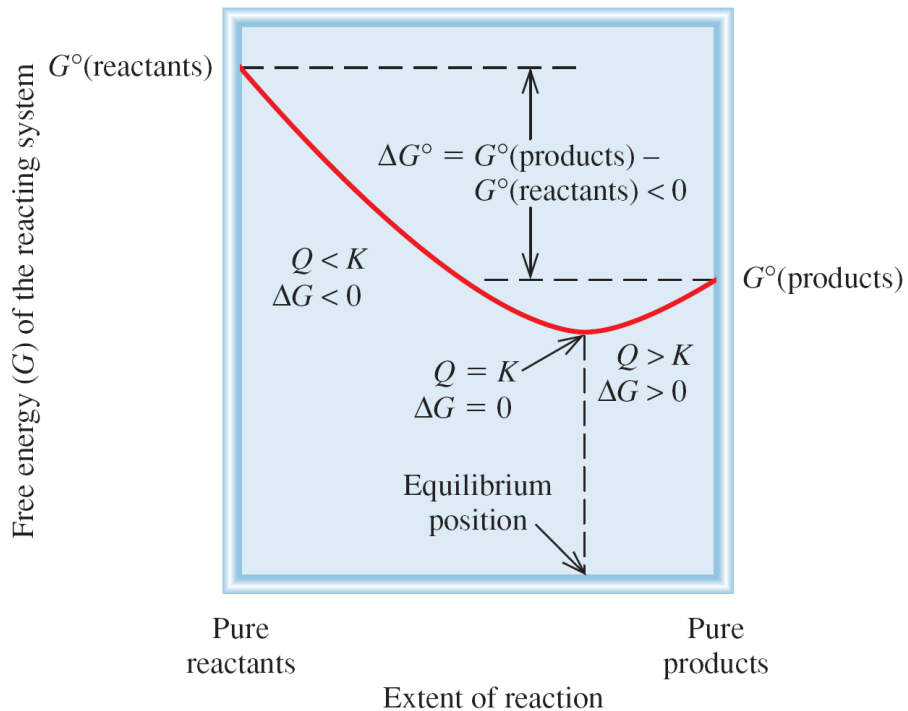
At Equilibrium

$$\Delta G = 0 \quad Q = K$$

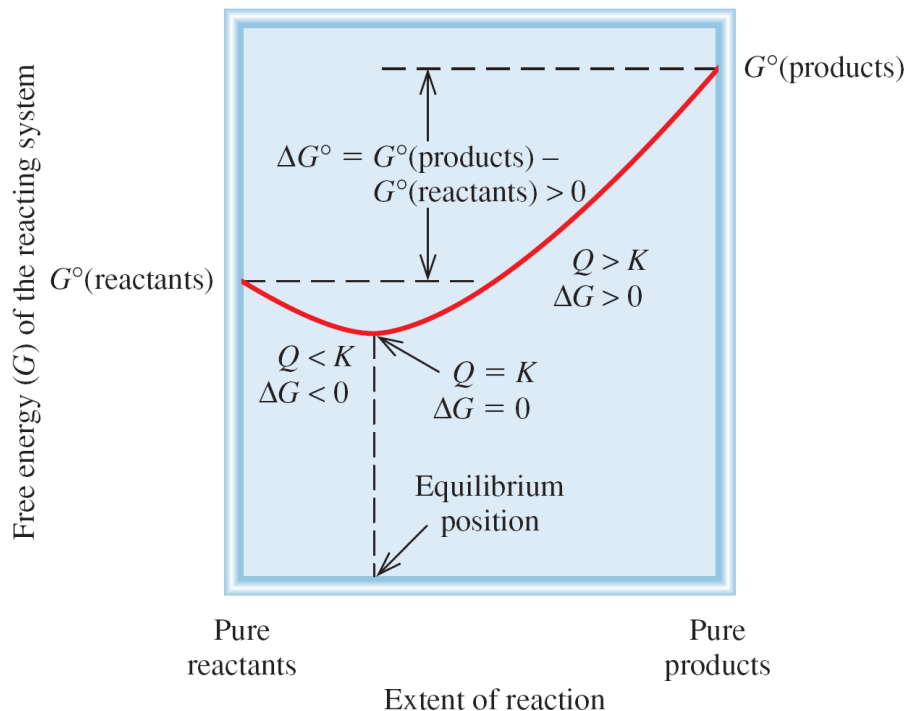
$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = - RT \ln K$$

