Chapter 16

Spontaneity, Entropy, and Free Energy

Chapter 16 Preview

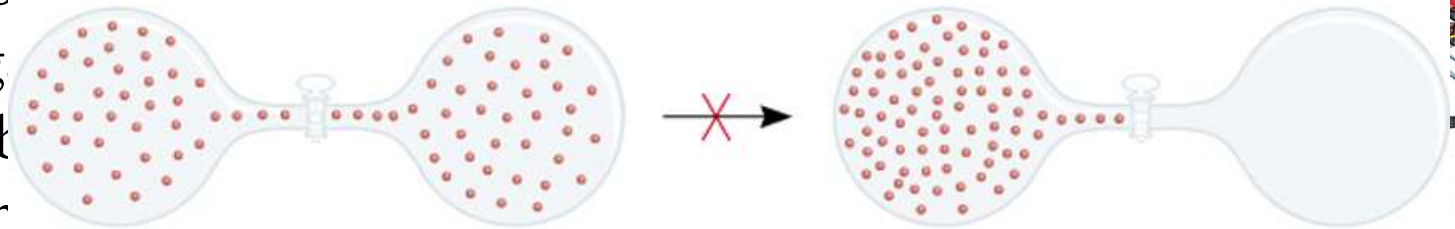
Spontaneity, Entropy, and Free Energy

- Spontaneous Processes and Entropy
  - Second law of Thermodynamic, Entropy, Effect of temperature on spontaneity, Entropy change in Chemical reacdtion
- Free Energy and Chemical Reaction
  - Dependence of Free energy on pressure
- Free Energy and Equilibrium
  - The temperature dependence
- Free Energy and Work

16.1 Spontaneous Processes and Entropy

- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1
  abc
- Hea
  a cc
- A g
  bull
- Iror
  forr

spontaneous



nonspontaneous

Does a decrease in enthalpy mean a reaction proceeds spontaneously?

Spontaneous reactions

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

$H^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) \quad \Delta H^0 = -56.2\ kJ$

