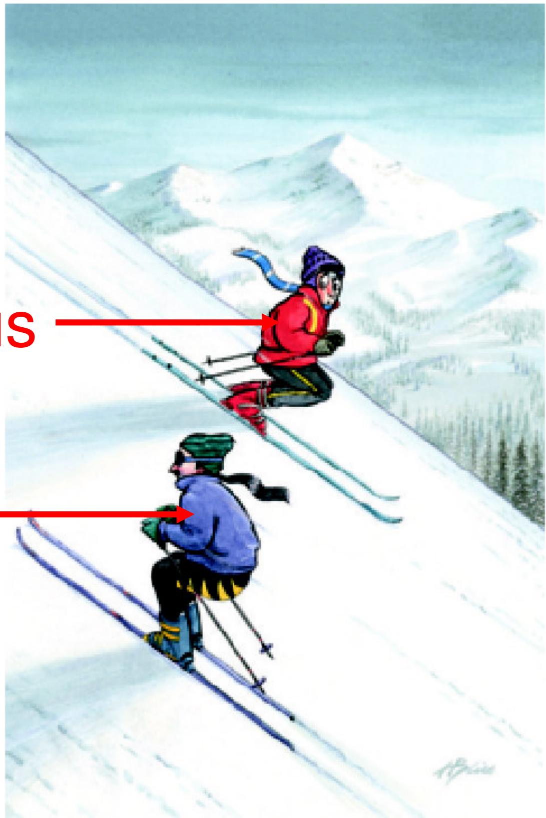
Entropy, Free Energy, and Equilibrium

Chapter 18

Spontaneous Physical and Chemical Processes

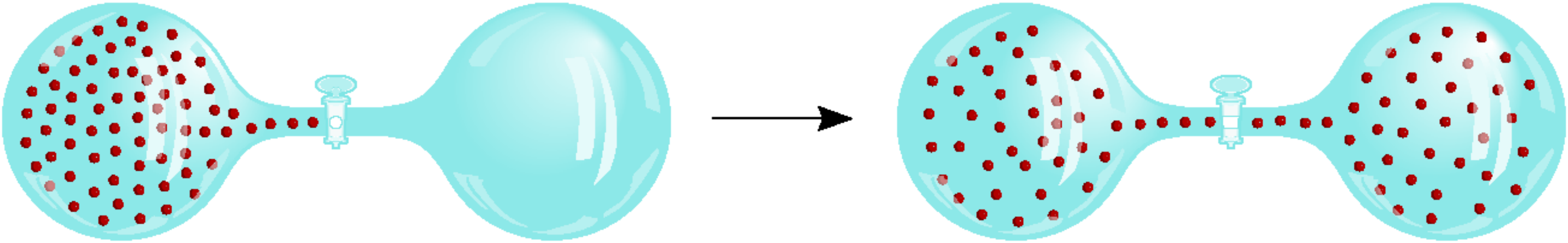
- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0 ^{o}C and ice melts above 0 ^{o}C
- Heat flows from a hotter object to a colder object
- A gas expands in an evacuated bulb
- Iron exposed to oxygen and water forms rust



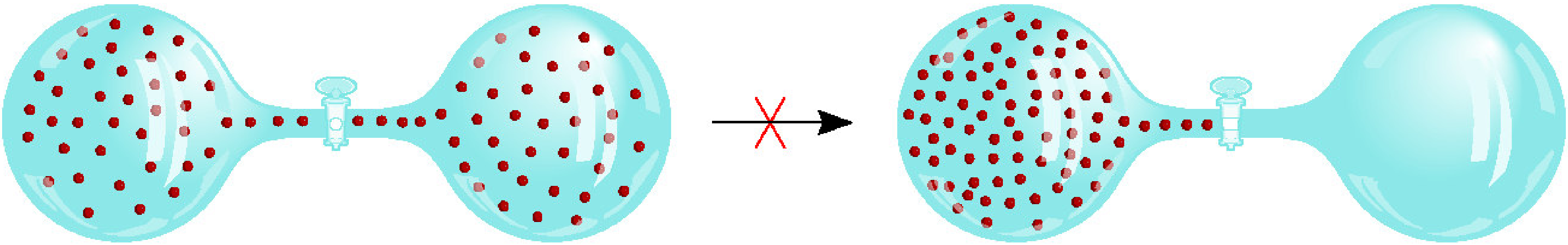
spontaneous

nonspontaneous

spontaneous



nonspontaneous



Does a decrease in enthalpy mean a reaction proceeds spontaneously?

Spontaneous reactions

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l) \quad \Delta H^0 = -890.4\ \text{kJ/mol}$$

$$H^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) \quad \Delta H^0 = -56.2\ \text{kJ/mol}$$

$$H_2O\ (s) \longrightarrow H_2O\ (l) \quad \Delta H^0 = 6.01\ \text{kJ/mol}$$

$$NH_4NO_3\ (s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-\ (aq) \quad \Delta H^0 = 25\ \text{kJ/mol}$$