Free Energy Versus Extent of Reaction



$$\Delta G^\circ < 0$$



$$\Delta G^\circ > 0$$

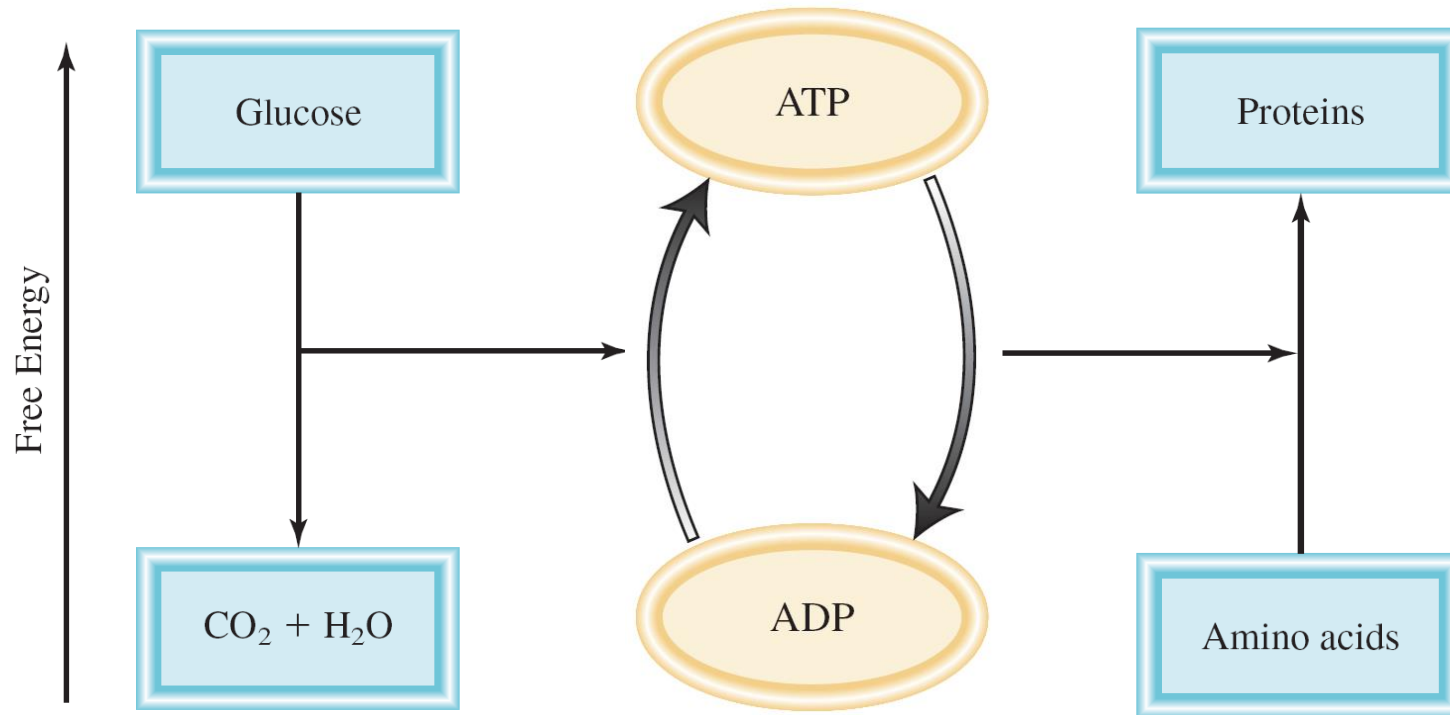
$$\Delta G^0 = -RT \ln K$$

TABLE 18.4

Relation Between ΔG° and K as Predicted by the Equation
 $\Delta G^\circ = -RT \ln K$

