

Petrucci • Harwood • Herring • Madura

Ninth  
Edition

# GENERAL CHEMISTRY

Principles and Modern Applications



## Chapter 19: Spontaneous Change: Entropy and Free Energy

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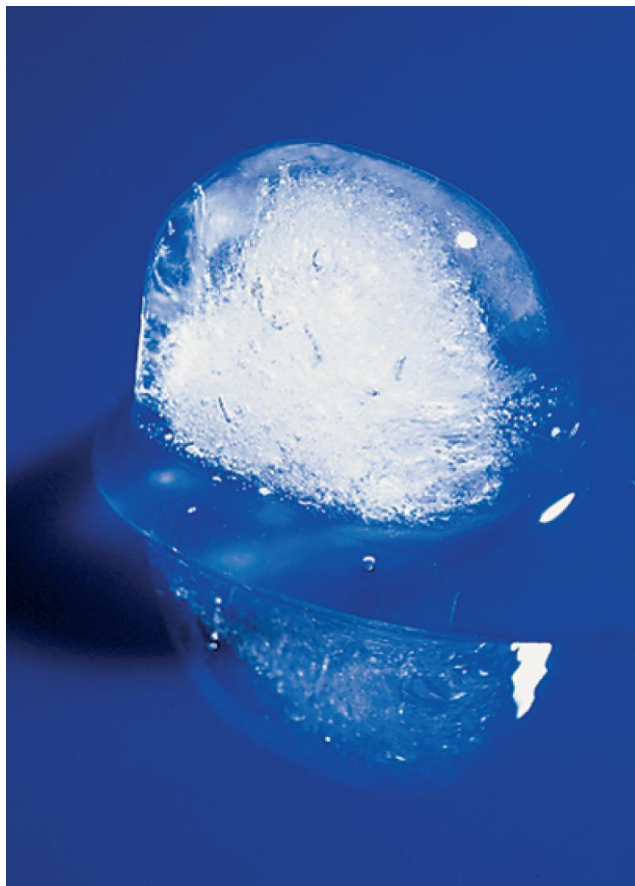
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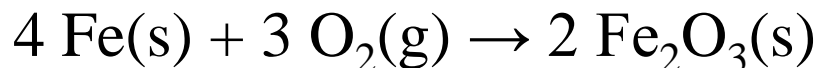
➤ *Focus On Coupled Reactions in Biological Systems*

# 19-1 Spontaneity: The Meaning of Spontaneous Change



# Spontaneous Process

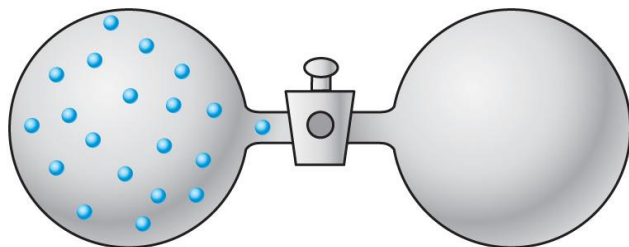
- ◆ A process that occurs in a system left to itself.
  - Once started, no external actions is necessary to make the process continue.
- ◆ A non-spontaneous process will not occur without external action continuously applied.



# Spontaneous Process

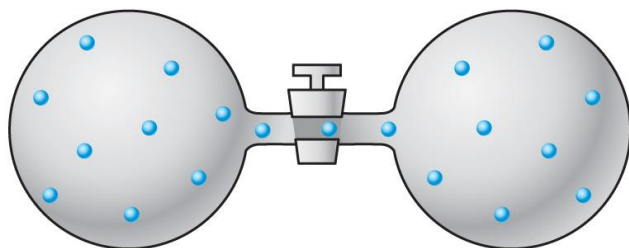
- ◆ Potential energy decreases.
- ◆ For chemical systems the internal energy  $U$  is equivalent to potential energy.
- ◆ Berthelot and Thomsen 1870's.
  - Spontaneous change occurs in the direction in which the enthalpy of a system decreases.
  - Mainly true but there are exceptions.

# 19-2 The Concept of Entropy



(a) Initial condition

$$\Delta U = \Delta H = 0$$



(b) After expansion into vacuum

## ◆ Entropy, $S$ .

- The greater the number of configurations of the microscopic particles among the energy levels in a particular system, the greater the entropy of the system.

