

# Entropy, Free Energy, and Equilibrium

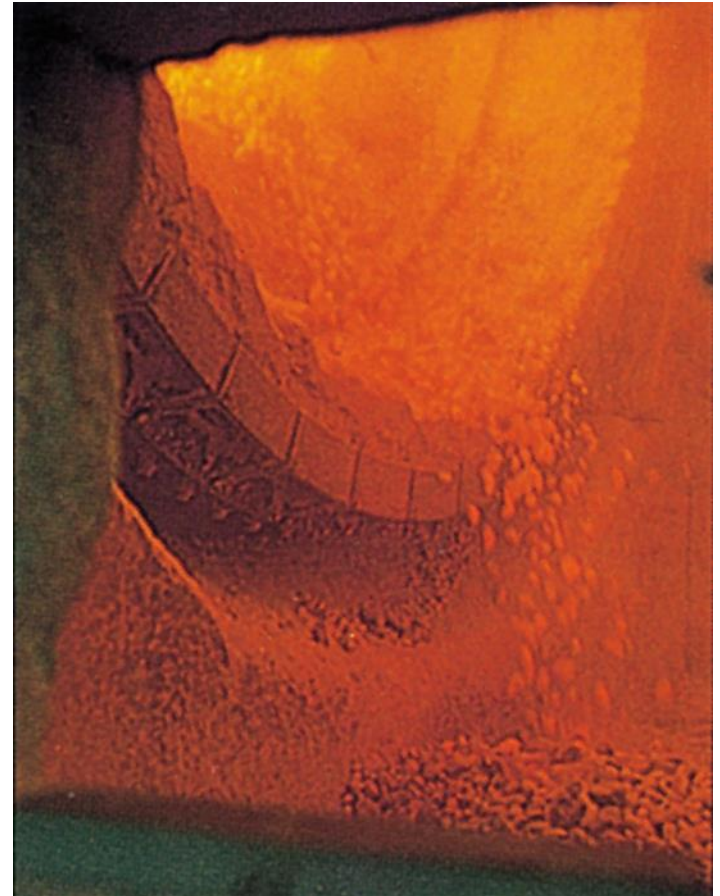
Chemical Thermodynamics

để biết 1 pứ có khả năng xảy ra hay không

Gibbs Free Energy and Chemical Equilibrium



Spontaneous process:  
Equilibrium process:

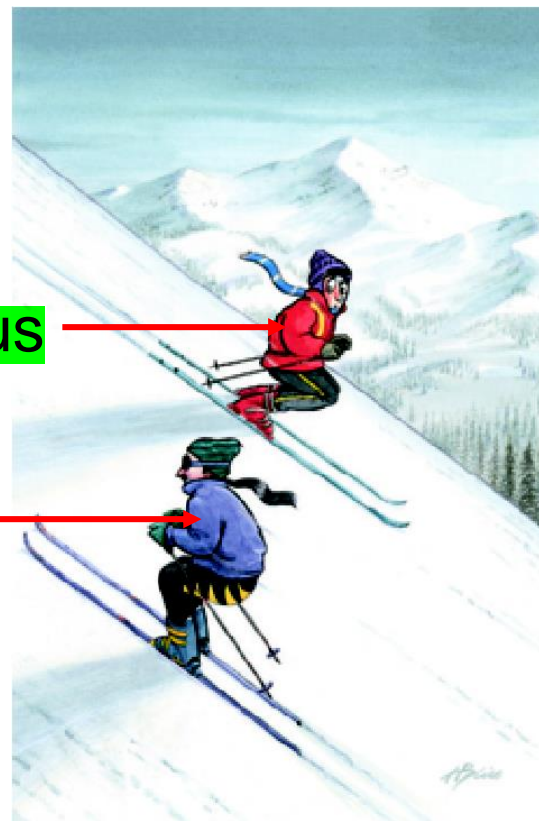


# **Spontaneous** Physical and Chemical Processes

- 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

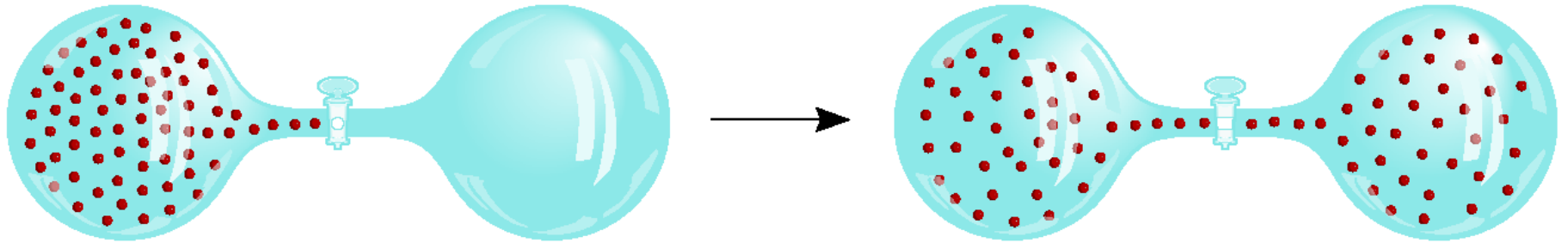
**spontaneous**

**nonspontaneous**

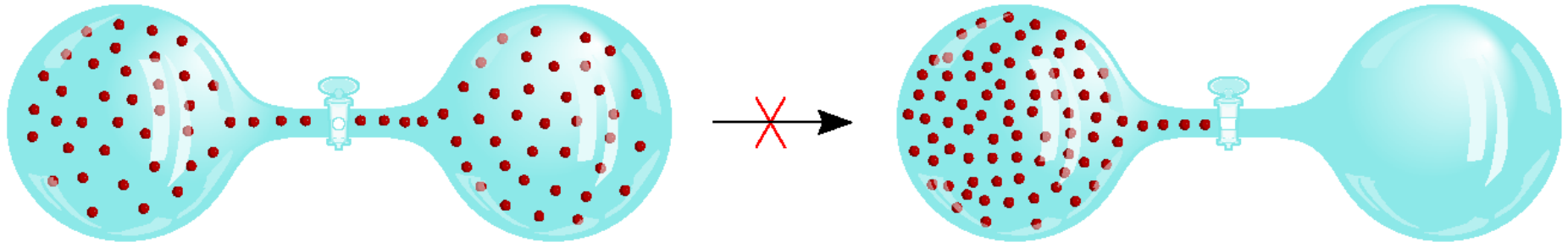


- Một thác nước chảy xuống đồi
- Một miếng đường tan trong một tách cà phê
- Ở 1 atm, nước đóng băng dưới 0 oC và băng tan trên 0 oC
- Nhiệt chảy từ vật nóng hơn sang vật lạnh hơn
- Khí mở rộng trong bóng thủy tinh được bơm chân không
- Sắt tiếp xúc với oxy và nước tạo thành gỉ