$H_2O\ (s) \longrightarrow H_2O\ (l) \quad \Delta H^0 = 6.01\ kJ$

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

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

spontaneous

Entropy

W = number of microstates

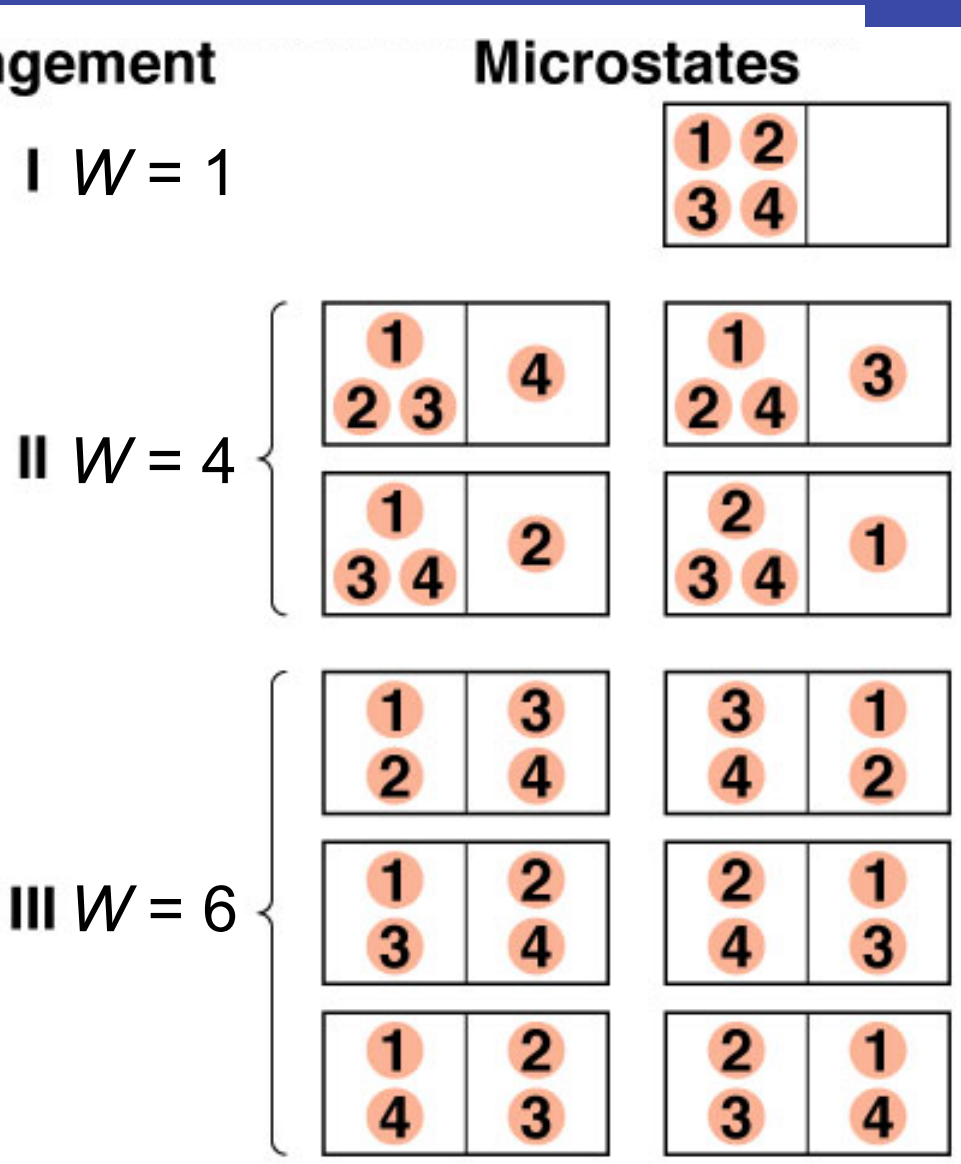
$$S = k \ln W$$

$$\Delta S = S_f - S_i$$

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

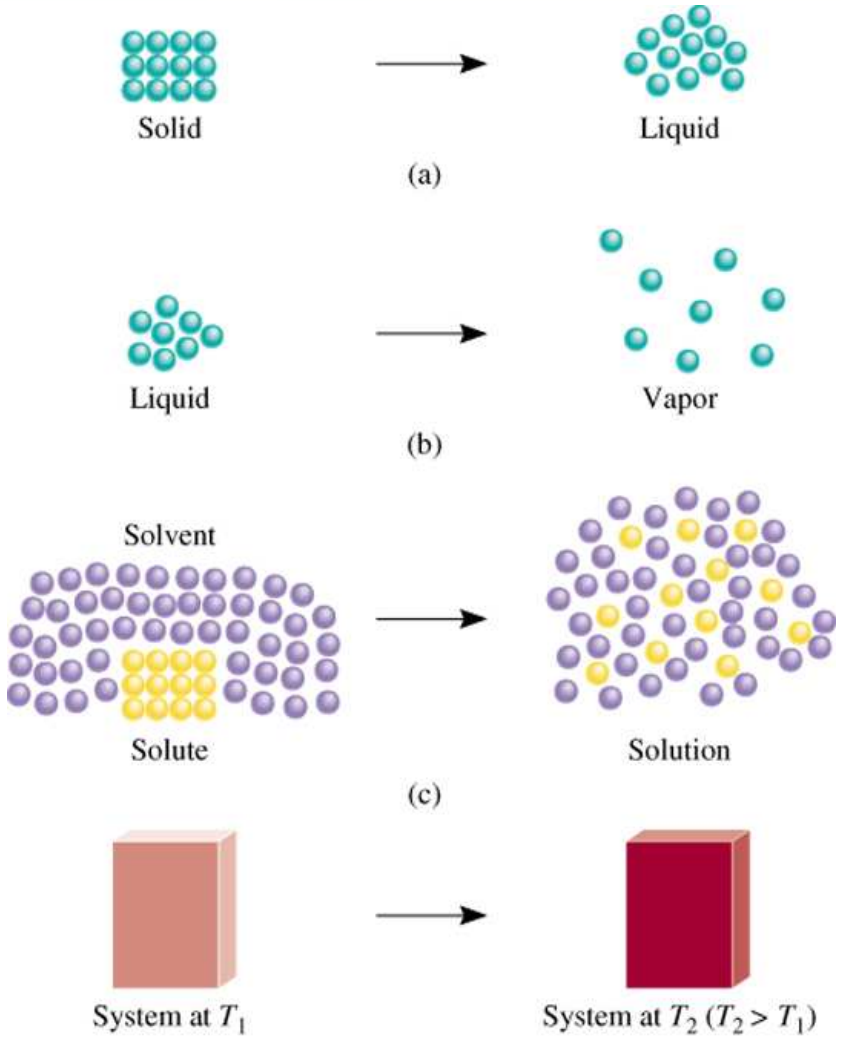
$W_f > W_i$ then $\Delta S > 0$

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



Entropy

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



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

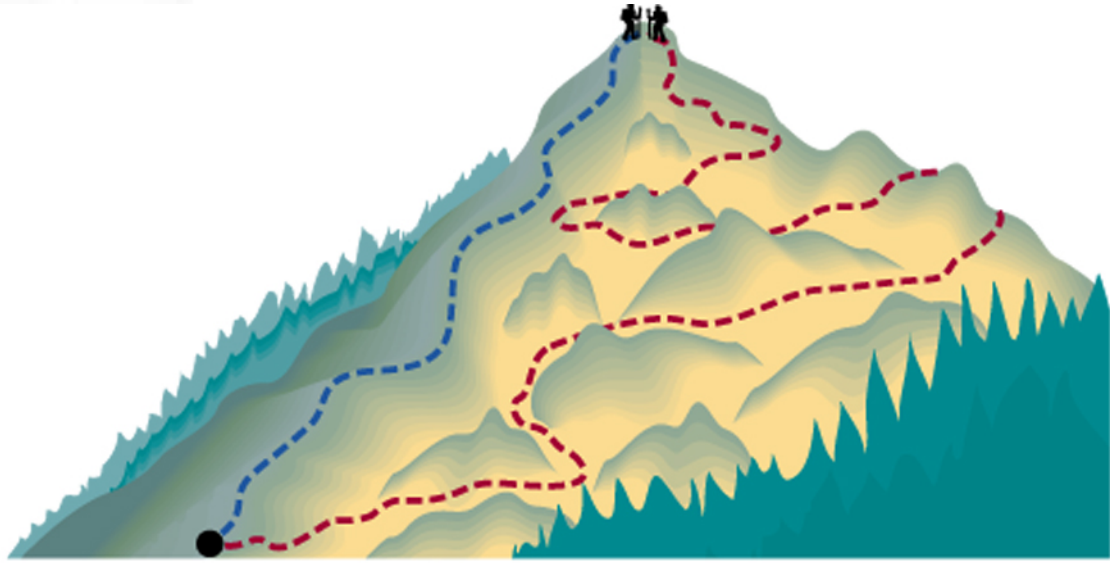
Randomness increases Entropy increases ($\Delta S > 0$)

(d) Subliming dry ice

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

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

energy, enthalpy, pressure, volume, temperature, entropy



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

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

TABLE 18.1

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

16.2 Entropy

First Law of Thermodynamics

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

Second Law of Thermodynamics

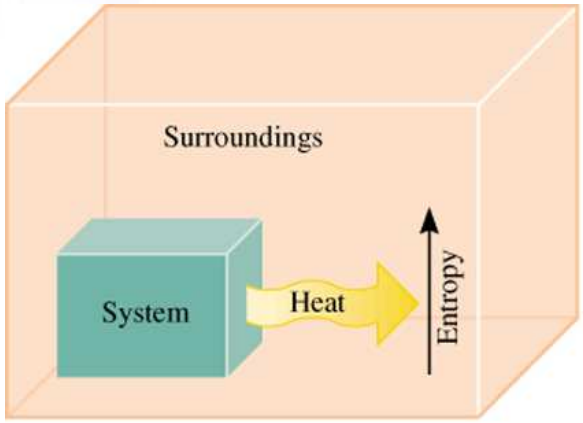
In any spontaneous process there is alaways an increase in the entropy of the **universe** and remains unchanged in an equilibrium process.