K	$\ln K$	ΔG°	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

Coupled Reactions



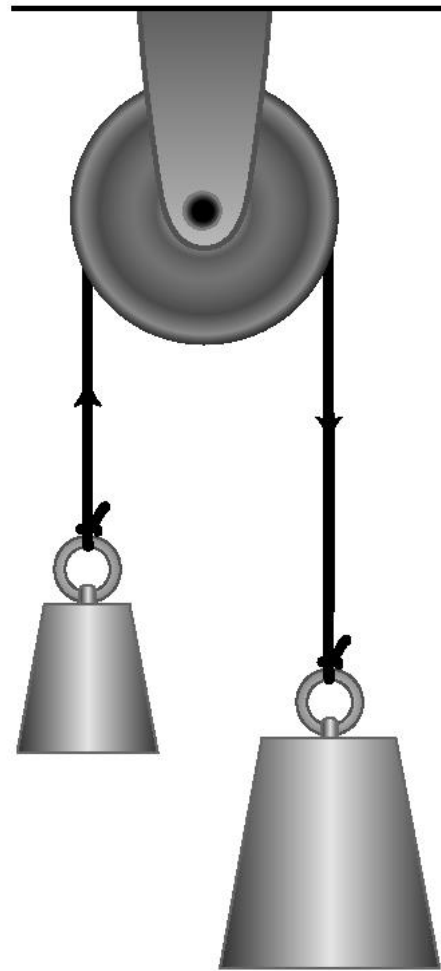
Example: Alanine + Glycine \longrightarrow Alanylglycine

$$\Delta G^0 = +29 \text{ kJ} \qquad K < 1$$



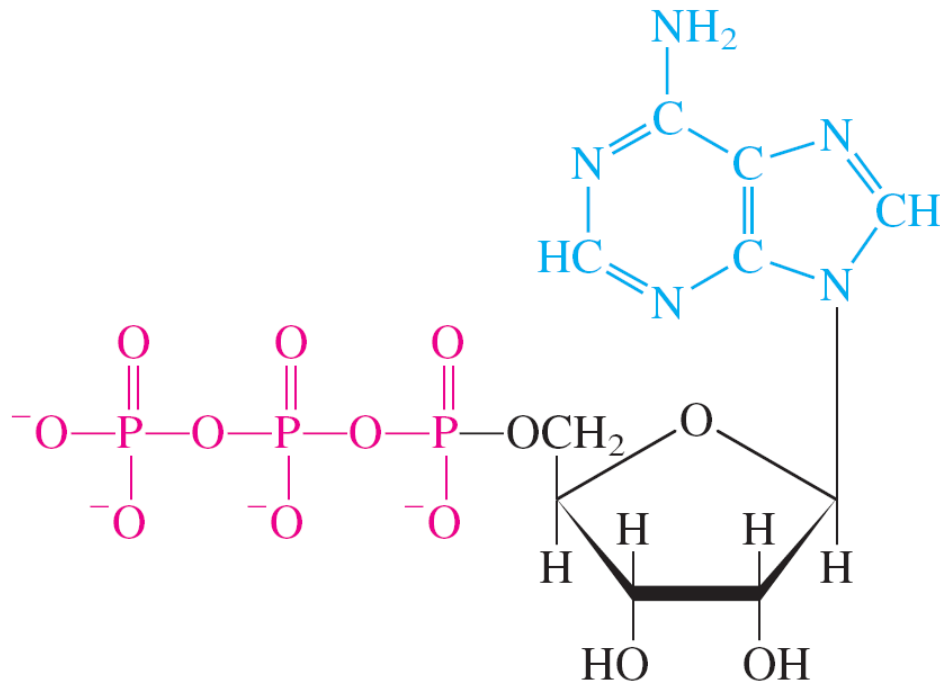
$$\Delta G^0 = -2 \text{ kJ} \qquad K > 1$$