spontaneous

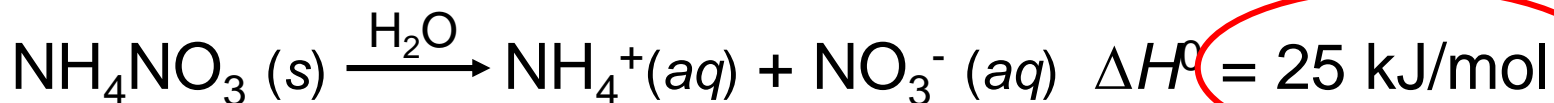
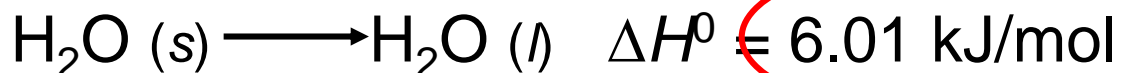
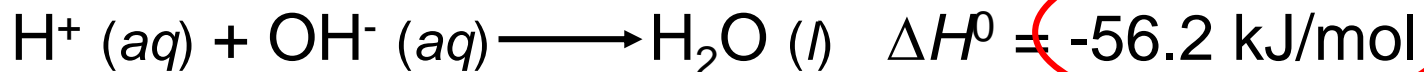
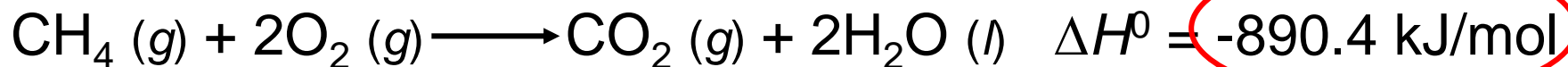


nonspontaneous



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

$$S = k \ln W \quad W = \text{number of microstates}$$


$$\Delta S = S_f - S_i \quad \Delta S = k \ln \frac{W_f}{W_i} \quad (k \text{ is the Boltzmann constant})$$

$$W_f > W_i \text{ then } \Delta S > 0$$

$$W_f < W_i \text{ then } \Delta S < 0$$

(a)  Distributing four particles among two boxes will result in  $2^4 = 16$  different microstates

(b) 

(c) 

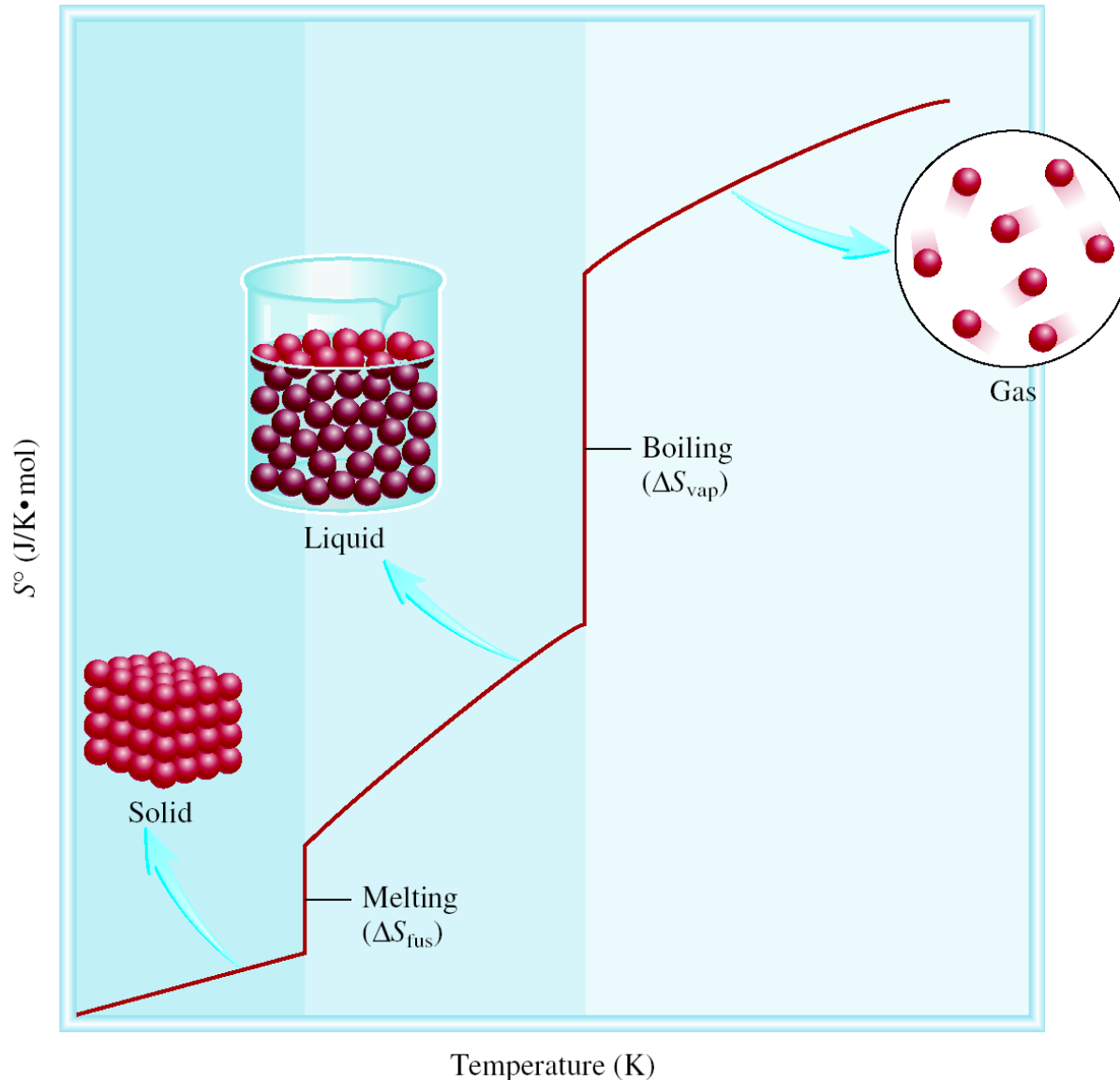
(d) 