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

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

16.3 The Effect of Temperature on Spontaneity

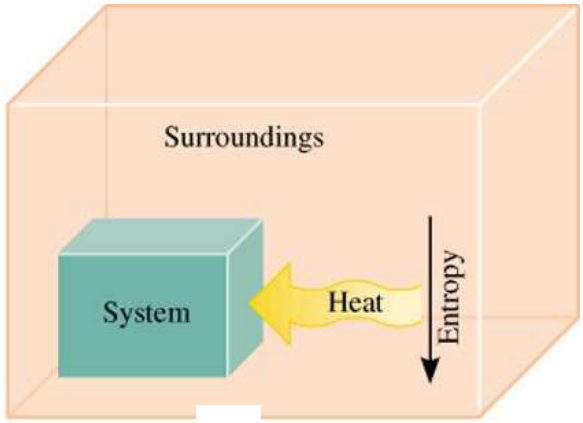
Entropy Changes in the Surroundings (ΔS_{surr})



(a)

Exothermic Process

$\Delta S_{surr} > 0$



(b)

Endothermic Process

$\Delta S_{surr} < 0$

$$\Delta S_{surr} = \pm \frac{Heat\ quantity}{temperature}$$

Heat = enthalpy

Endo: +

Exo: -

Enthalpy of System

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

1. The sign of ΔS_{surr} depends on the direction of heat flow.
2. The magnitude of ΔS_{surr} depends on the temperature

16.4 Gibbs Free Energy

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

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

For a constant-temperature process:

Gibbs free energy (G) $\Delta G = \Delta H_{sys} - T\Delta S_{sys}$

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.	$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

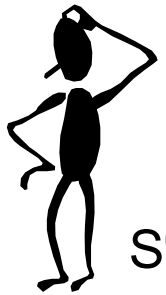
16.5 Entropy Changes in Chemical Reaction (ΔS_{sys})

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

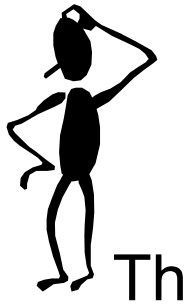
$$\Delta S^0_{rxn} = 2 \times S^0(CO_2) - [2 \times S^0(CO) + S^0(O_2)]$$

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

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.