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

order ↑ S ↓ disorder ↑ S ↑

$$\Delta S = S_f - S_i$$

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

$$S_{solid} < S_{liquid} << S_{gas}$$

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta S > 0$$

Entropy

W = number of microstates

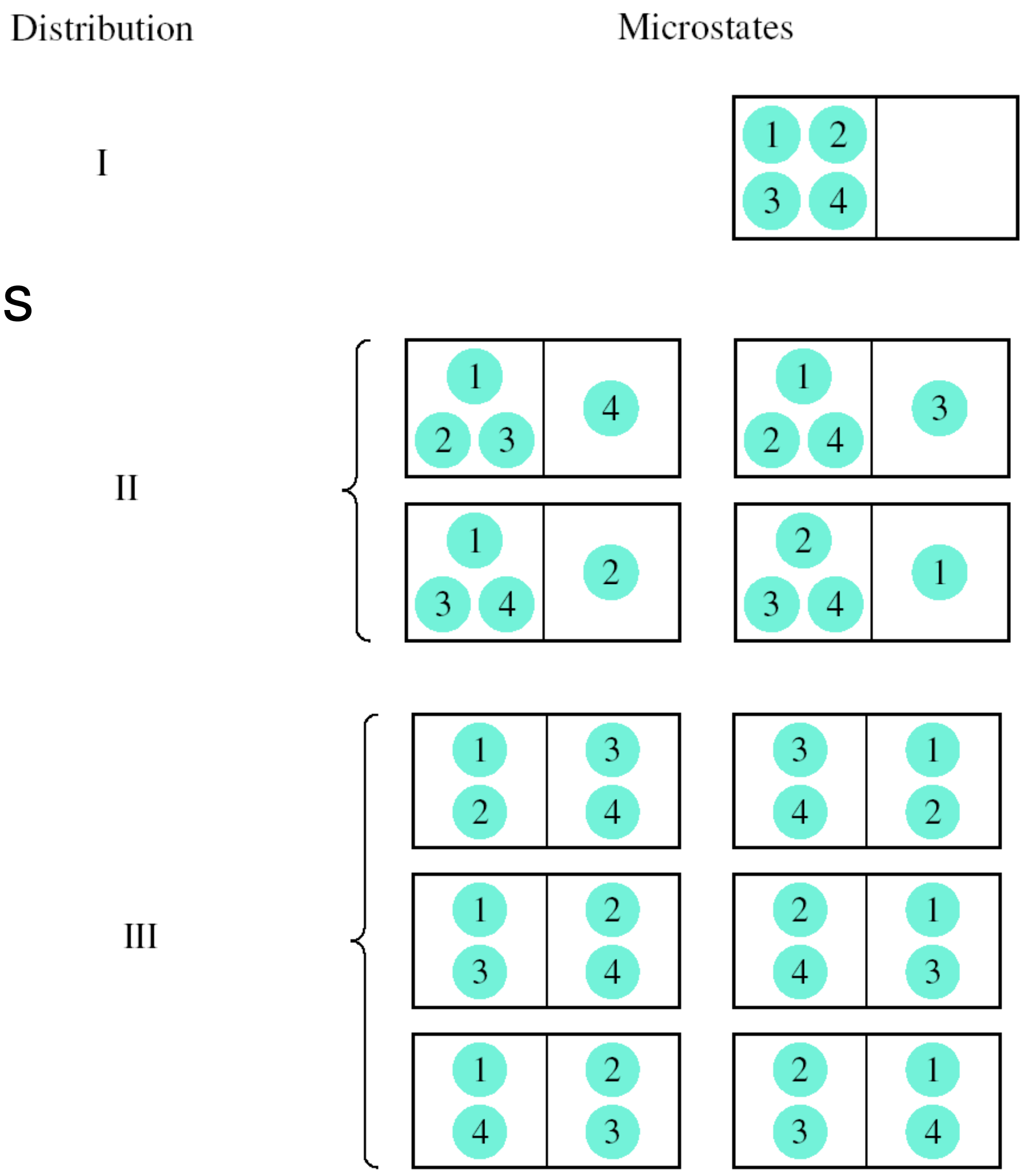
$$S = k \ln W$$

$$\Delta S = S_f - S_i$$

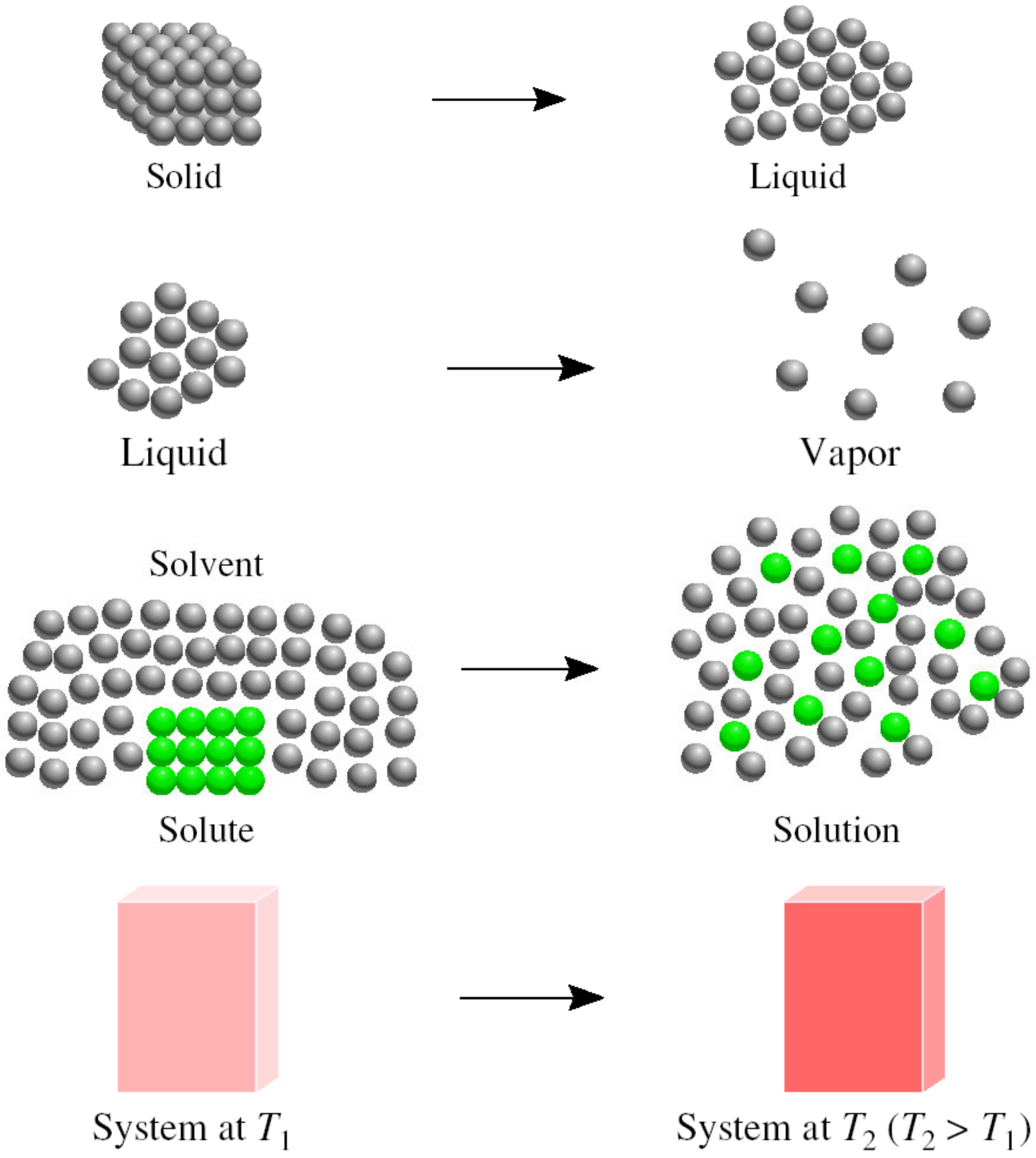
$$\Delta S = k \ln \frac{W_f}{W_i}$$

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

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

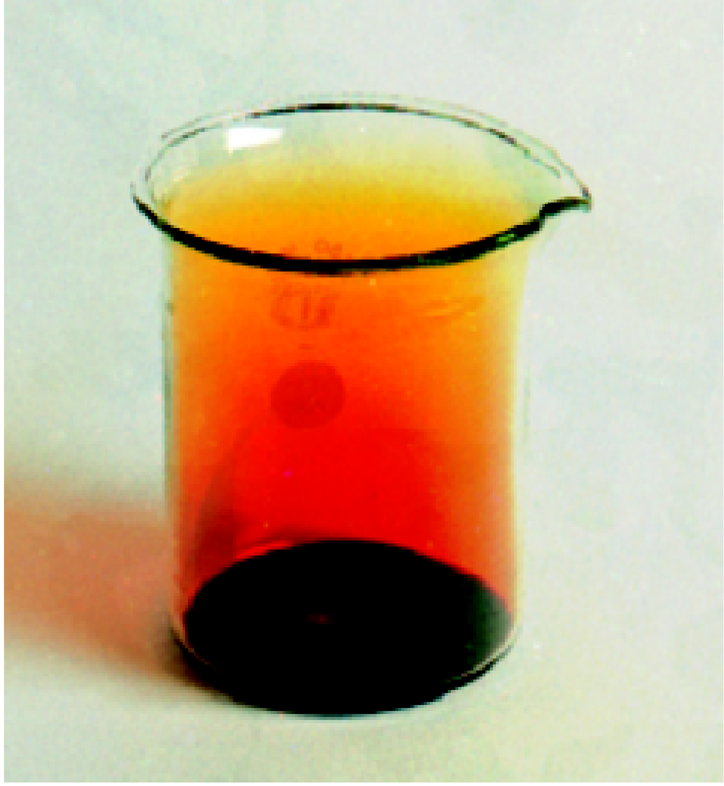


Processes that lead to an increase in entropy ($\Delta S > 0$)



Example: $Br_2(l) \longrightarrow Br_2(g)$

Example: $I_2(s) \longrightarrow I_2(g)$



$\Delta S > 0$

$\Delta S > 0$

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 60^0C to 80^0C

Randomness increases Entropy increases ($\Delta S > 0$)

(d) Subliming dry ice

Randomness increases Entropy increases ($\Delta S > 0$)

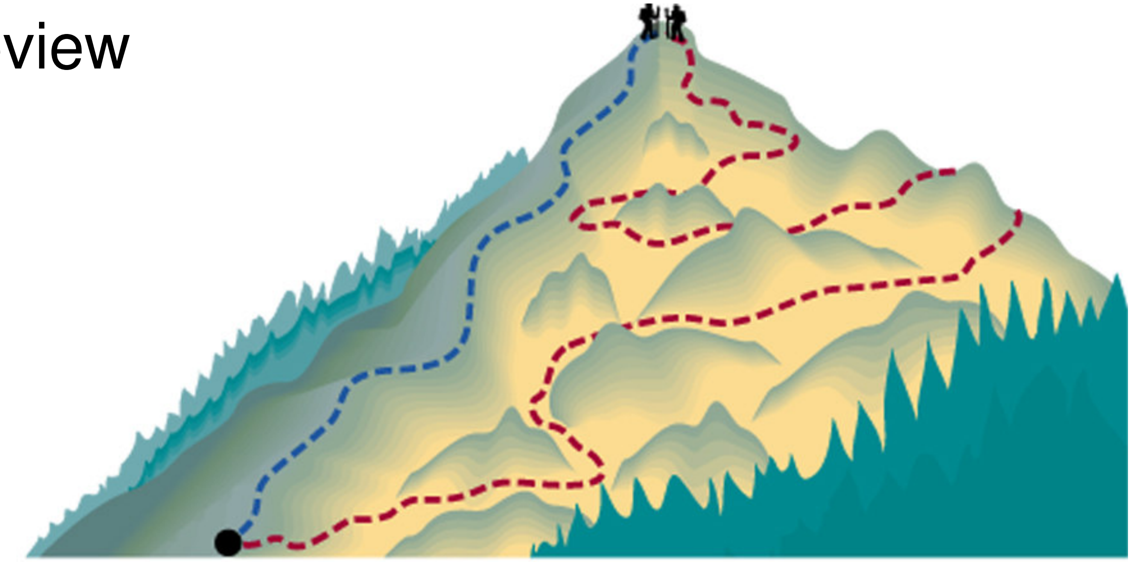
Entropy

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.