(e) 

“most probable distribution”

# Third Law of Thermodynamics

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

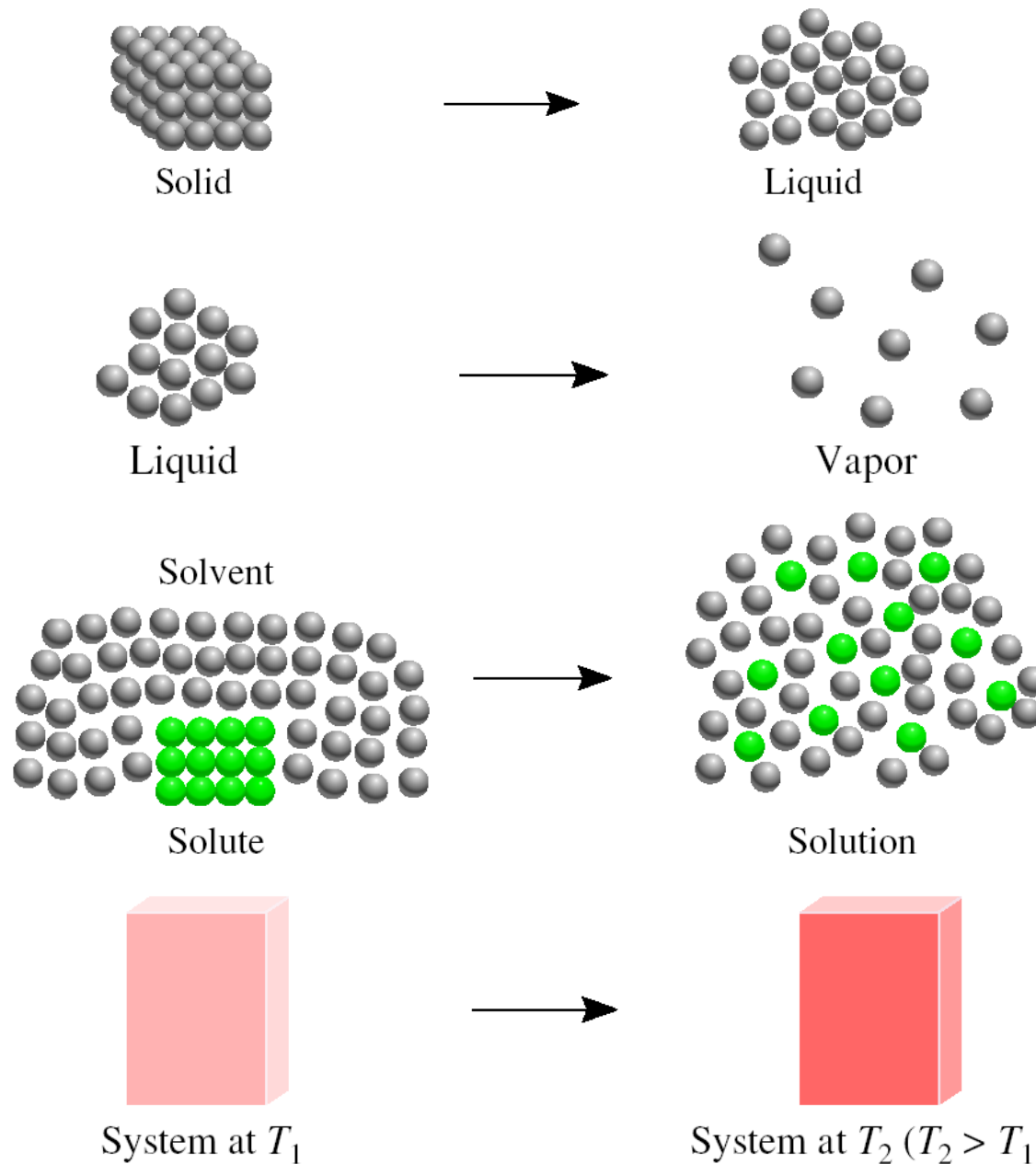


$$S = k \ln W$$

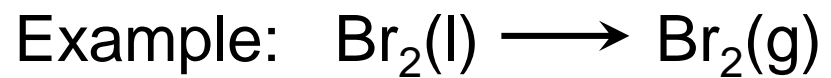
$$W = 1$$

$$S = 0$$

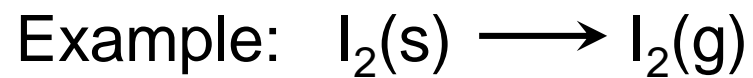
# Processes that lead to an increase in entropy ( $\Delta S > 0$ )







$$\Delta S > 0$$



$$\Delta S > 0$$

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 °C to 80 °C

Randomness increases

Entropy increases ( $\Delta S > 0$ )

(d) Subliming dry ice

Randomness increases

Entropy increases ( $\Delta S > 0$ )