Exercise

Predict whether the entropy change of the system in each of the following reactions is positive or negative.

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

(b) $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$

(c) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Solution (a) Two reactant molecules combine to form one product molecule. Even though H_2O is a more complex molecule than either H_2 and O_2, the fact that there is a net decrease of one molecule and gases are converted to liquid ensures that the number of microstates will be diminished and hence ΔS° is negative.

(b) A solid is converted to two gaseous products. Therefore, ΔS° is positive.

(c) The same number of molecules is involved in the reactants as in the product. Furthermore, all molecules are diatomic and therefore of similar complexity. As a result, we cannot predict the sign of ΔS°, but we know that the change must be quite small in magnitude.

16.6 Free Energy in Chemical Reaction (ΔG_{sys})

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

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

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

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

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.

Conventions for Standard States

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

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

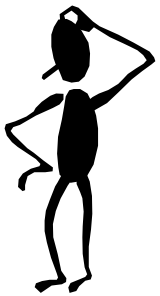
What is the standard free-energy change for the following reaction at 25 ^{0}C?

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

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

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

$$\Delta G^0_{rxn} = [12x{-}394.4 + 6x{-}237.2] - [2x124.5] = -6405\ \text{kJ}$$



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

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

spontaneous

16.7 Dependence of ΔG_{rxn} on Pressure

Temperature and Spontaneity of Chemical Reactions

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

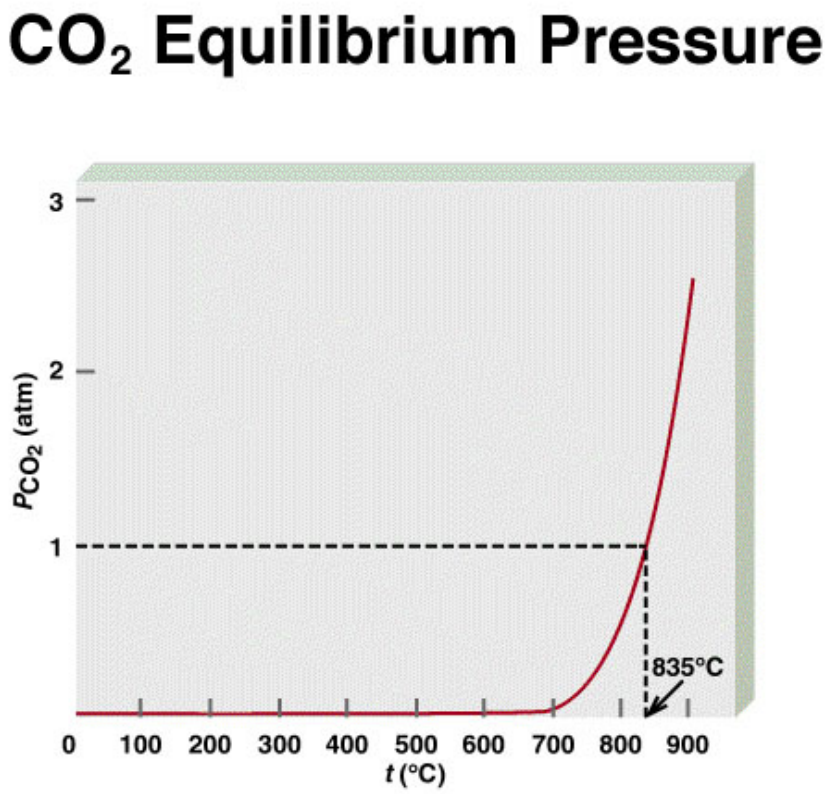
$\Delta H^0 = 177.8$ kJ

$\Delta S^0 = 160.5$ J/K

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

At 25 ^{0}C, $\Delta G^0 = 130.0$ kJ

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



Special Cases of (ΔG_{rxn})