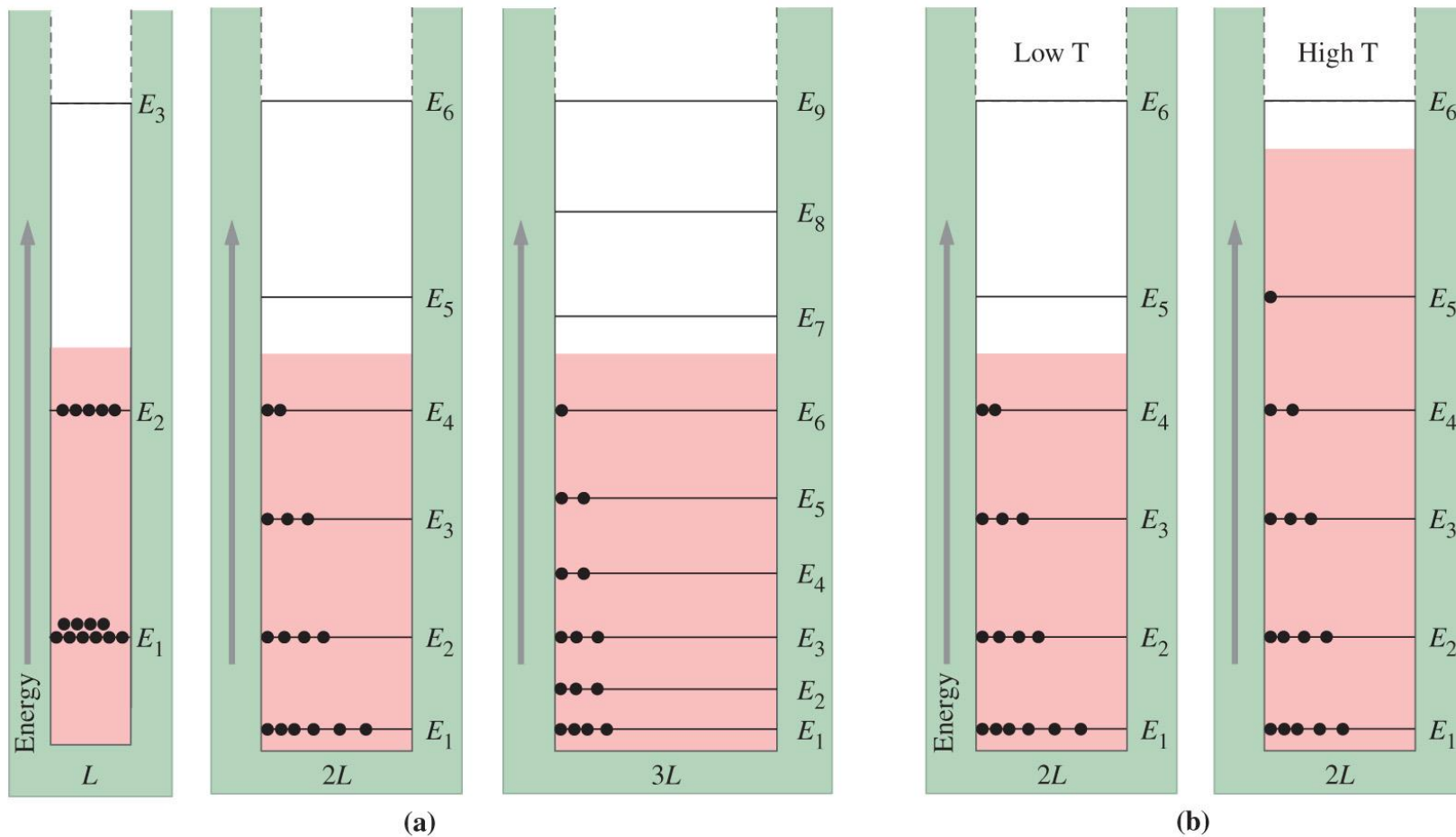
$$\Delta S > 0 \text{ spontaneous}$$

# The Boltzmann Equation for Entropy

$$S = k \ln W$$

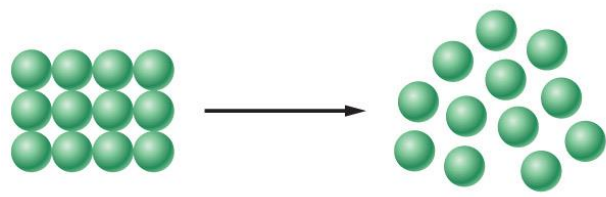
- ◆ Entropy,  $S$
- ◆ States.
  - The microscopic energy levels available in a system.
- ◆ Microstates,  $W$ .
  - The particular way in which particles are distributed amongst the states. Number of microstates =  $W$ .
- ◆ The Boltzmann constant,  $k$ .
  - Effectively the gas constant per molecule =  $R/N_A$ .