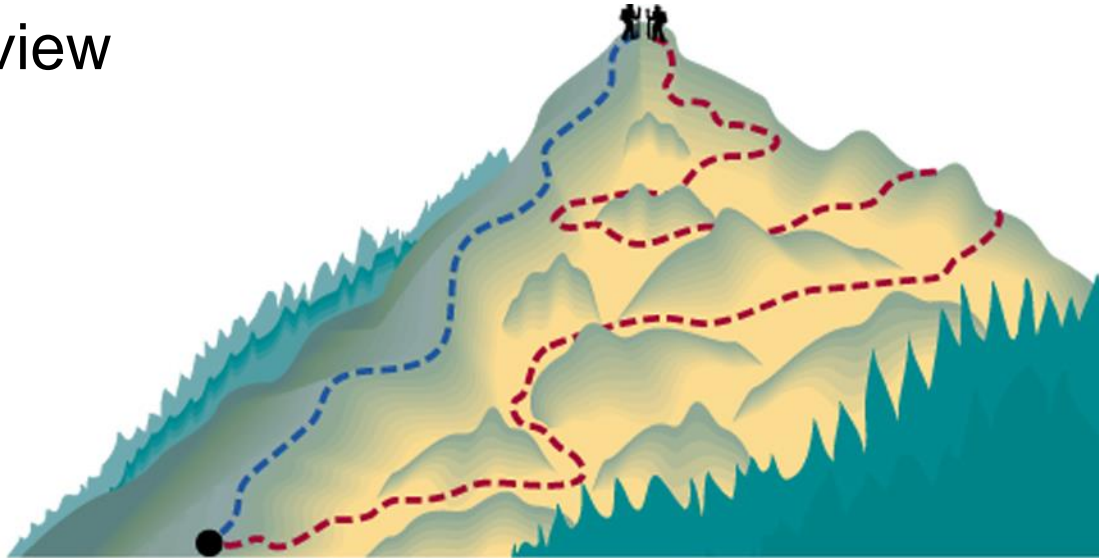
# Entropy

***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**

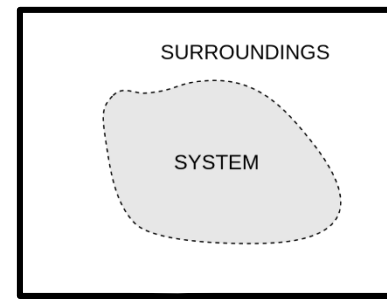
Review



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

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

<b>Substance</b>	<b><math>S^\circ</math> (J/K · mol)</b>
$\text{H}_2\text{O}(l)$	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
$\text{CH}_4$ (methane)	186.2
$\text{C}_2\text{H}_6$ (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:

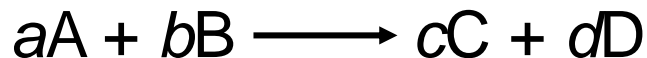
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

**Equilibrium** process:

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

# Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

The **standard entropy of reaction** ( $\Delta S_{\text{rxn}}^0$ ) 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?  $2\text{CO} (g) + \text{O}_2 (g) \longrightarrow 2\text{CO}_2 (g)$

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

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

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

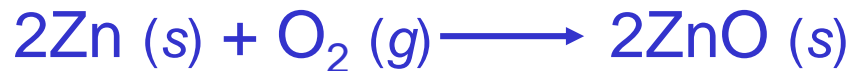
$$\Delta S_{\text{rxn}}^0 = 427.2 - [395.8 + 205.0] = -173.6 \text{ J/K}\cdot\text{mol}$$

# Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

When gases are produced (or consumed)

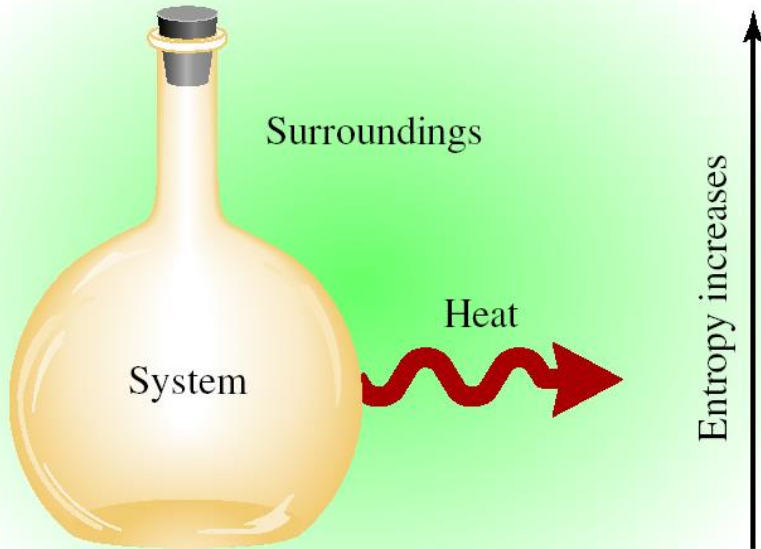
- If a reaction produces more gas molecules than it consumes,  $\Delta S^0 > 0$ .
- If the total number of gas molecules diminishes,  $\Delta S^0 < 0$ .
- If there is no net change in the total number of gas molecules, then  $\Delta S^0$  may be positive or negative BUT  $\Delta S^0$  will be a small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

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



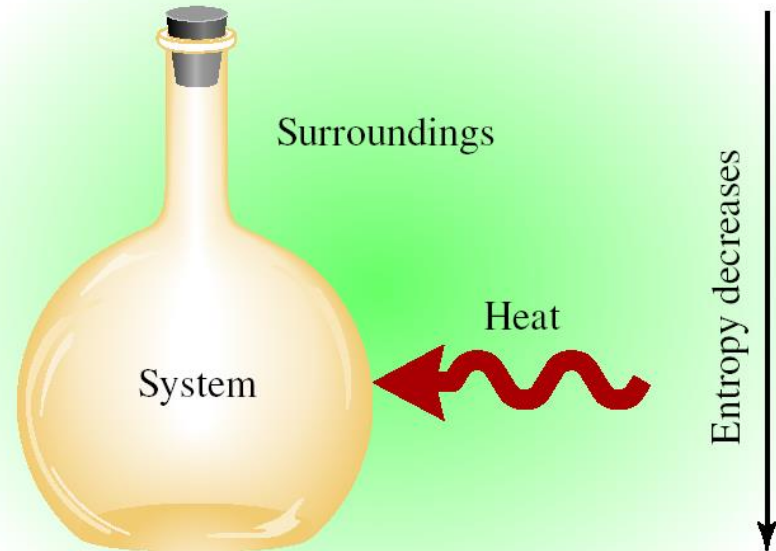
The total number of gas molecules goes down,  $\Delta S$  is negative.