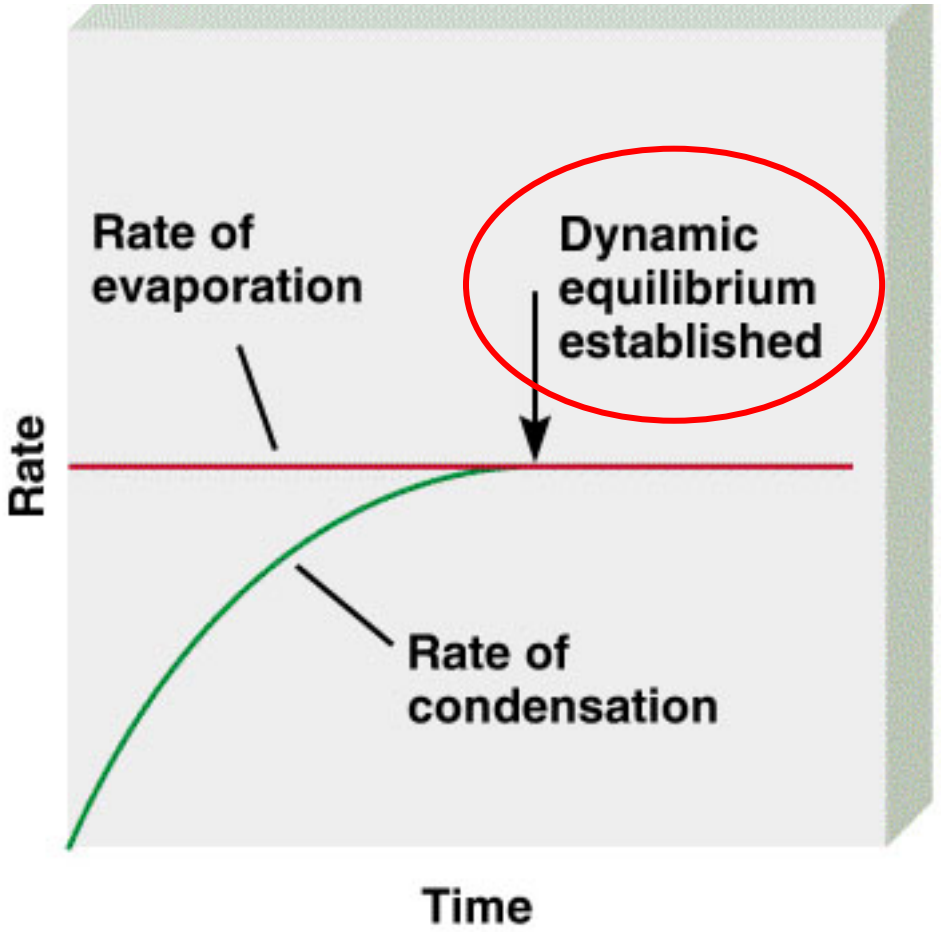
Gibbs Free Energy and Phase Transitions

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

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

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

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



Exercise

The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid → liquid and liquid → vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

Solution The entropy change for melting 1 mole of benzene at 5.5°C is

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{\Delta T_f} = \frac{(10.9\ \text{kJ/mol})(1000\ \text{J/1 kJ})}{(5.5 + 273)\ \text{K}} = 39.1\ \text{J/K} \cdot \text{mol}$$

Similarly, the entropy change for boiling 1 mole of benzene at 80.1°C is

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{bp}} = \frac{(31.0\ \text{kJ/mol})(1000\ \text{J/1 kJ})}{(80.1 + 273)\ \text{K}} = 87.8\ \text{J/K} \cdot \text{mol}$$

Check Because vaporization creates more microstates than the melting process, $\Delta S_{vap} > \Delta S_{fus}$.

16.8 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

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

K	ln *K*	$\Delta G°$	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.

Exercise

the solubility product of silver chloride at 25°C (1.6×10^{-10}), calculate $\Delta G°$ for the process

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

Solution The solubility equilibrium for AgCl is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

Using Equation (18.14) we obtain

$$\begin{aligned}\Delta G° &= -(8.314\ \text{J/K} \cdot \text{mol})(298\ \text{K})\ \ln\ (1.6 \times 10^{-10}) \\ &= 5.6 \times 10^4\ \text{J/mol} \\ &= 56\ \text{kJ/mol}\end{aligned}$$

Check The large, positive $\Delta G°$ indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

Ex 18.8

The equilibrium constant (K_P) for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Solution Equation (18.13) can be written as