# Boltzmann Distribution





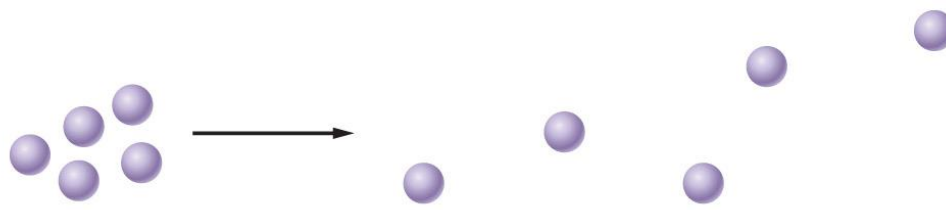
# Entropy Change



Solid

Liquid

(a) Melting:  $S_{\text{liquid}} > S_{\text{solid}}$



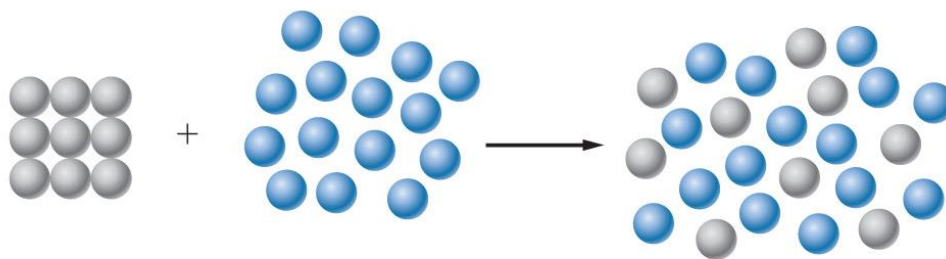
Liquid

Vapor

(b) Vaporization:  $S_{\text{vapor}} > S_{\text{liquid}}$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

For changes occurring  
at constant temperature



Solute

Solvent

Solution

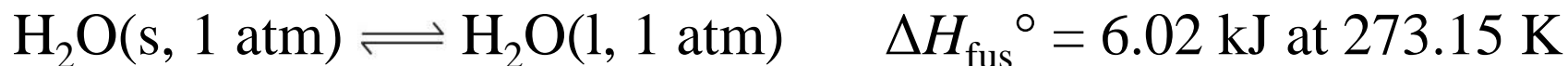
(c) Dissolving:  $S_{\text{soln}} > (S_{\text{solvent}} + S_{\text{solute}})$

## 19-3 Evaluating Entropy and Entropy Changes

### ◆ Phase transitions.

- Exchange of heat can be carried out reversibly.

$$\Delta S = \frac{\Delta H}{T_{\text{tr}}}$$



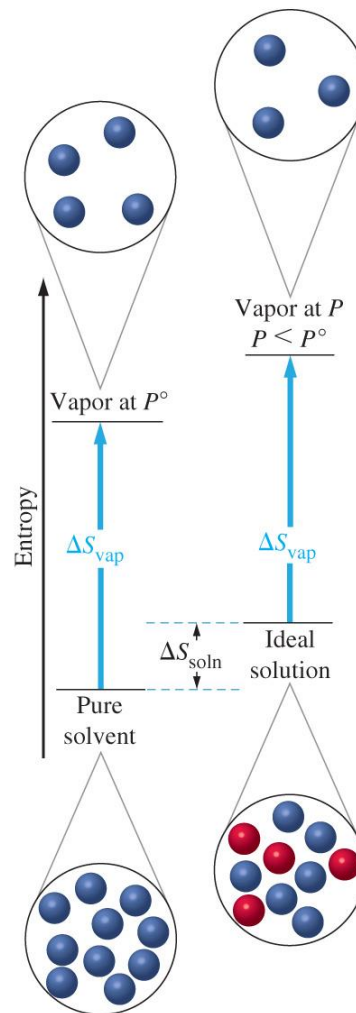
$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}^\circ}{T_{\text{tr}}} = \frac{6.02 \text{ kJ mol}^{-1}}{273.15 \text{ K}} = 2.20 \times 10^{-2} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

# Trouton's Rule

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} \approx 87 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