# Entropy Changes in the Surroundings ( $\Delta S_{\text{surr}}$ )



**Exo**thermic Process

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



**Endo**thermic Process

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



# Entropy Changes in the System and Surroundings

Why does **crystallization of a solute occur?**

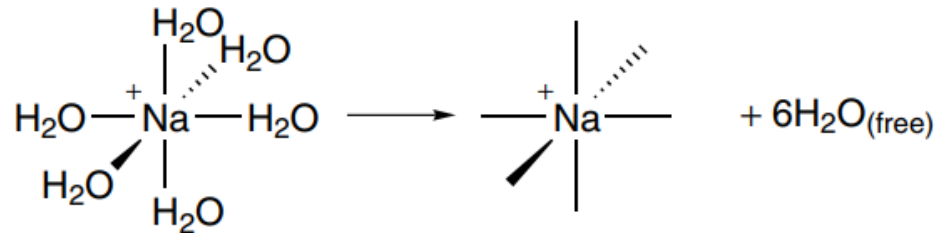
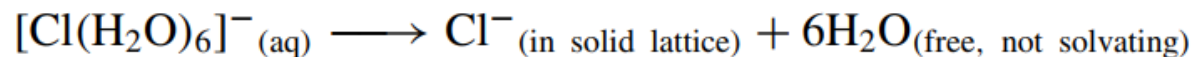
1. Entropy of **system**:  $\Delta S_{\text{sys}} < 0$

‘solute disorder(initial) > solute disorder(final)’

2. Entropy of **surrounding**:  $\Delta S_{\text{surr}} > 0$

‘solvent disorder(initial) < solvent disorder(final)’

3. Entropy of **universe**:  $\Delta S_{\text{surr}} + \Delta S_{\text{sys}} > 0$



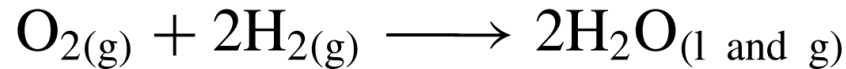
Mobile aquo ion

Ion immobilized  
within a 3-D  
repeat lattice

Mobile water  
molecules

# Entropy Changes in the System and Surroundings

Why is burning hydrogen gas in air (to form liquid water) a spontaneous reaction?



1. **Entropy of system:**  $\Delta S_{\text{sys}} < 0$ , easily quantified
  - Three gas molecules (initial) > Two molecules (final)
2. **Entropy of surrounding:**  $\Delta S_{\text{surr}} > 0$ 
  - Surrounding air absorbs the energy (heat and sound) liberated during the reaction:
  - Quantification of the influence of the surroundings on the reaction is usually **not a trivial problem**.
3. **Entropy of universe:**  $\Delta S_{\text{surr}} + \Delta S_{\text{sys}} > 0$

# Gibbs Free Energy

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

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T \quad \Longrightarrow \quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + -\Delta H_{\text{sys}}/T$$

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

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

Spontaneous process:  $\Delta S_{\text{univ}} > 0$

$$\Delta G = -T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

Nonspontaneous process:  $\Delta S_{\text{univ}} < 0$

$$\Delta G = -T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} > 0$$

Nonspontaneous process:  $\Delta S_{\text{univ}} = 0$  ,  $\Delta G = 0$

# Gibbs Free Energy

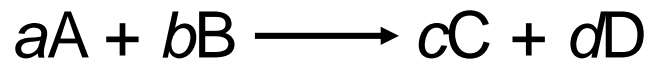
For a constant temperature and constant pressure process:

**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 ( $\Delta G_{\text{rxn}}^0$ )** 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 ( $\Delta G_{\text{f}}^0$ )** is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

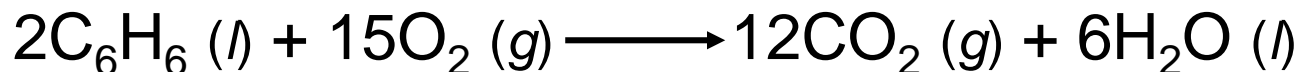
$\Delta G_{\text{f}}^0$  of any element in its stable form is zero.

**TABLE 18.2****Conventions for Standard States**

<b>State of Matter</b>	<b>Standard State</b>
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**

- When  $\Delta G$  is negative, a process will proceed spontaneously and is referred to as exergonic.

- The spontaneity of a process can depend on the temperature.

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

$\Delta H$	$\Delta S$	$\Delta G$	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$
+	−	$\Delta G$ is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
−	+	$\Delta G$ 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