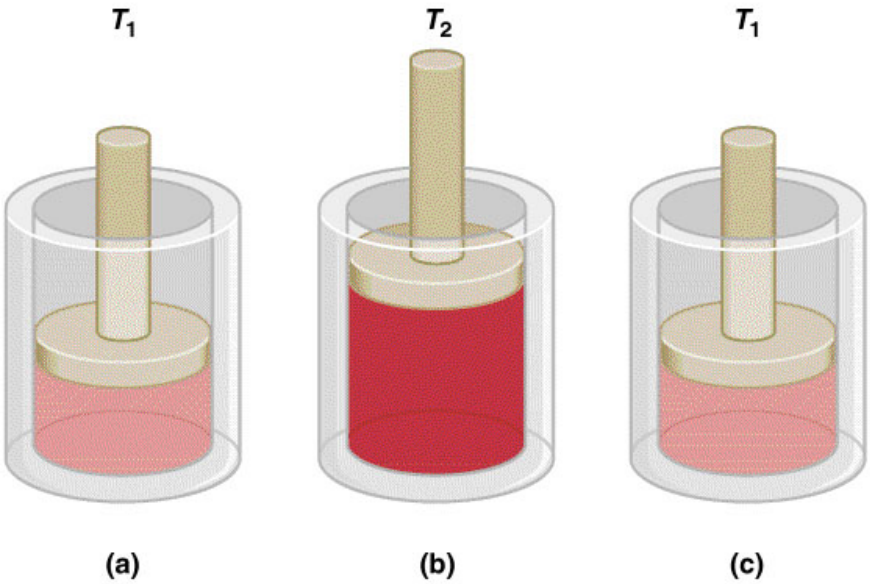
$$\begin{aligned}
\Delta G &= \Delta G^\circ + RT \ln Q_P \\
&= \Delta G^\circ + RT \ln \frac{P_{NO_2}^2}{P_{N_2O_4}} \\
&= 5.40 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\
&= 5.40 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\
&= -3.06 \times 10^3 \text{ J/mol} = -3.06 \text{ kJ/mol}
\end{aligned}$$

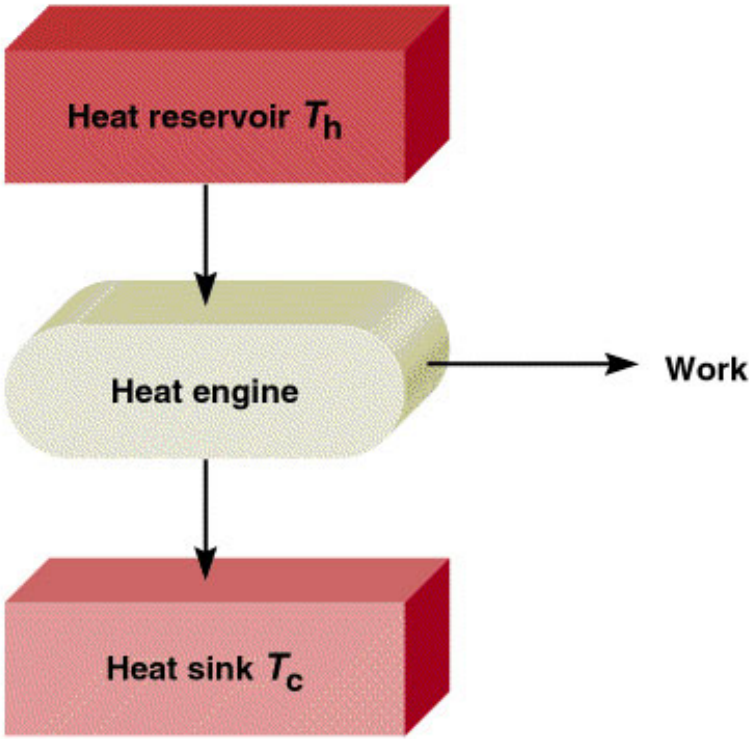
Because $\Delta G < 0$, the net reaction proceeds from left to right to reach equilibrium.

Check Note that although $\Delta G^\circ > 0$, the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm the prediction by showing that $Q_P < K_P$.