# Raoult's Law

$$P_A = \chi_A P_A^\circ$$

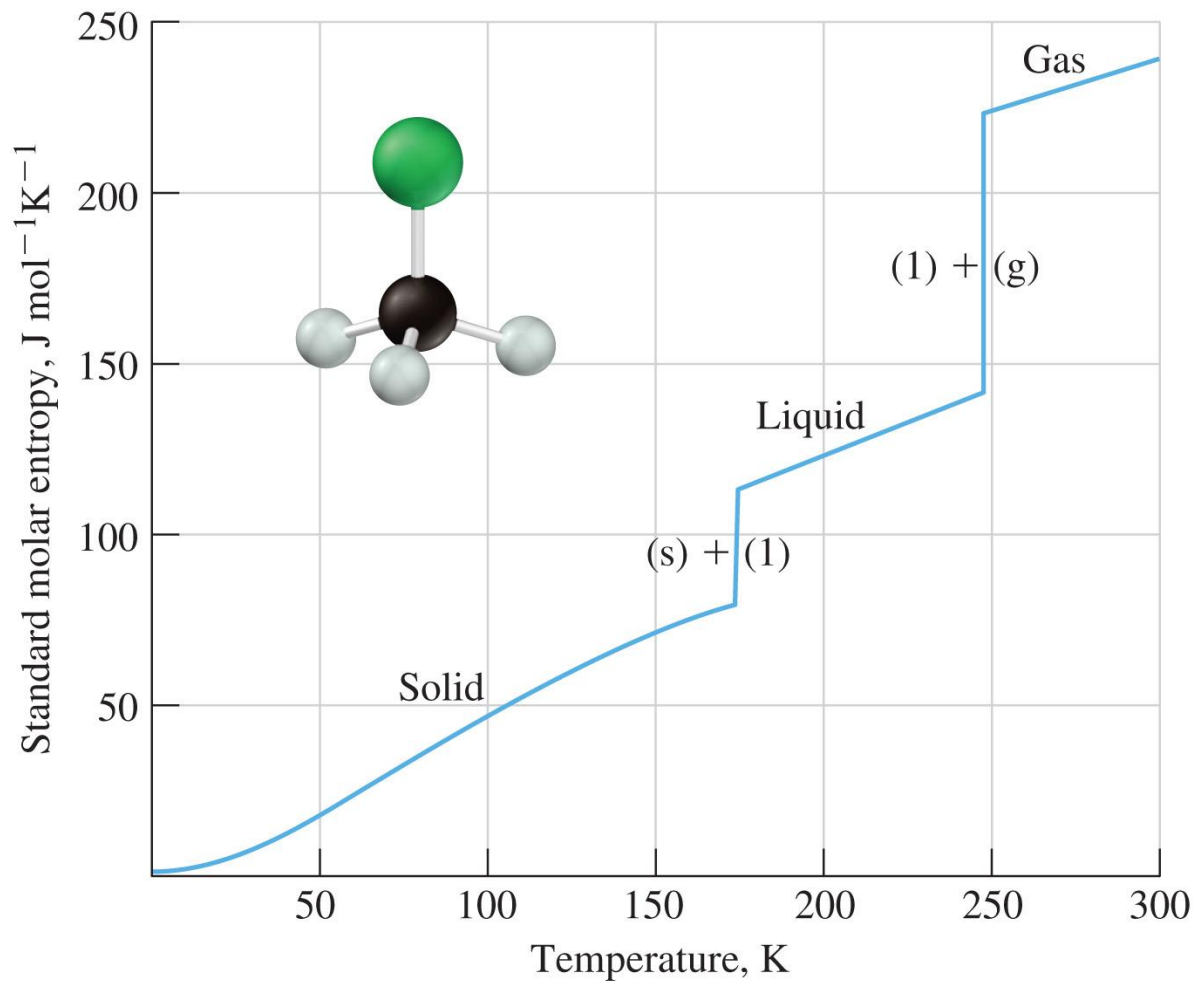


# Absolute Entropies

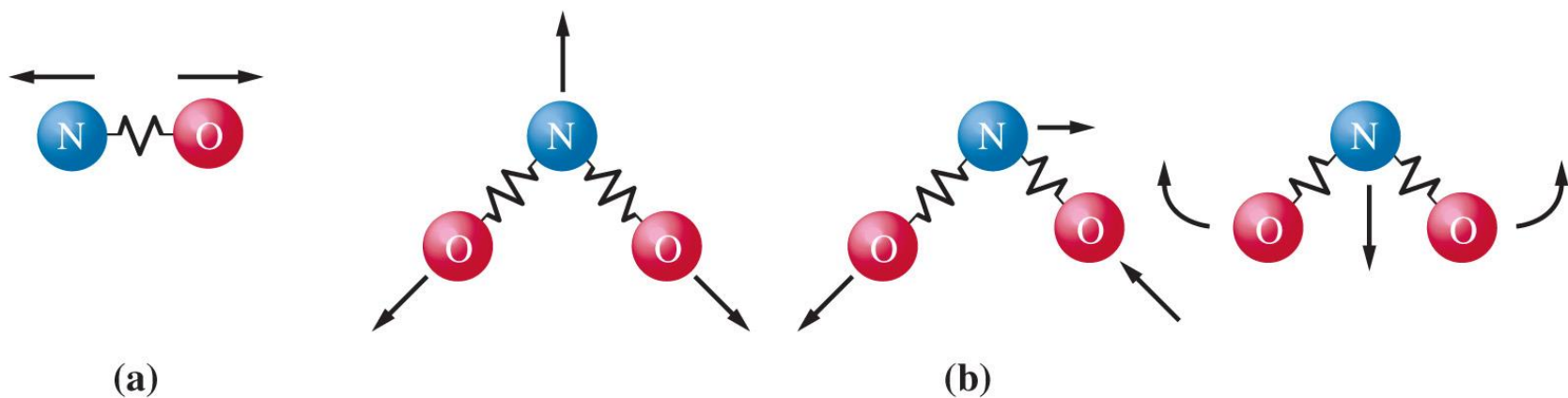
- ◆ Third law of thermodynamics.
  - The entropy of a pure perfect crystal at 0 K is zero.
- ◆ Standard molar entropy.
  - Tabulated in Appendix D.

$$\Delta S = [ \sum v_p S^\circ(\text{products}) - \sum v_r S^\circ(\text{reactants}) ]$$

# Entropy as a Function of Temperature



# Vibrational Energy and Entropy



## 19-4 Criteria for Spontaneous Change: The Second Law of Thermodynamics.

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

The Second Law of Thermodynamics:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

All spontaneous processes produce an increase in the entropy of the universe.