Mechanical Analog of Couple Reactions

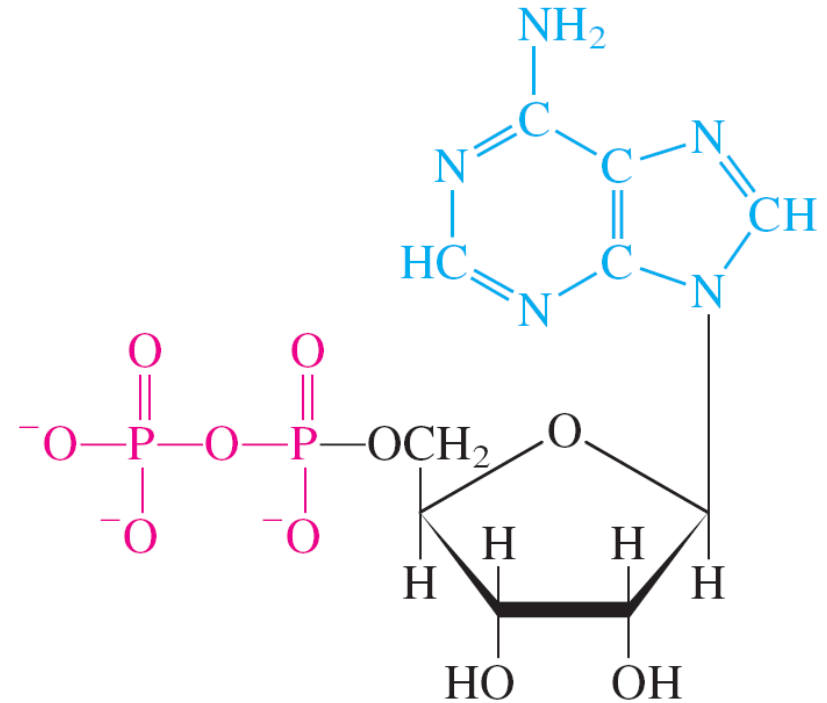


Make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

The Structure of ATP and ADP in Ionized Forms



Adenosine triphosphate
(ATP)

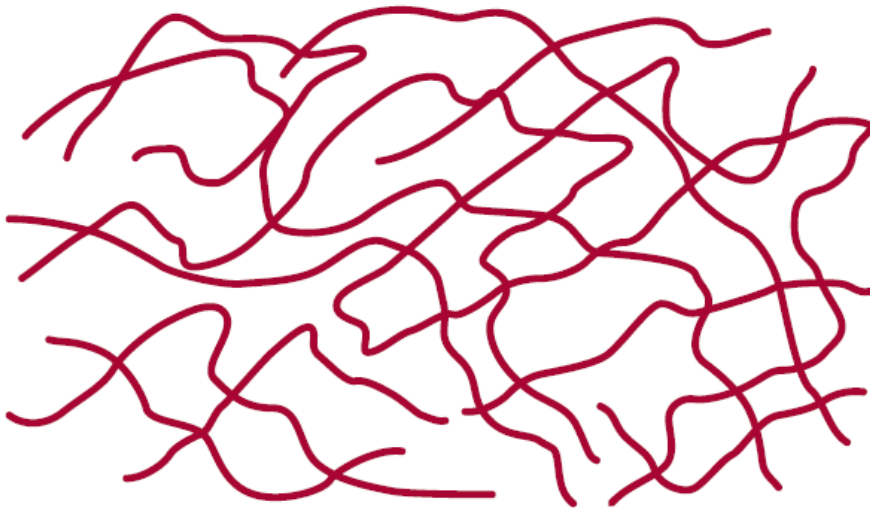


Adenosine diphosphate
(ADP)

Chemistry In Action: The Thermodynamics of a Rubber Band

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

High Entropy



Low Entropy