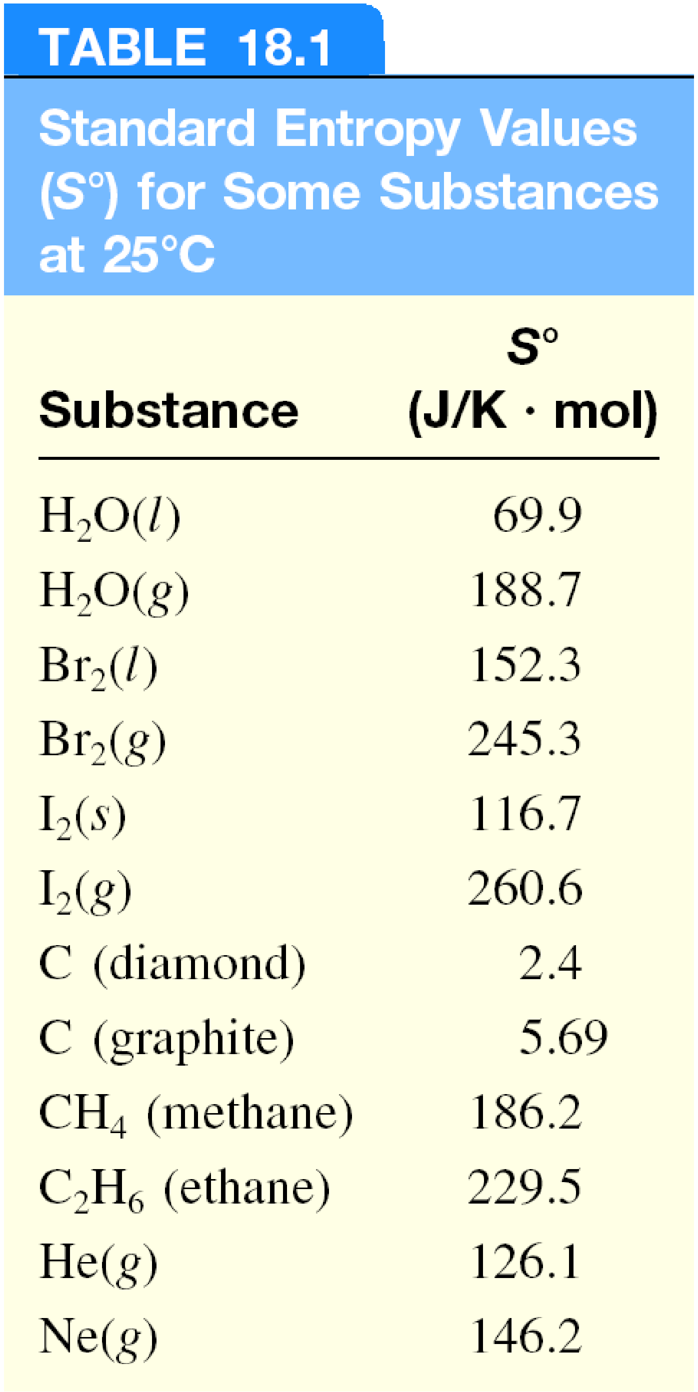


TABLE 18.1

Standard Entropy Values ($S°$) for Some Substances at 25°C

Substance	$S°$ (J/K · mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
$He(g)$	126.1
$Ne(g)$	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: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

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

Entropy Changes in the System (ΔS_{sys})

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

$$aA + bB \longrightarrow cC + dD$$

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

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

What is the standard entropy change for the following reaction at 25^{0}C? $2CO\ (g) + O_2\ (g) \longrightarrow 2CO_2\ (g)$

$S^0(CO) = 197.9$ J/K•mol $S^0(CO_2) = 213.6$ J/K•mol
$S^0(O_2) = 205.0$ J/K•mol

$$\Delta S^0_{rxn} = 2 \times S^0(CO_2) - [2 \times S^0(CO) + S^0\ (O_2)]$$

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

Entropy Changes in the System (ΔS_{sys})

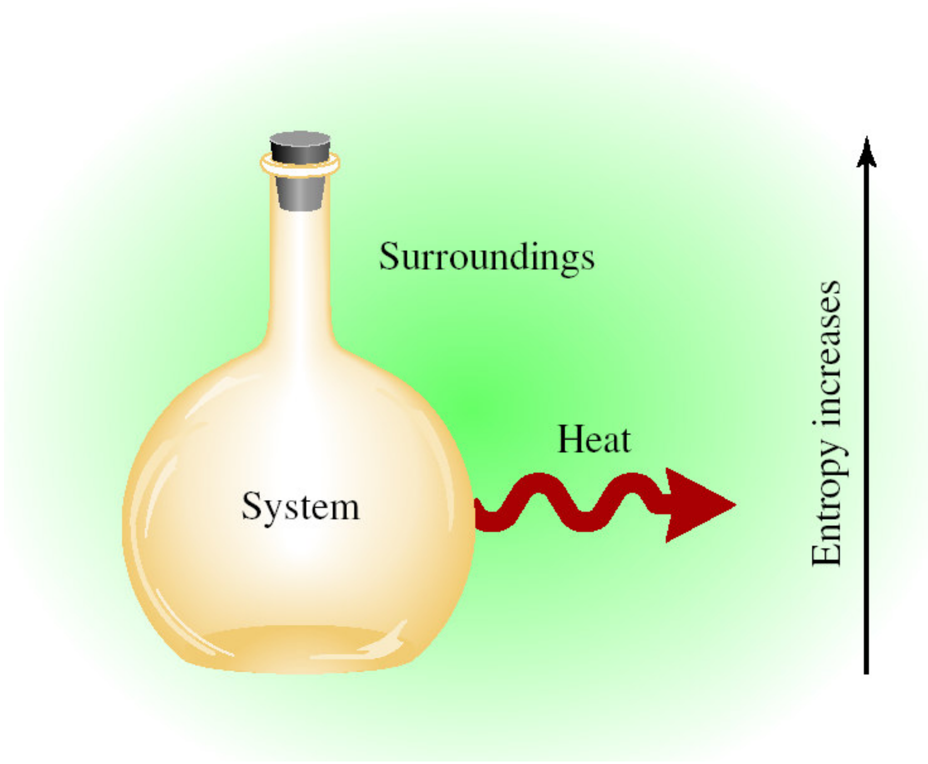
When gases are produced (or consumed)

- 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.