# Free Energy and Free Energy Change

## ◆ Hypothetical process:

- only pressure-volume work, at constant  $T$  and  $P$ .

$$q_{\text{surroundings}} = -q_p = -\Delta H_{\text{sys}}$$

## ◆ Make the enthalpy change reversible.

- large surroundings, infinitesimal change in temperature.

## ◆ Under these conditions we can calculate entropy.

# Free Energy and Free Energy Change

*For the universe:*

$$T\Delta S_{\text{univ.}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} = -(\Delta H_{\text{sys}} - T\Delta S_{\text{sys}})$$

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

*For the system:*

$$G = H - TS$$

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

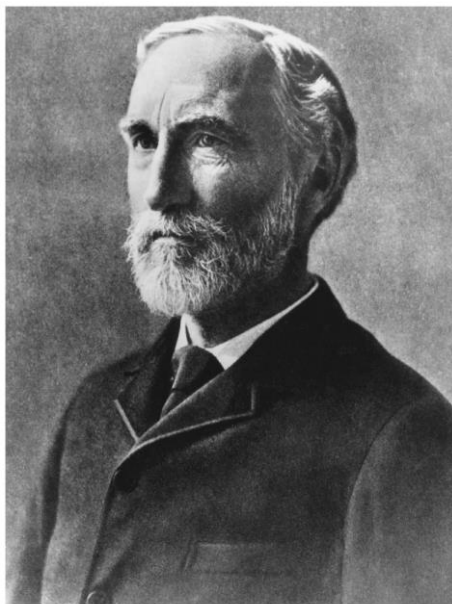
$$\Delta G_{\text{sys}} = -T\Delta S_{\text{universe}}$$

# Criteria for Spontaneous Change

$\Delta G_{\text{sys}} < 0$  (negative), the process is spontaneous.

$\Delta G_{\text{sys}} = 0$  (zero), the process is at equilibrium.

$\Delta G_{\text{sys}} > 0$  (positive), the process is non-spontaneous.



J. Willard Gibbs

1839-1903

**TABLE 19.1 Criteria for Spontaneous Change:  $\Delta G = \Delta H - T\Delta S$** 

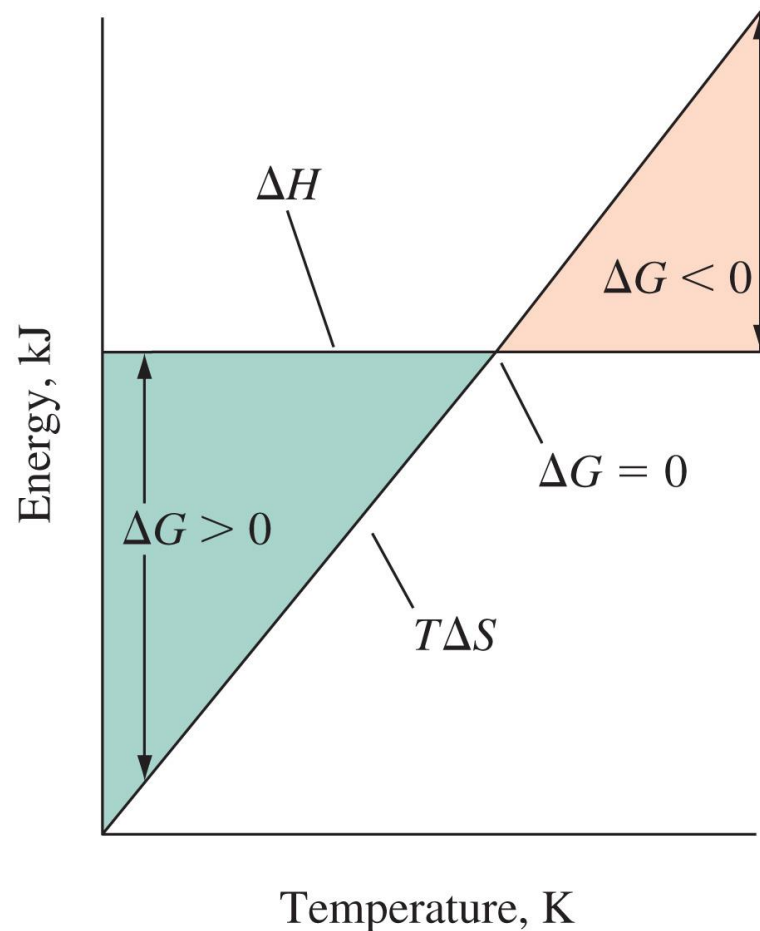
Case	$\Delta H$	$\Delta S$	$\Delta G$	Result	Example
1.	–	+	–	spontaneous at all temp.	$2 \text{ N}_2\text{O(g)} \longrightarrow 2 \text{ N}_2\text{(g)} + \text{O}_2\text{(g)}$
2.	–	–	$\begin{cases} - \\ + \end{cases}$	$\begin{cases} \text{spontaneous at low temp.} \\ \text{nonspontaneous at high temp.} \end{cases}$	$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(s)}$
3.	+	+	$\begin{cases} + \\ - \end{cases}$	$\begin{cases} \text{nonspontaneous at low temp.} \\ \text{spontaneous at high temp.} \end{cases}$	$\text{NH}_3\text{(g)} \longrightarrow \text{N}_2\text{(g)} + 3 \text{ H}_2\text{(g)}$
4.	+	–	+	nonspontaneous at all temp.	$3 \text{ O}_2\text{(g)} \longrightarrow 2 \text{ O}_3\text{(g)}$