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

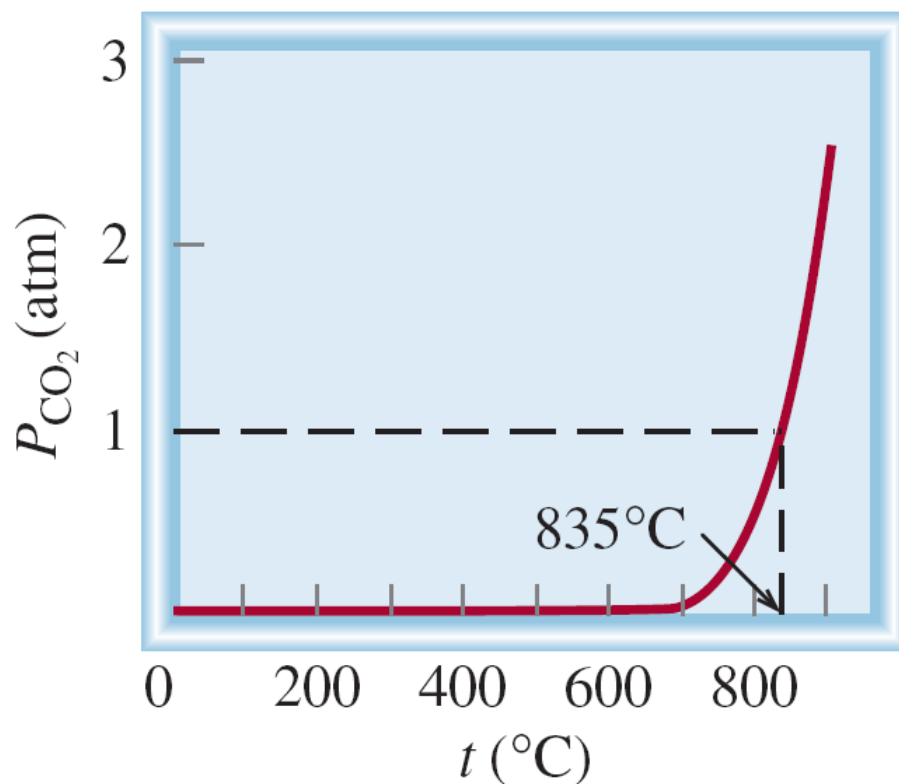
$$\Delta S^0 = 160.5 \text{ J/K}\cdot\text{mol}$$

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

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

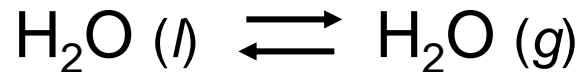
$$\Delta G^0 = 0 \text{ at } 835^\circ\text{C}$$

## Equilibrium Pressure of $\text{CO}_2$



# Gibbs Free Energy and Phase Transitions

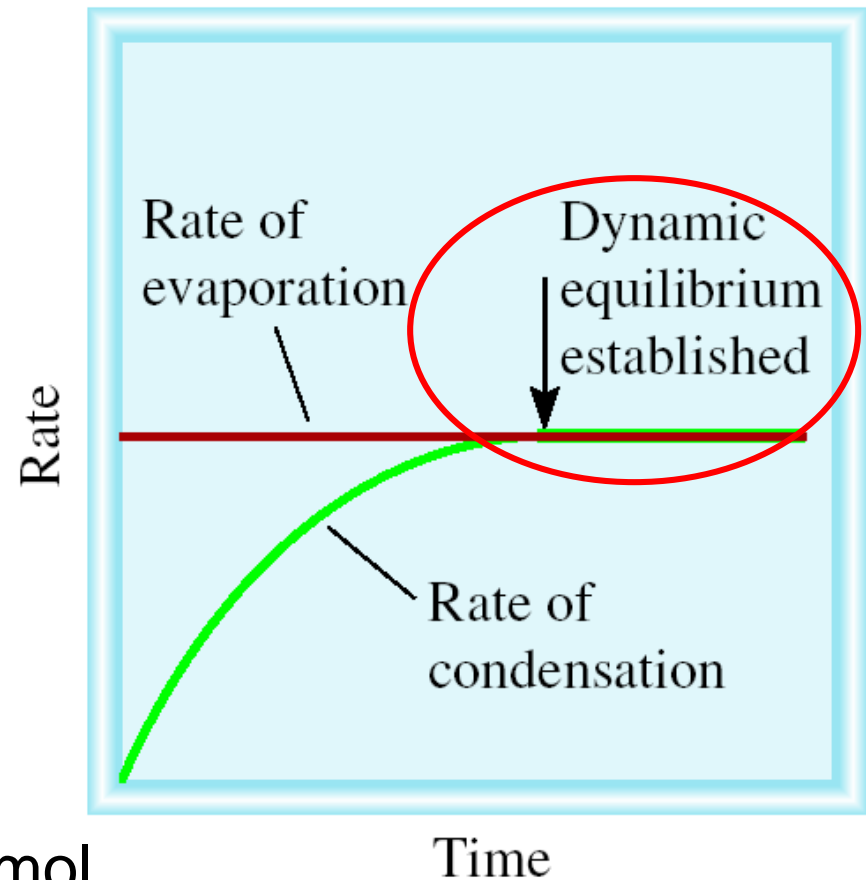
$$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$$