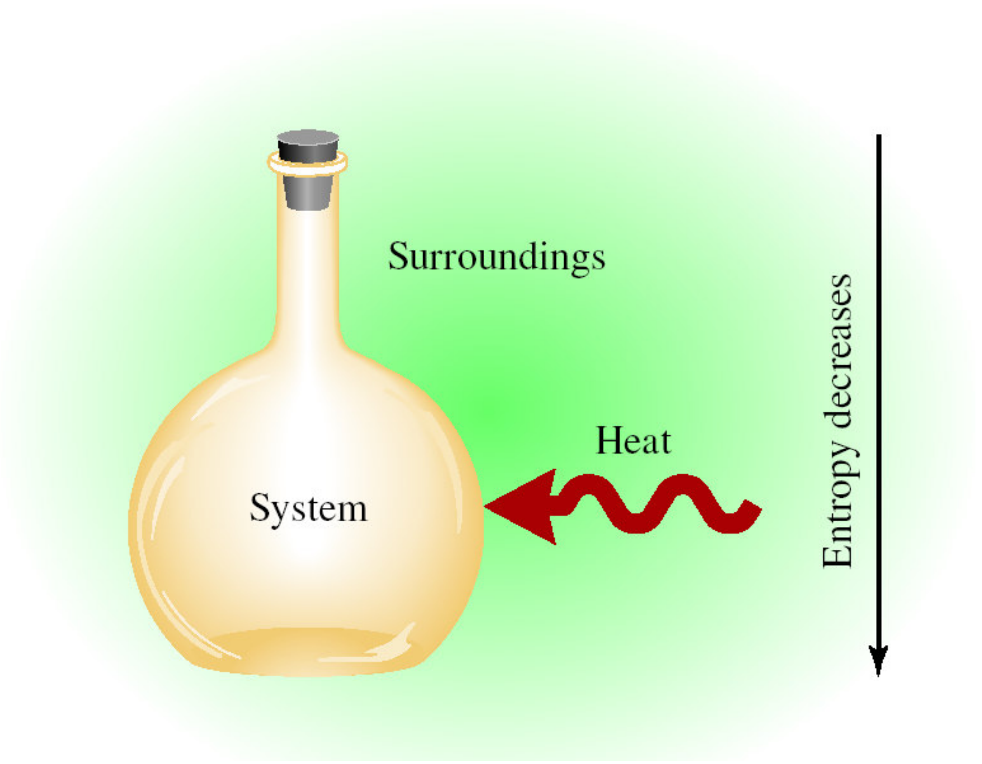
What is the sign of the entropy change for the following reaction? $2Zn\ (s) + O_2\ (g) \longrightarrow 2ZnO\ (s)$

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

Entropy Changes in the Surroundings (ΔS_{surr})



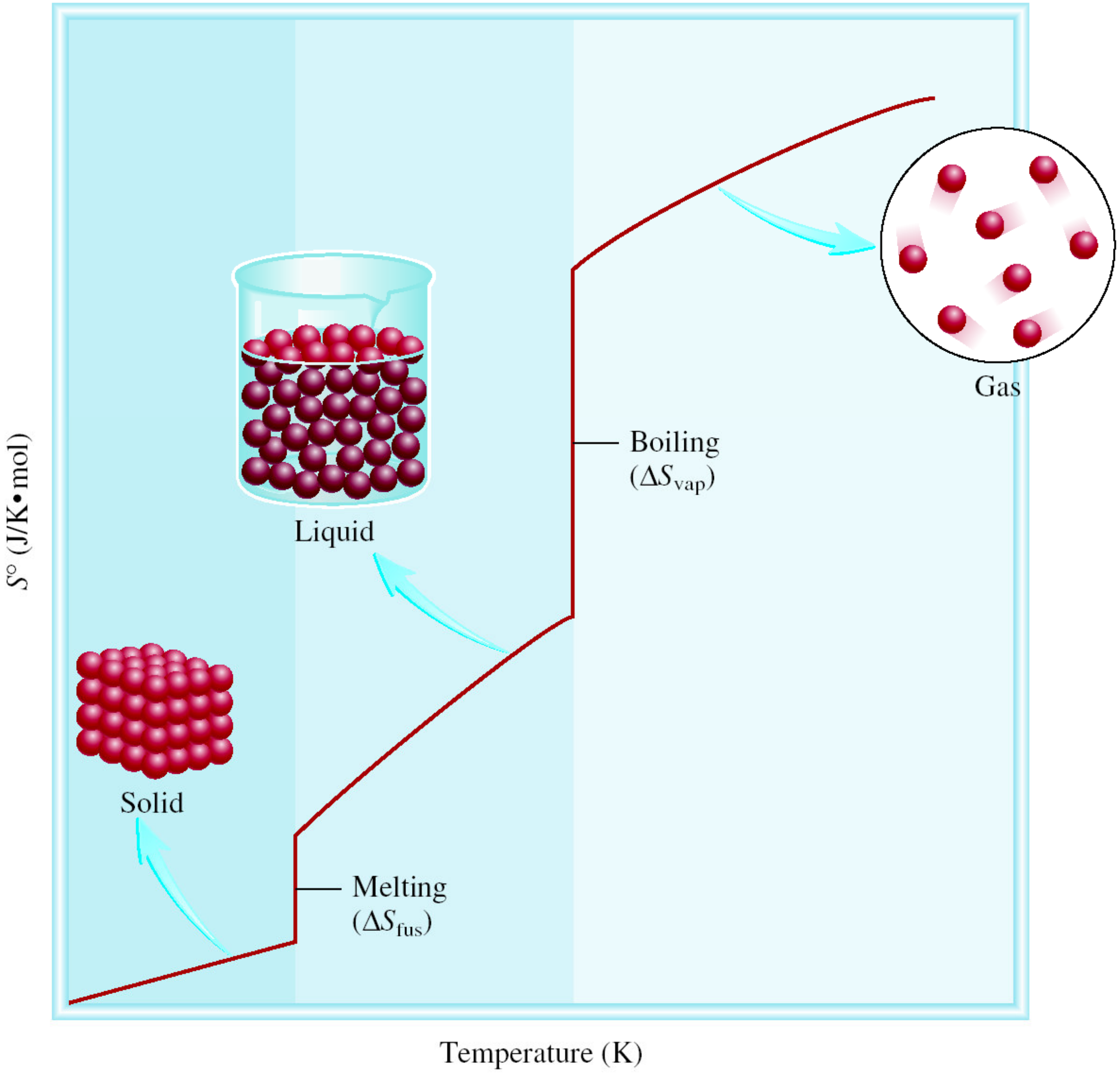
Exothermic Process
$\Delta S_{\text{surr}} > 0$



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

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

<u>For a constant temperature and constant pressure process:</u>

Gibbs free energy (G)

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

$\Delta G < 0$ 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 ($\Delta G^0_{\mathrm{rxn}}$)*** is the free-energy change for a reaction when it occurs under standard-state conditions.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^0_{\mathrm{rxn}} = [c\Delta G^0_f(C) + d\Delta G^0_f(D)] - [a\Delta G^0_f(A) + b\Delta G^0_f(B)]$$

$$\Delta G^0_{\mathrm{rxn}} = \Sigma n\Delta G^0_f(\text{products}) - \Sigma m\Delta G^0_f(\text{reactants})$$

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

ΔG^0_f of any element in its stable form is zero.