## 19-5 Standard Free Energy Change, $\Delta G^\circ$

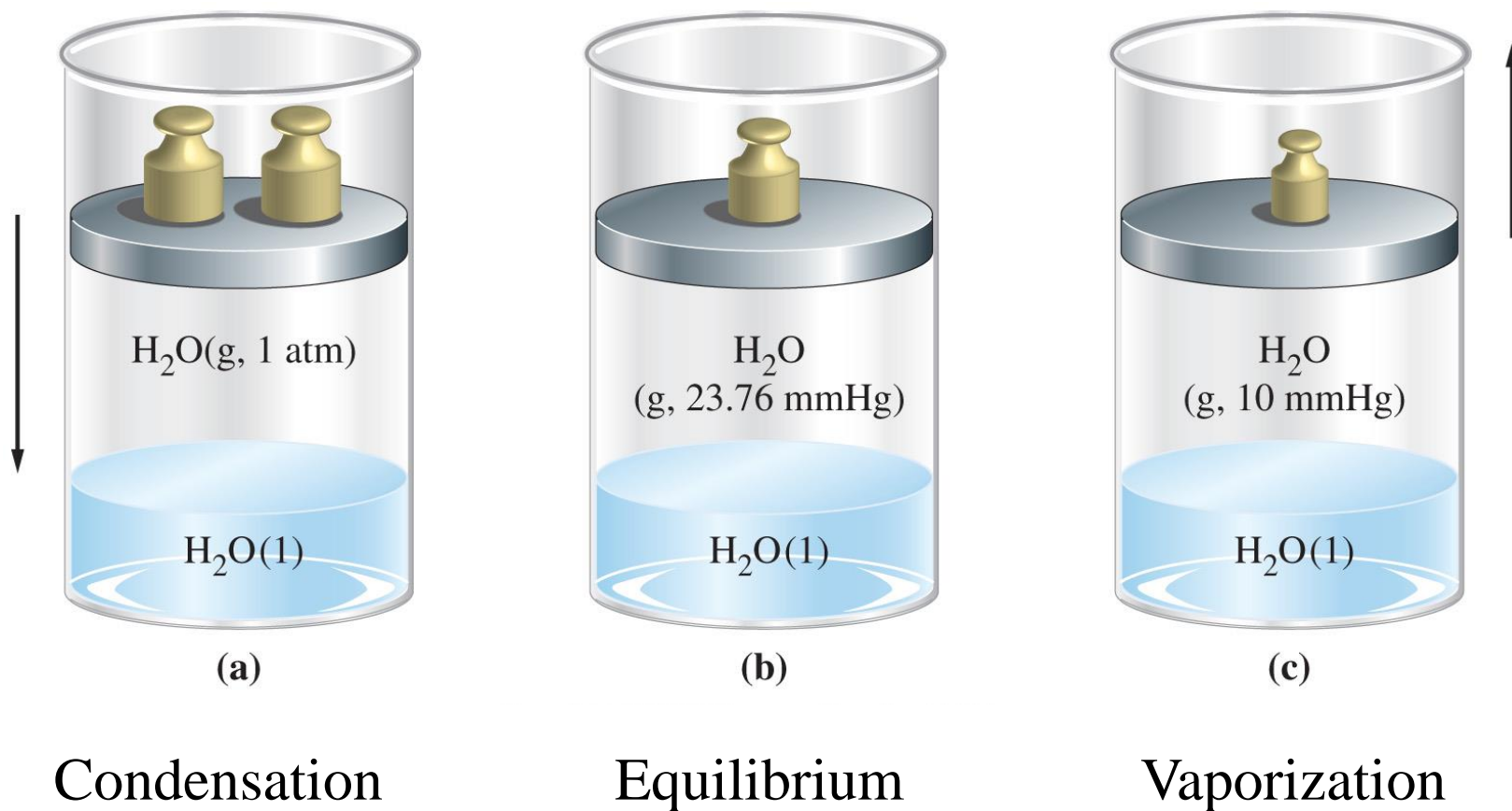
- ◆ The standard free energy of formation,  $\Delta G_f^\circ$ .
  - The change in free energy for a reaction in which a substance in its standard state is formed from its elements in reference forms in their standard states.
- ◆ The standard free energy of reaction,  $\Delta G^\circ$ .