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

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

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



# 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

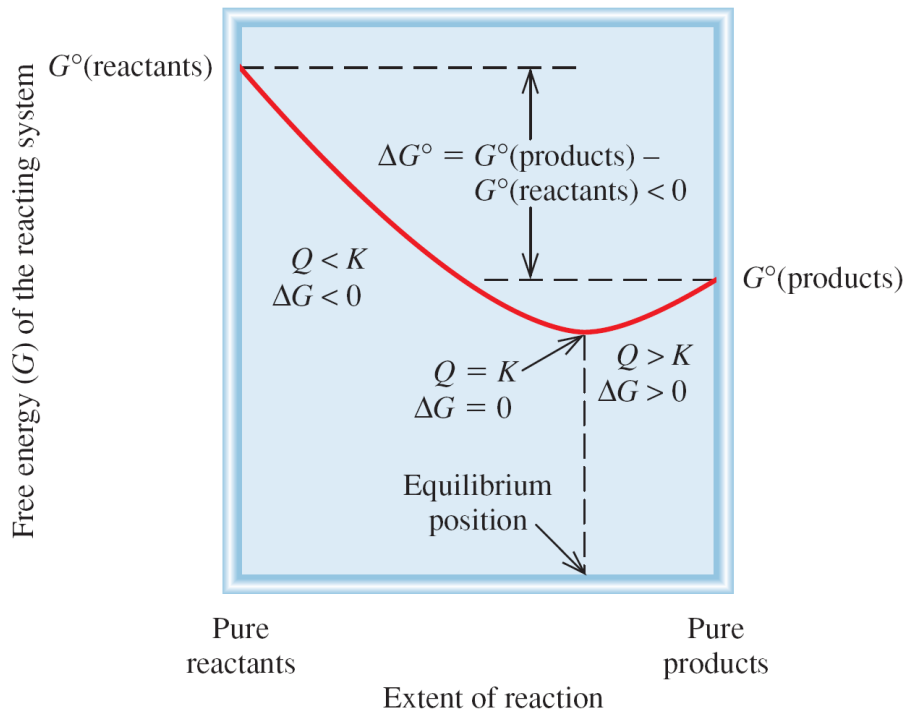
At Equilibrium

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

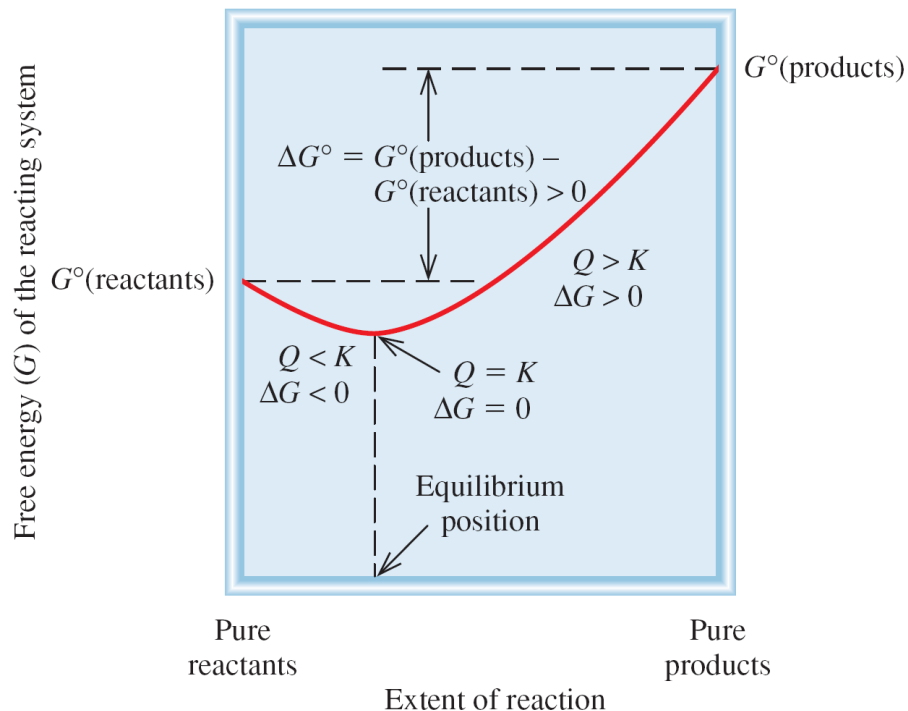
$$0 = \Delta G^0 + RT \ln K$$

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

# Free Energy Versus Extent of Reaction



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



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

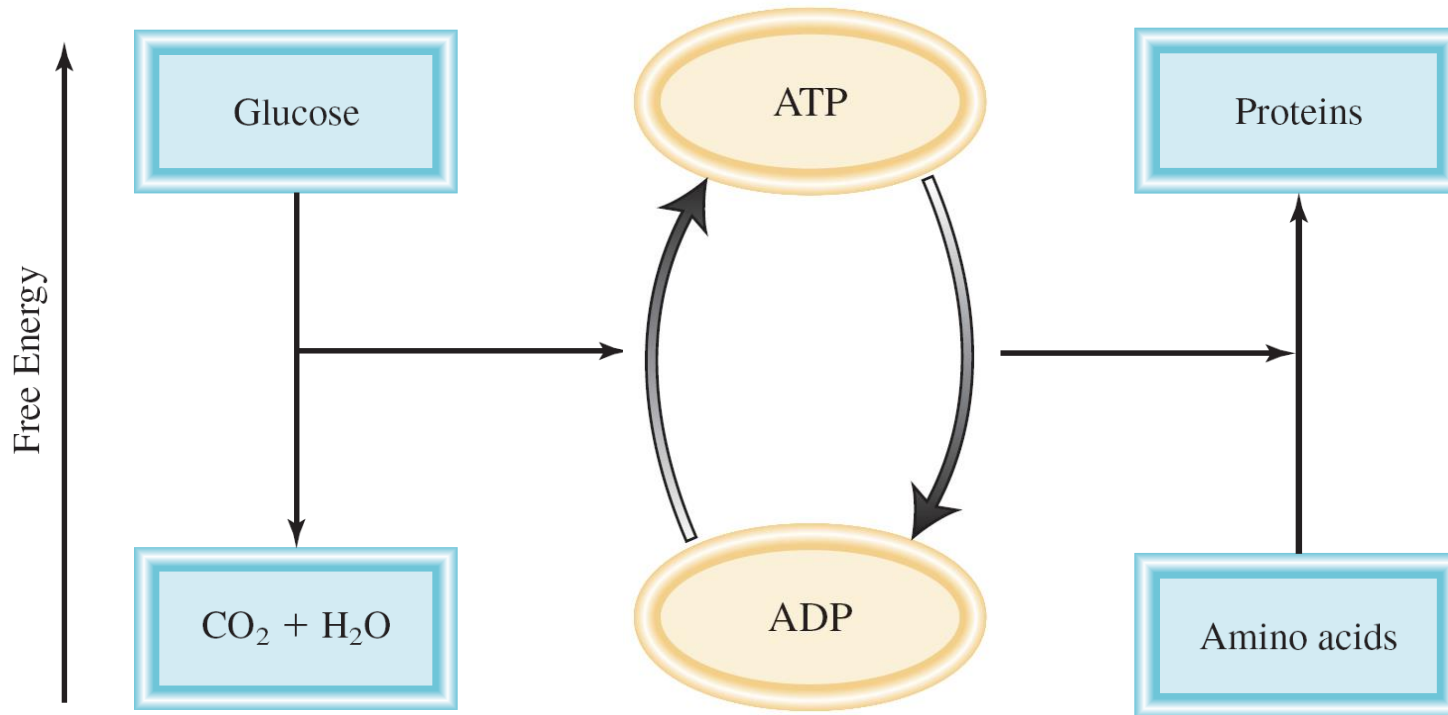
$$\Delta G^{\circ} = -RT \ln K$$

**TABLE 18.4**

**Relation Between  $\Delta G^{\circ}$  and  $K$  as Predicted by the Equation  $\Delta G^{\circ} = -RT \ln K$**

$K$	$\ln K$	$\Delta G^{\circ}$	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