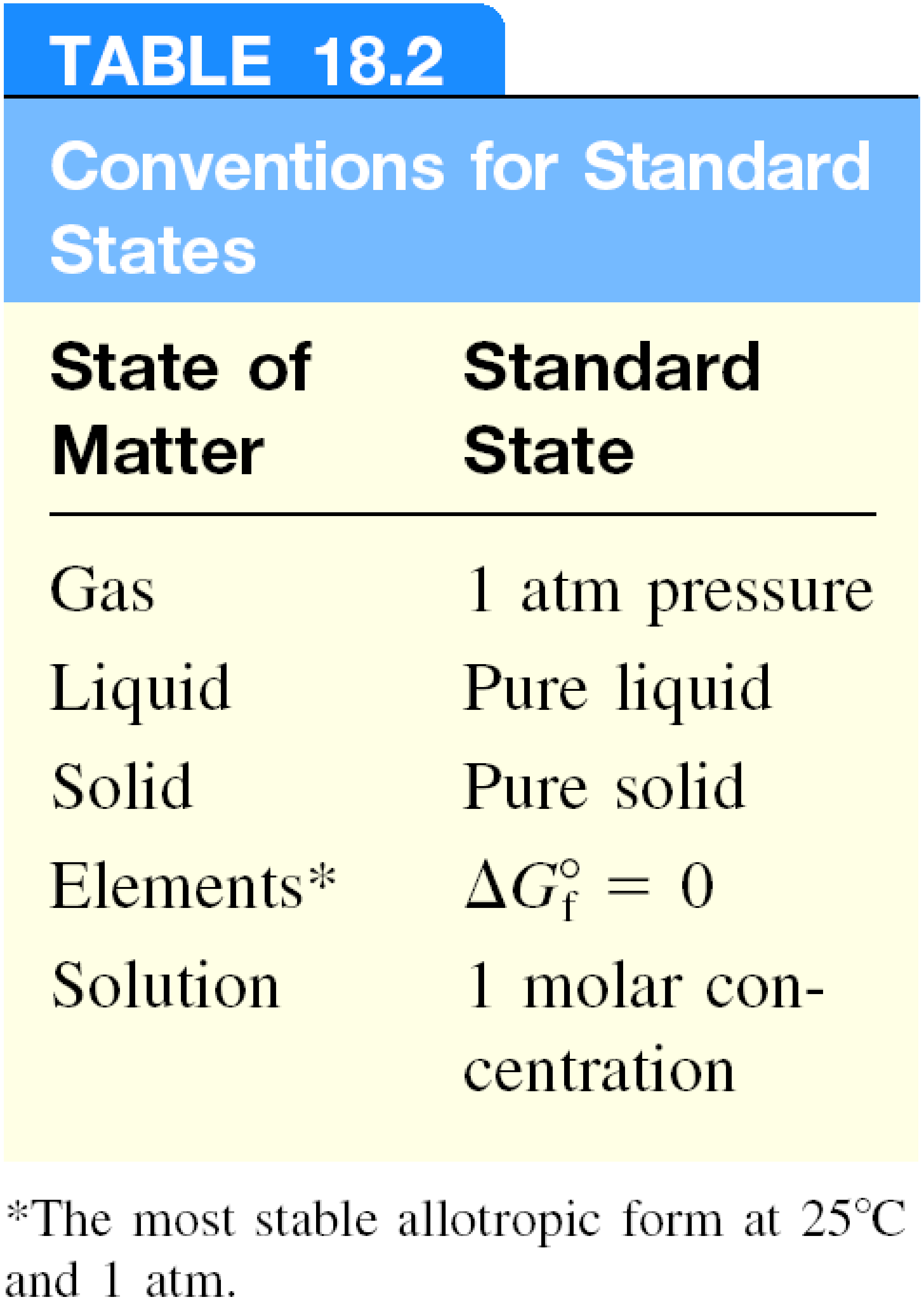


TABLE 18.2

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 ^{0}C?

$$2C_6H_6\,(l) + 15O_2\,(g) \longrightarrow 12CO_2\,(g) + 6H_2O\,(l)$$

$$\Delta G^0_{rxn} = \Sigma n\Delta G^0_f\,(\text{products}) - \Sigma m\Delta G^0_f\,(\text{reactants})$$

$$\Delta G^0_{rxn} = [12\Delta G^0_f\,(CO_2) + 6\Delta G^0_f\,(H_2O)] - [2\Delta G^0_f\,(C_6H_6)]$$

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

Is the reaction spontaneous at 25 ^{0}C?

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

spontaneous

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

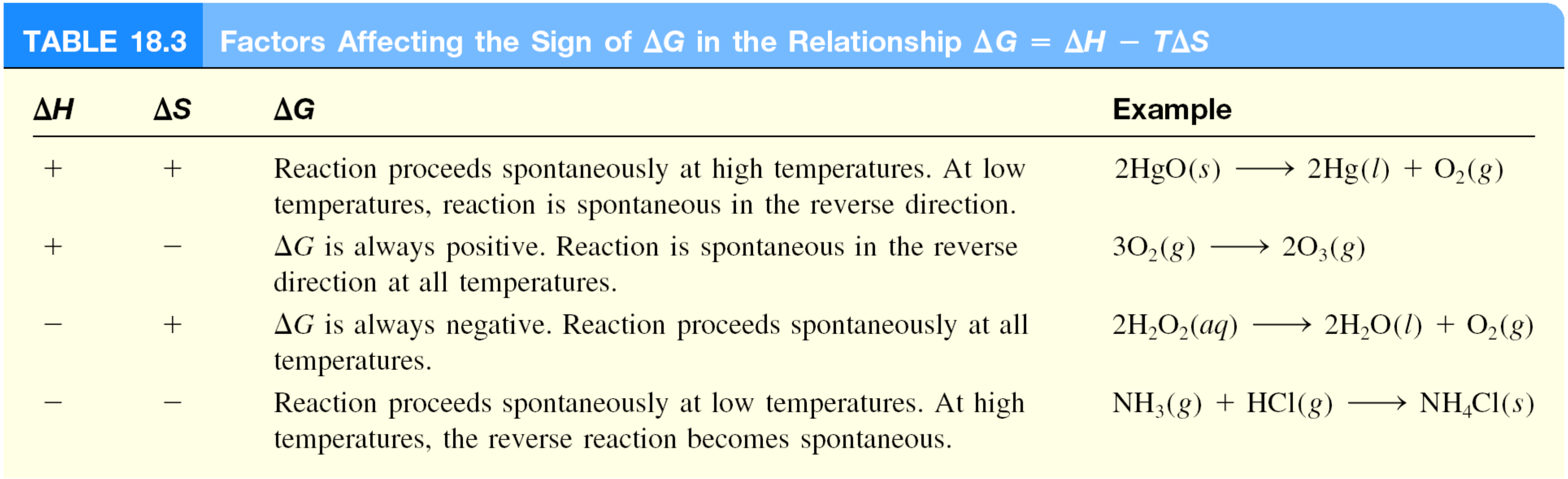


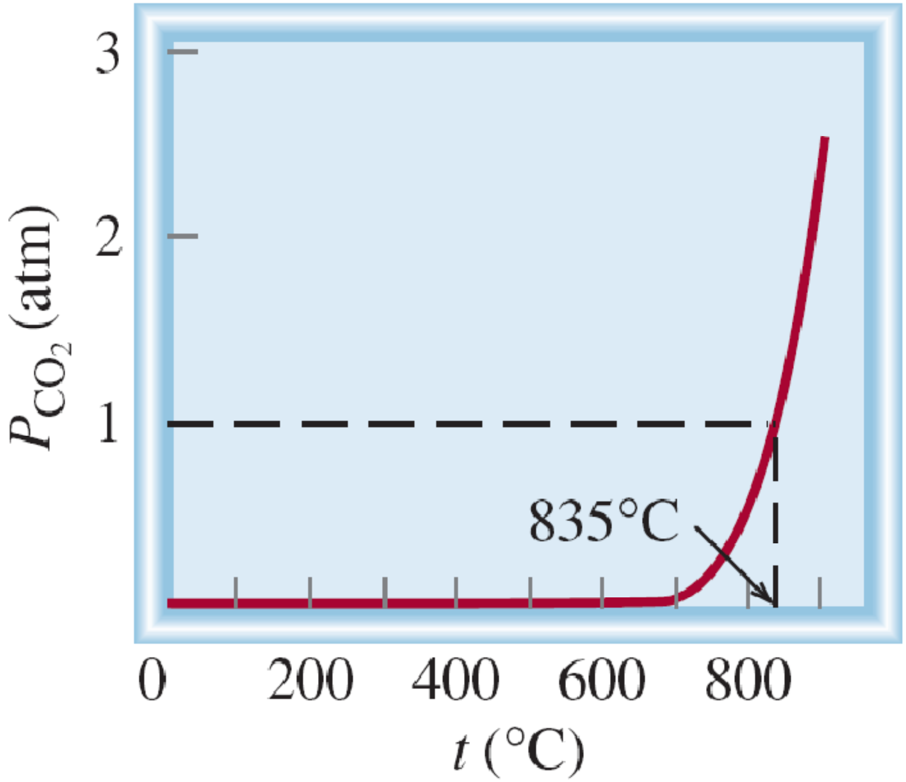
TABLE 18.3 **Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$**

ΔH	ΔS	ΔG	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Temperature and Spontaneity of Chemical Reactions

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Equilibrium Pressure of CO_2