$$\Delta G^\circ = [ \sum v_p \Delta G_f^\circ(\text{products}) - \sum v_r \Delta G_f^\circ(\text{reactants}) ]$$

## 19-6 Free Energy Change and Equilibrium



# Free Energy Change and Equilibrium



# Relationship of $\Delta G^\circ$ to $\Delta G$ for Non-standard Conditions



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

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

For ideal gases  $\Delta H = \Delta H^\circ$

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



# Relationship Between $S$ and $S^\circ$

$$q_{\text{rev}} = -w = RT \ln \frac{V_f}{V_i}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = R \ln \frac{V_f}{V_i}$$

$$\Delta S = S_f - S_i = R \ln \frac{V_f}{V_i} = R \ln \frac{P_i}{P_f} = -R \ln \frac{P_f}{P_i}$$

$$S = S^\circ - R \ln \frac{P}{P^\circ} = S^\circ - R \ln \frac{P}{1} = S^\circ - R \ln P$$



$$S_{\text{N}_2}^{\text{red}} = S_{\text{N}_2} - R \ln P_{\text{N}_2}$$

$$S_{\text{H}_2}^{\text{red}} = S_{\text{H}_2} - R \ln P_{\text{H}_2}$$

$$S_{\text{NH}_3}^{\text{red}} = S_{\text{NH}_3} - R \ln P_{\text{NH}_3}$$

$$\Delta S_{\text{rxn}} = 2 \times (S_{\text{NH}_3} - R \ln P_{\text{NH}_3}) - (S_{\text{N}_2} - R \ln P_{\text{N}_2}) - 3 \times (S_{\text{H}_2} - R \ln P_{\text{H}_2})$$

$$\Delta S_{\text{rxn}} = 2 S_{\text{NH}_3} - S_{\text{N}_2} - 3 S_{\text{H}_2} + R \ln \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

$$\Delta S_{\text{rxn}} = \Delta S_{\text{rxn}}^{\circ} + R \ln \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

# $\Delta G$ Under Non-standard Conditions

$$\Delta G = \Delta H^\circ - T\Delta S \qquad \Delta S_{\text{rxn}} = \Delta S^\circ_{\text{rxn}} + R \ln \frac{P_{\text{N}_2}^2 P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ_{\text{rxn}} - TR \ln \frac{P_{\text{N}_2}^2 P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2}^2 P_{\text{H}_2}^3}$$

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

# $\Delta G$ and the Equilibrium Constant $K_{\text{eq}}$

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

*If the reaction is at equilibrium then:*

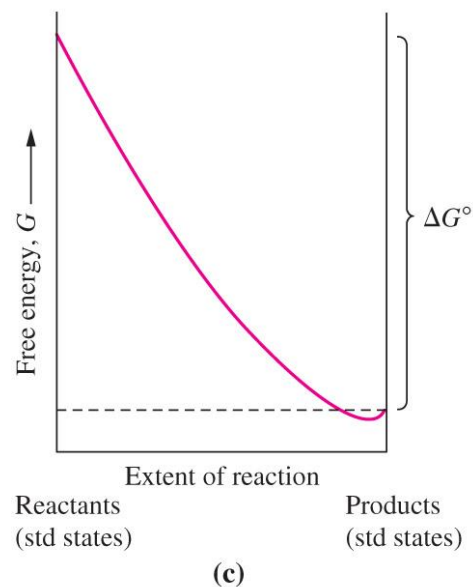
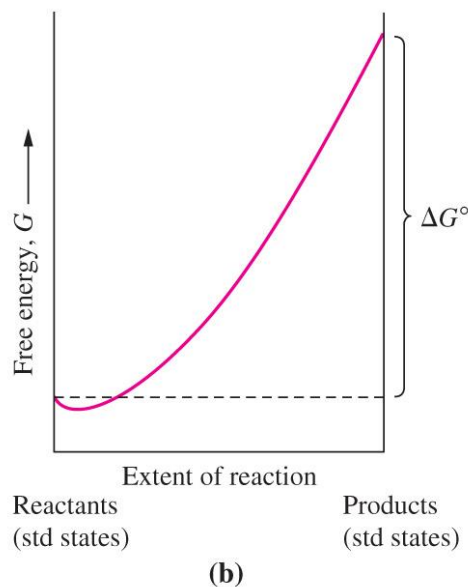
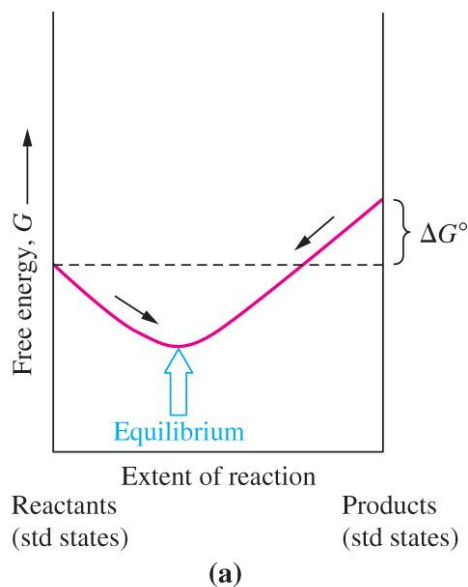
$$\Delta G = \Delta G^{\circ} + RT \ln K_{\text{eq}} = 0$$