Chemistry In Action: The Efficiency of Heat Engines

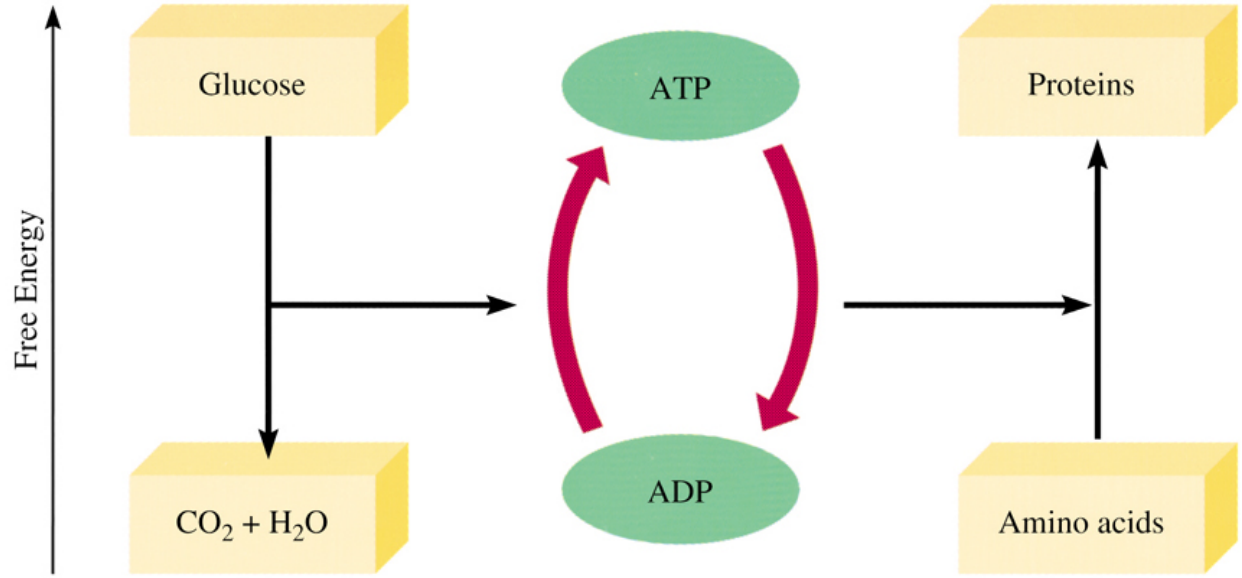
Simple Heat Engine





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

Chemistry In Action: The Efficiency of Heat Engines



$$\text{Alanine + Glycine} \longrightarrow \text{Alanylglycine}$$

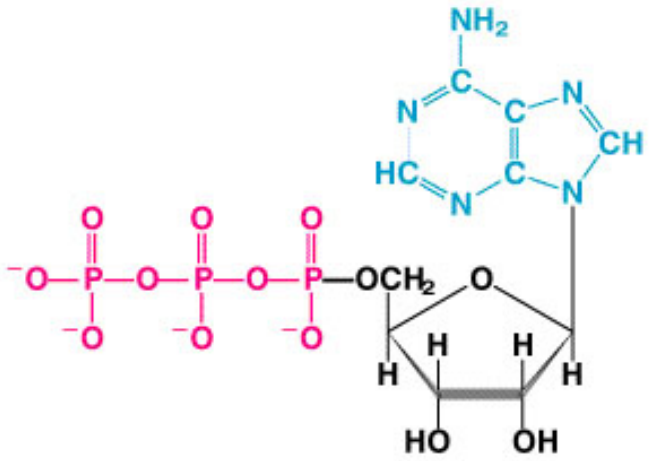
$$\Delta G^0 = +29 \text{ kJ} \qquad K < 1$$

$$\text{ATP} + H_2O + \text{Alanine + Glycine} \longrightarrow \text{ADP} + H_3PO_4 + \text{Alanylglycine}$$

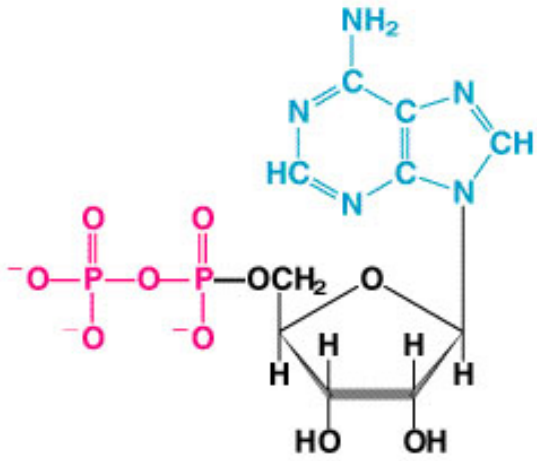
$$\Delta G^0 = -2 \text{ kJ} \qquad K > 1$$

Chemistry In Action: The Efficiency of Heat Engines

Structure of ATP and ADP in Ionized Forms



Adenosine triphosphate (ATP)



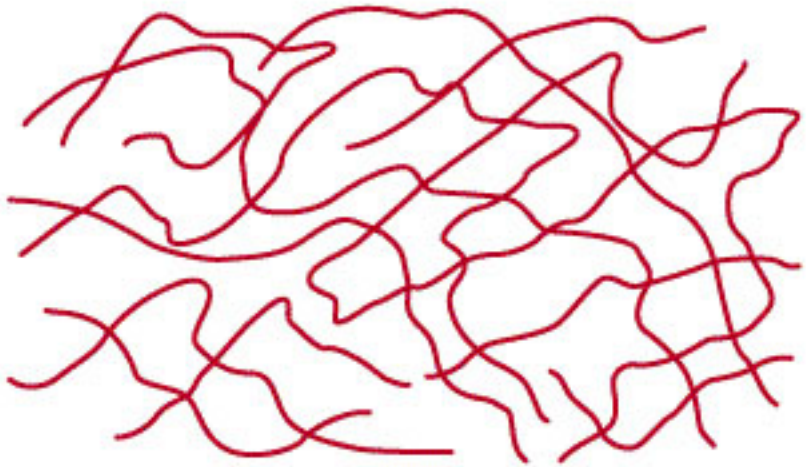
Adenosine diphosphate (ADP)