$\Delta H^0 = 177.8$ kJ/mol

$\Delta S^0 = 160.5$ J/K·mol

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

At 25 °C, $\Delta G^0 = 130.0$ kJ/mol

$\Delta G^0 = 0$ at 835 °C

Gibbs Free Energy and Phase Transitions

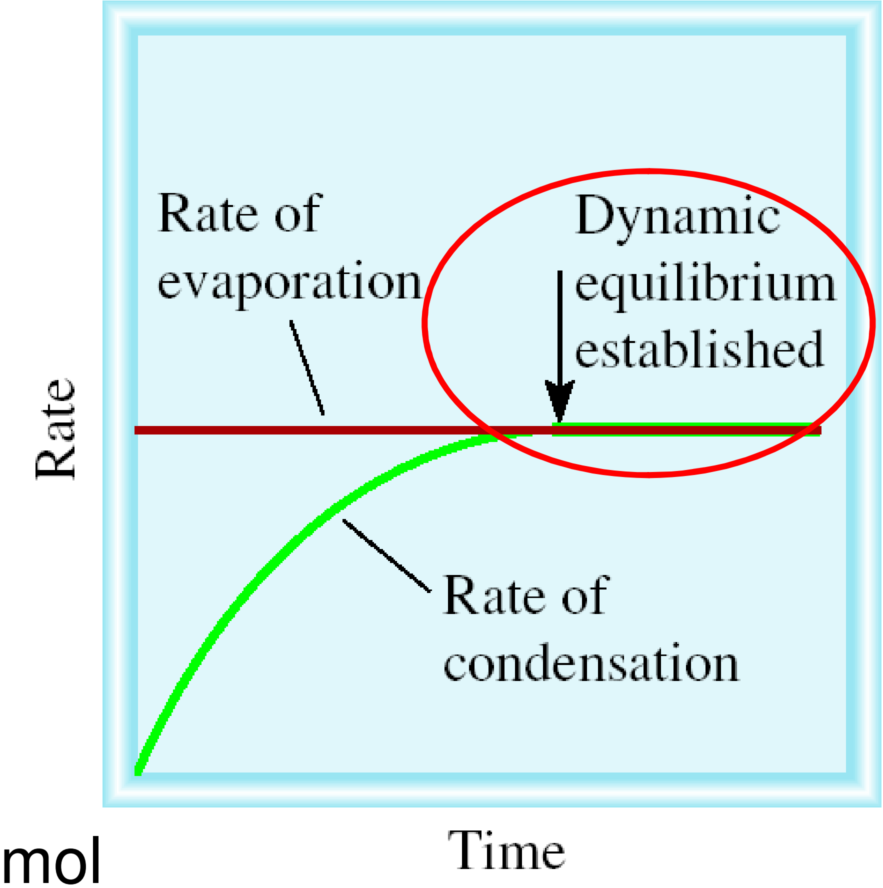
$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$

$H_2O\ (l) \rightleftarrows H_2O\ (g)$

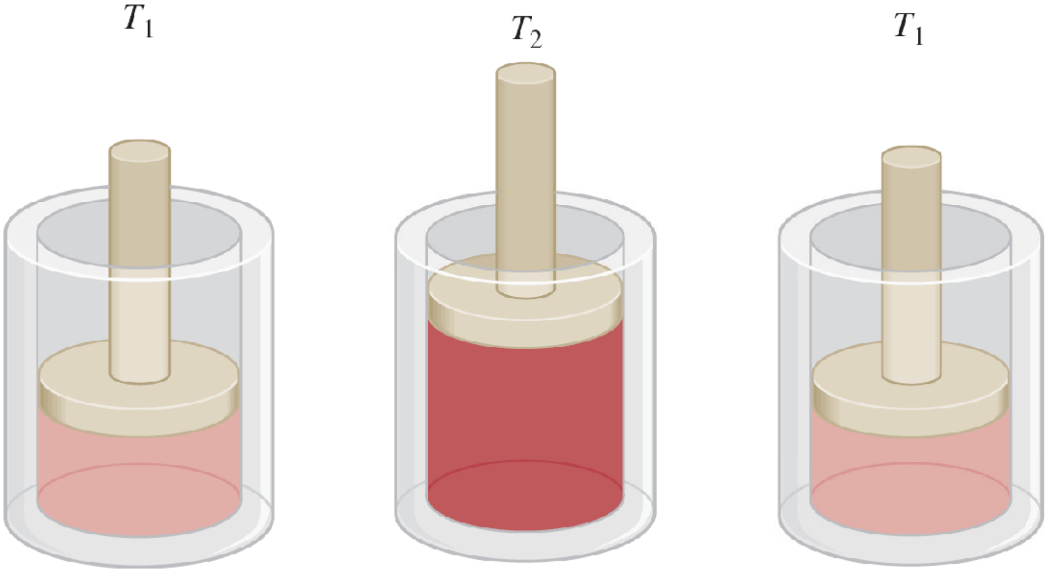
$$\Delta S = \frac{\Delta H}{T} = \frac{40.79 \text{ kJ/mol}}{373 \text{ K}}$$