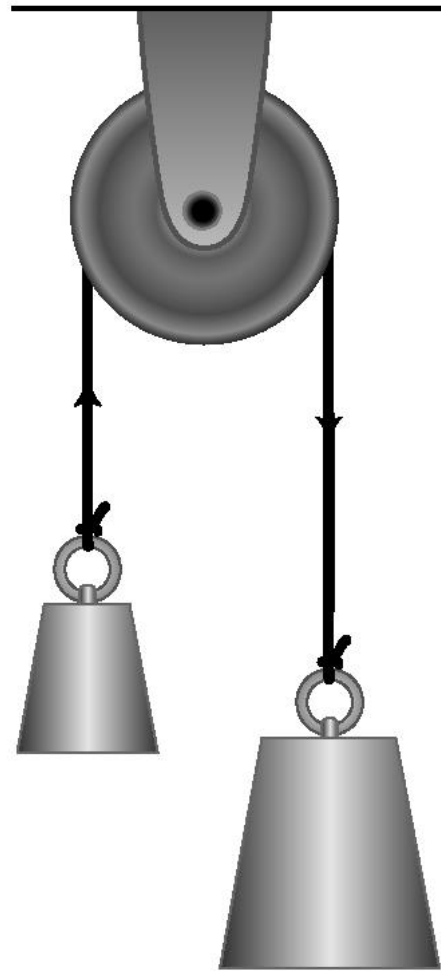
Example:            Alanine + Glycine  $\longrightarrow$  Alanylglycine

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



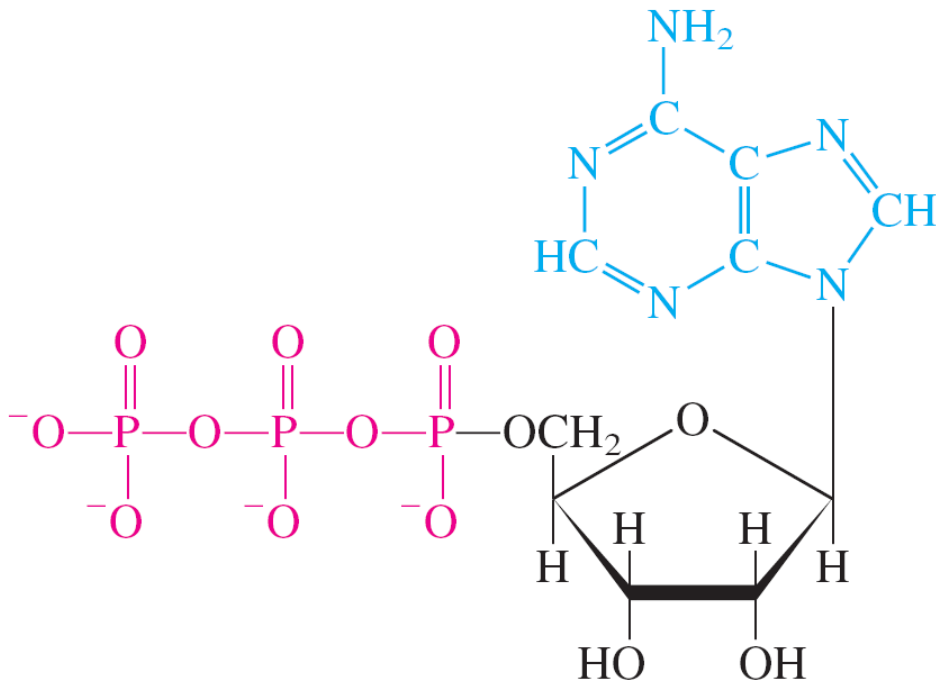
$$\Delta G^0 = -2 \text{ kJ} \qquad K > 1$$

# Mechanical Analog of Couple Reactions

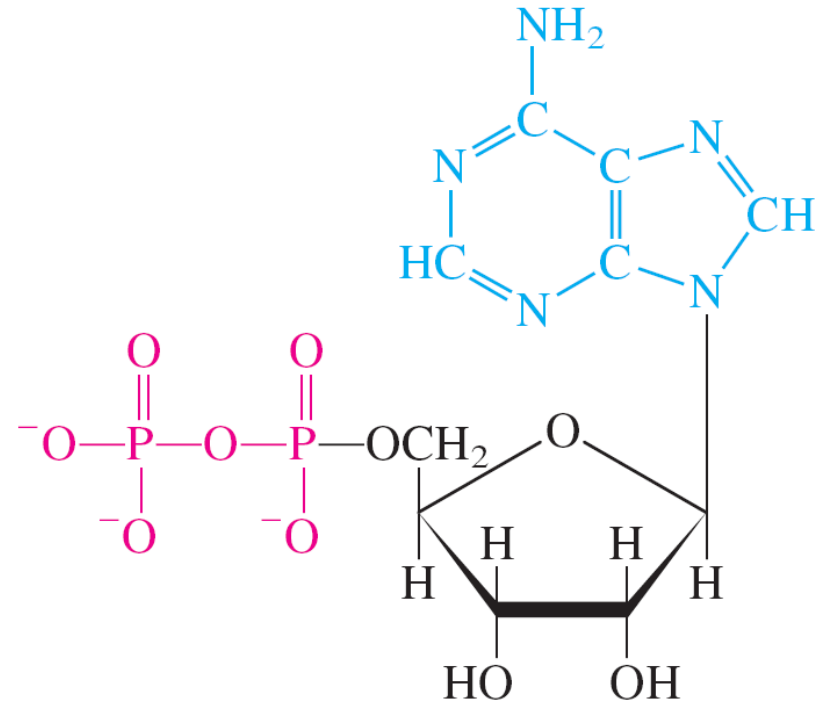


Make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

# The Structure of ATP and ADP in Ionized Forms



Adenosine triphosphate  
(ATP)



Adenosine diphosphate  
(ADP)