Chemistry In Action: The Efficiency of Heat Engines

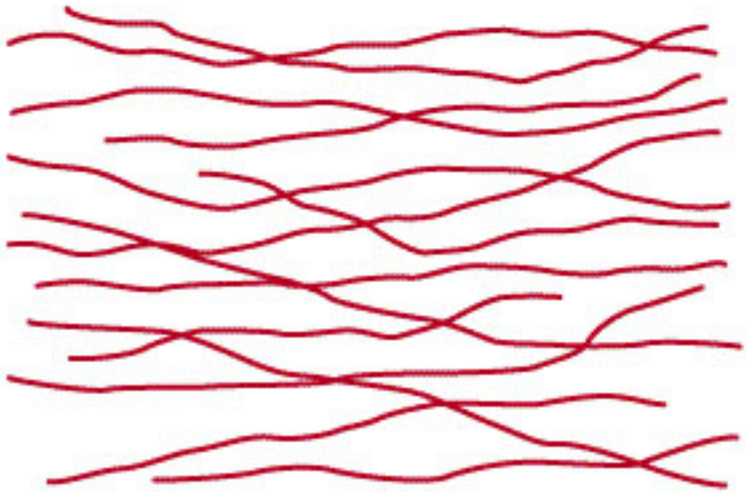
Chemistry In Action: The Thermodynamics of a Rubber Band

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

High Entropy



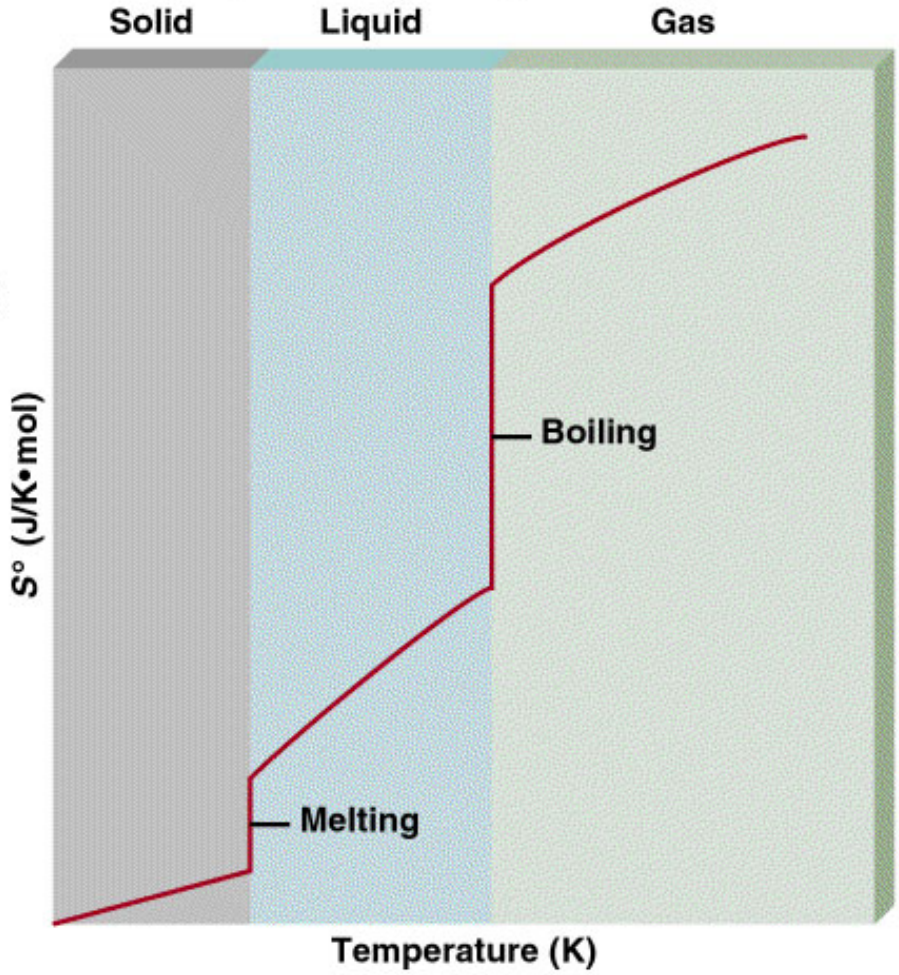
Low Entropy



Third Law of Thermodynamics

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

Entropy Increase of a Substance



$S = k \ln W$

$W = 1$

$S = 0$