$= 1.09 \times 10^{-1}$ kJ/K·mol

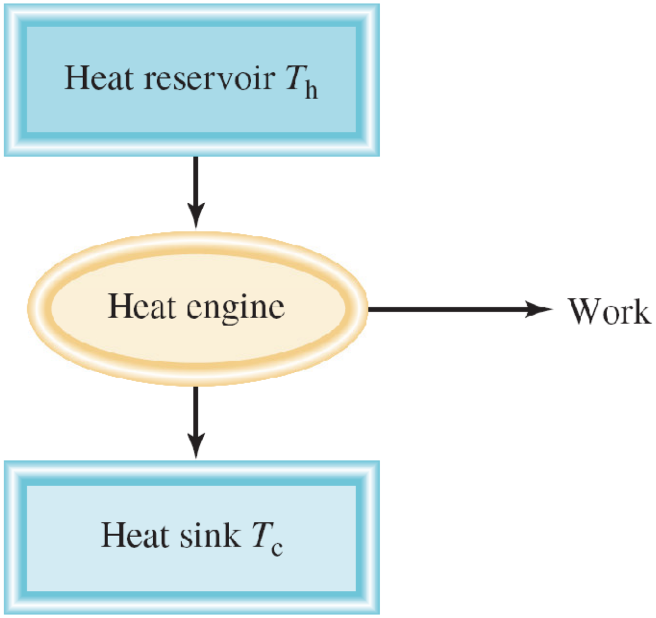
$= 109$ J/K·mol



Chemistry In Action: The Efficiency of Heat Engines



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



Heat reservoir T_h

Heat engine

Work

Heat sink T_c

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

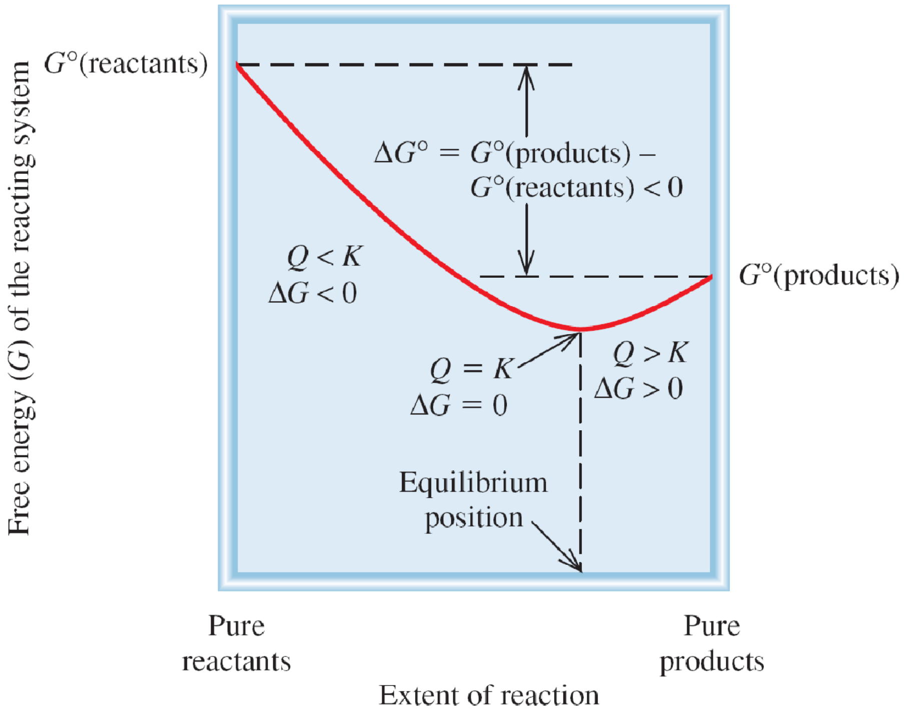
At Equilibrium

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

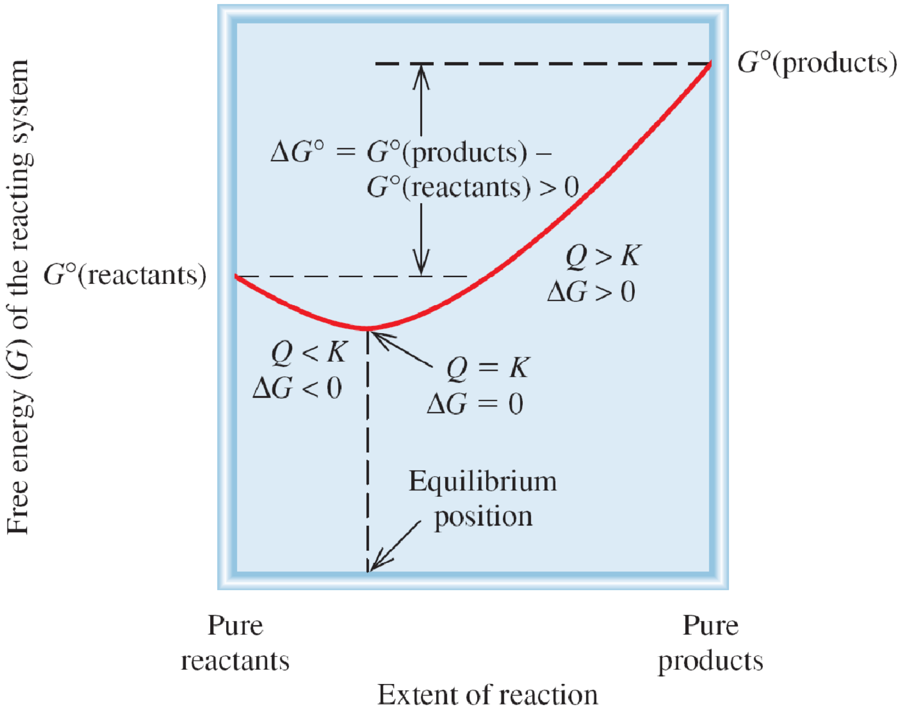
$$0 = \Delta G^0 + RT \ln K$$

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

Free Energy Versus Extent of Reaction



$\Delta G^0 < 0$



$\Delta G^0 > 0$

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

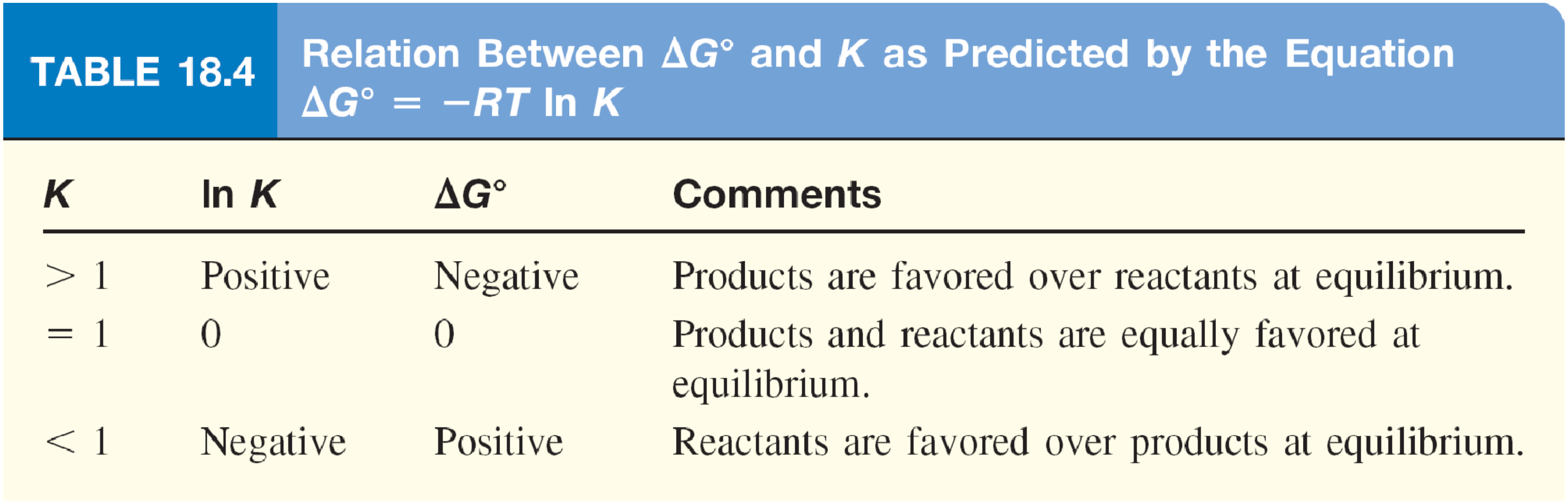
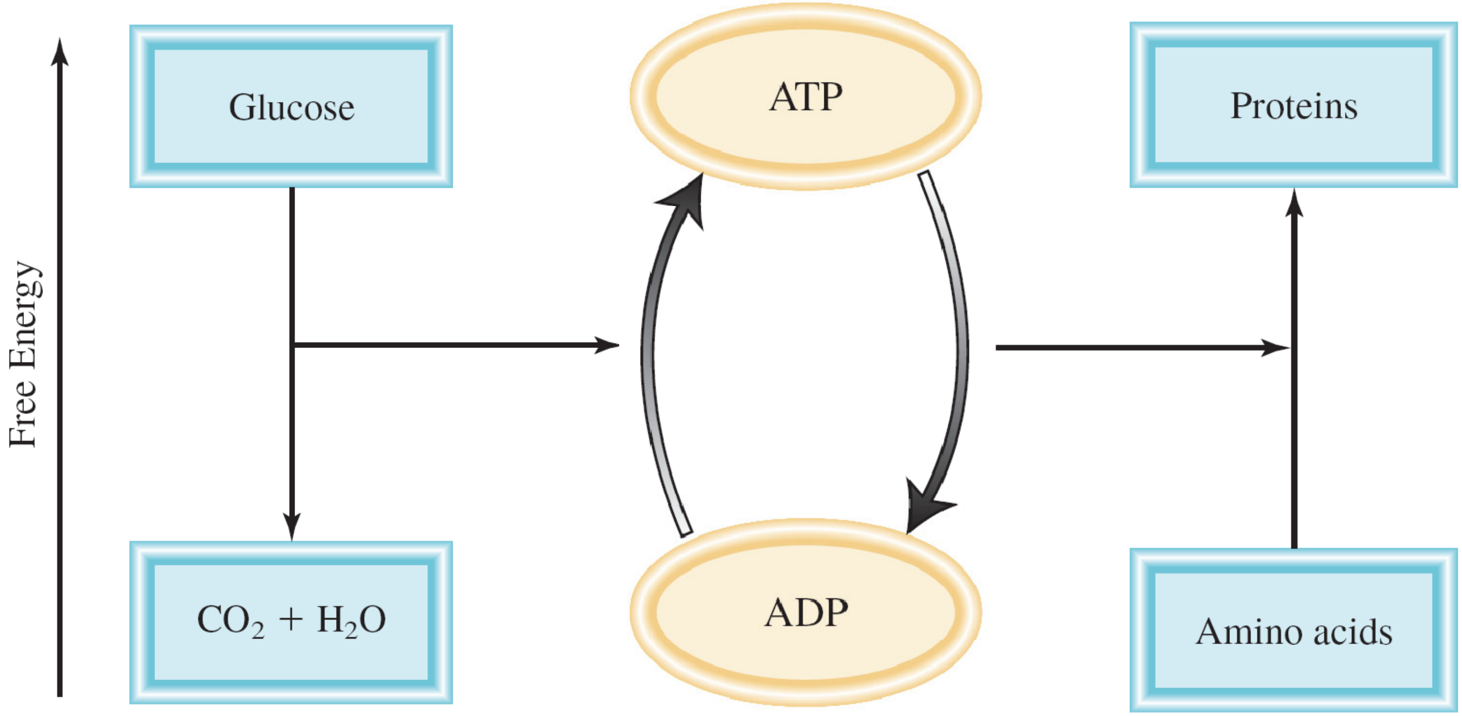


TABLE 18.4 Relation Between ΔG° and K as Predicted by the Equation $\Delta G^\circ = -RT \ln K$

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



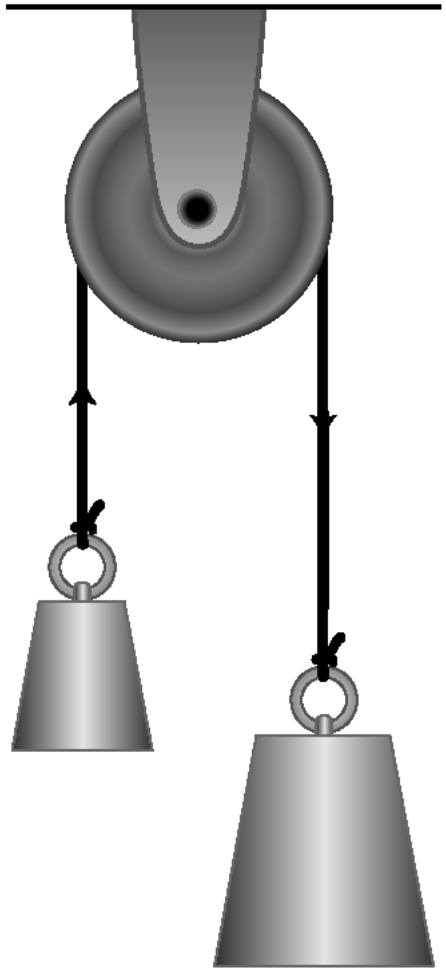
Example: Alanine + Glycine ⟶ Alanylglycine

$\Delta G^0 = +29$ kJ $K < 1$

$$ATP + H_2O + Alanine + Glycine \longrightarrow ADP + H_3PO_4 + Alanylglycine$$

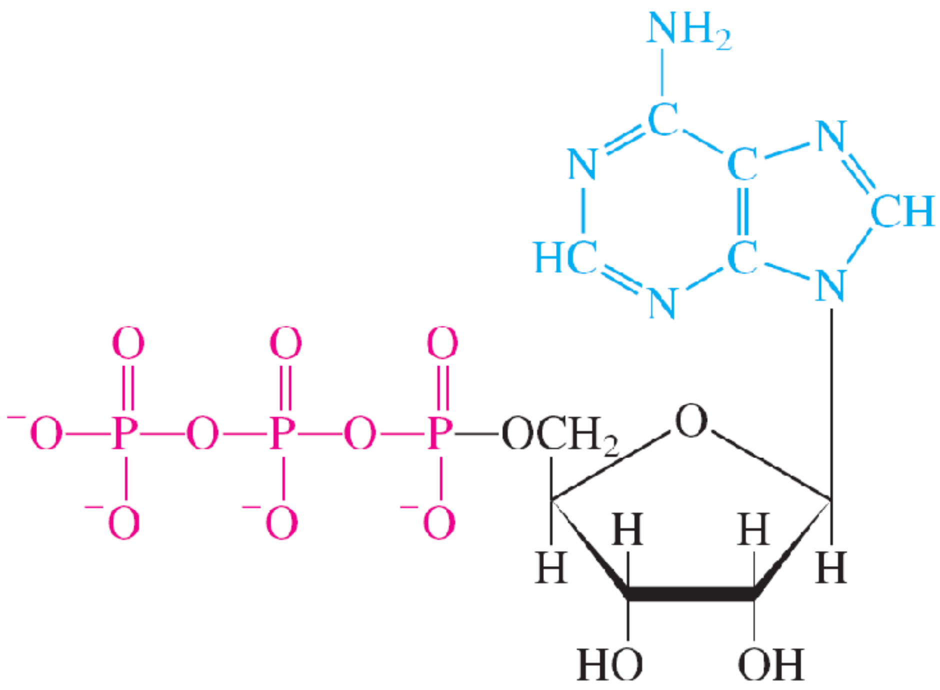
$\Delta G^0 = -2$ kJ $K > 1$

Mechanical Analog of Couple Reactions

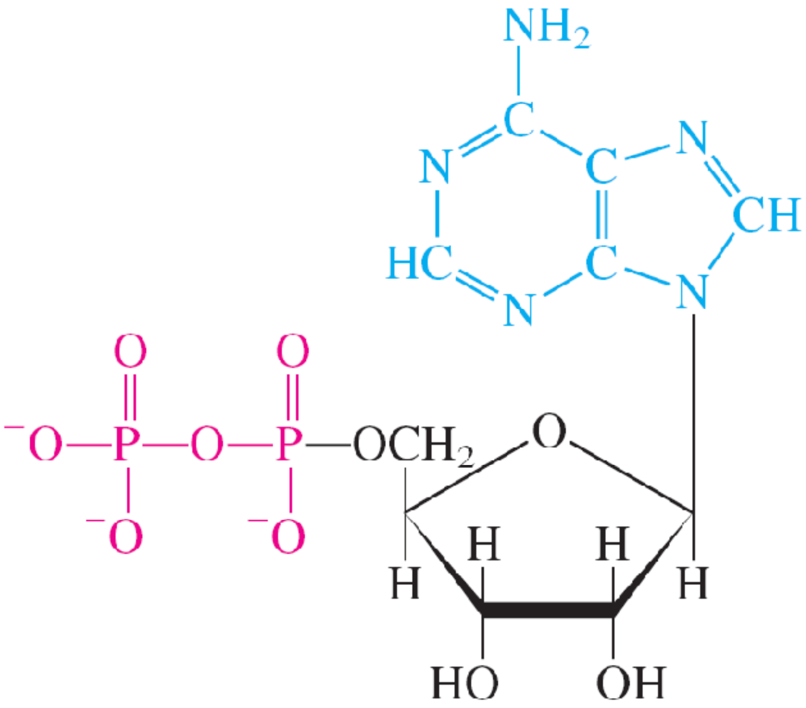


Make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

The Structure of ATP and ADP in Ionized Forms



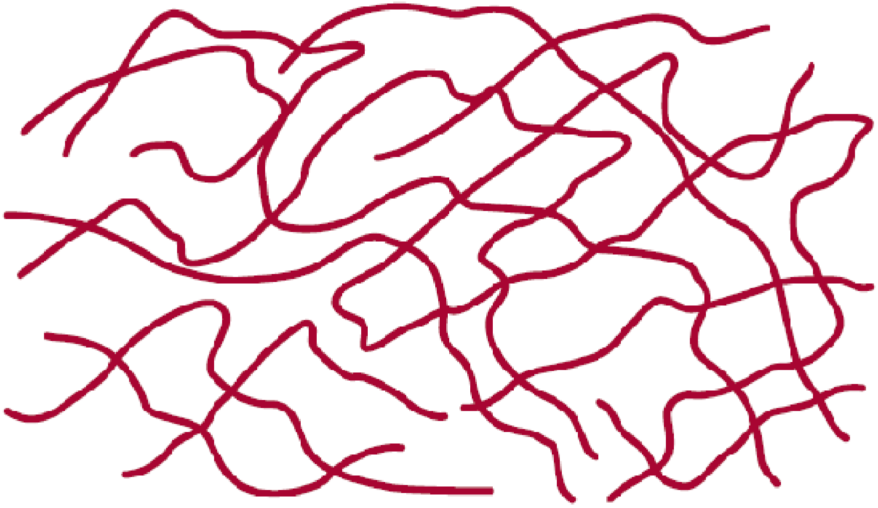
Adenosine triphosphate
(ATP)



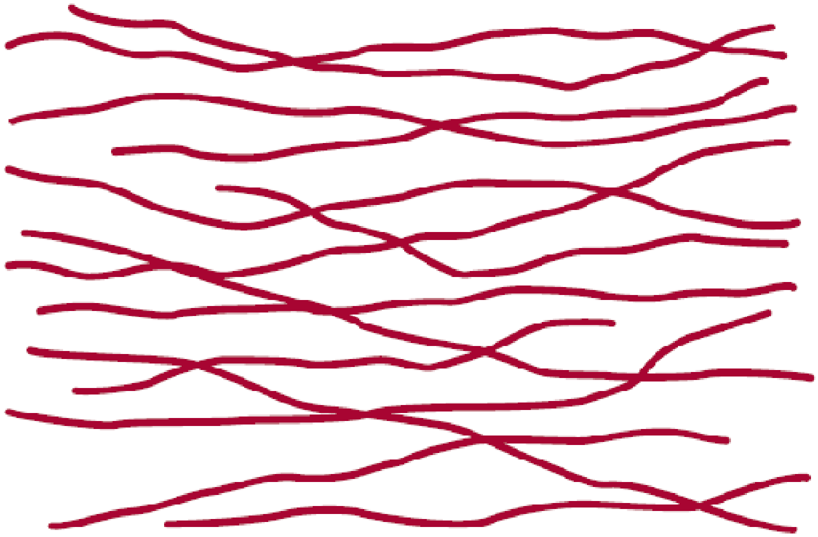
Adenosine diphosphate
(ADP)

Chemistry In Action: The Thermodynamics of a Rubber Band

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



High Entropy



Low Entropy