$$\Delta G^{\circ} = -RT \ln K_{\text{eq}}$$

# Criteria for Spontaneous Change

Every chemical reaction consists of both a forward and a reverse reaction.

The direction of spontaneous change is the direction in which the free energy decreases.



# Significance of the Magnitude of $\Delta G$

+200 kJ/mol	$9.1 \times 10^{-36}$	No reaction
+100	$3.0 \times 10^{-18}$	
+50	$1.7 \times 10^{-9}$	
+10	$1.8 \times 10^{-2}$	
+1.0	$6.7 \times 10^{-1}$	
0	1.0	Equilibrium calculation is necessary
-1.0	1.5	
-10	$5.6 \times 10^1$	
-50	$5.8 \times 10^8$	Reaction goes to completion
-100	$3.3 \times 10^{17}$	
-200	$1.1 \times 10^{35}$	

# The Thermodynamic Equilibrium Constant: Activities.

*For ideal gases at 1.0 bar:*

$$S = S^{\circ} - R \ln \frac{P}{P^{\circ}} = S^{\circ} - R \ln \frac{P}{1}$$

$PV=nRT$  or  $P=(n/V)RT$ , *pressure is an effective concentration*

*Therefore, in solution:*

$$S = S^{\circ} - R \ln \frac{c}{c^{\circ}} = S^{\circ} - R \ln a$$

The effective concentration in the standard state for an *ideal solution* is  $c^{\circ} = 1 \text{ M}$ .

# Activities

- ◆ For pure solids and liquids:
  - $a = 1$
- ◆ For ideal gases:
  - $a = P$  (in bars, 1 bar = 0.987 atm)
- ◆ For ideal solutes in aqueous solution:
  - $a = c$  (in mol L<sup>-1</sup>)



# The Thermodynamic Equilibrium Constant, $K_{\text{eq}}$

- ◆ A dimensionless equilibrium constant expressed in terms of *activities*.
- ◆ Often  $K_{\text{eq}} = K_{\text{c}}$  or  $K_{\text{p}}$ , but not always.
- ◆ Must be used to determine  $\Delta G$ .

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{a_{\text{g}} a_{\text{h}} \dots}{a_{\text{a}} a_{\text{b}} \dots}$$

## 19-7 $\Delta G^\circ$ and $K_{\text{eq}}$ as Functions of Temperature

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

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{T\Delta S^\circ}{RT}$$

$$\ln K_{\text{eq}} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

# Van't Hoff Equation

If we evaluate this equation for a change in temperature:

$$\ln \frac{K_{\text{eq}2}}{K_{\text{eq}1}} = \left( \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \right) - \left( \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \right)$$

$$\ln \frac{K_{\text{eq}2}}{K_{\text{eq}1}} = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

**TABLE 19.3**    **Equilibrium Constants,  $K_p$ , for the Reaction**  
 $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$   
**at Several Temperatures**

$T, \text{K}$	$1/T, \text{K}^{-1}$	$K_p$	$\ln K_p$
800	$12.5 \times 10^{-4}$	$9.1 \times 10^2$	6.81
850	$11.8 \times 10^{-4}$	$1.7 \times 10^2$	5.14
900	$11.1 \times 10^{-4}$	$4.2 \times 10^1$	3.74
950	$10.5 \times 10^{-4}$	$1.0 \times 10^1$	2.30
1000	$10.0 \times 10^{-4}$	$3.2 \times 10^0$	1.16
1050	$9.52 \times 10^{-4}$	$1.0 \times 10^{-4}$	0.00
1100	$9.09 \times 10^{-4}$	$3.9 \times 10^{-1}$	-0.94
1170	$8.5 \times 10^{-4}$	$1.2 \times 10^{-1}$	-2.12

# Temperature Dependence of $K_{eq}$

Assume  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary significantly with temperature.

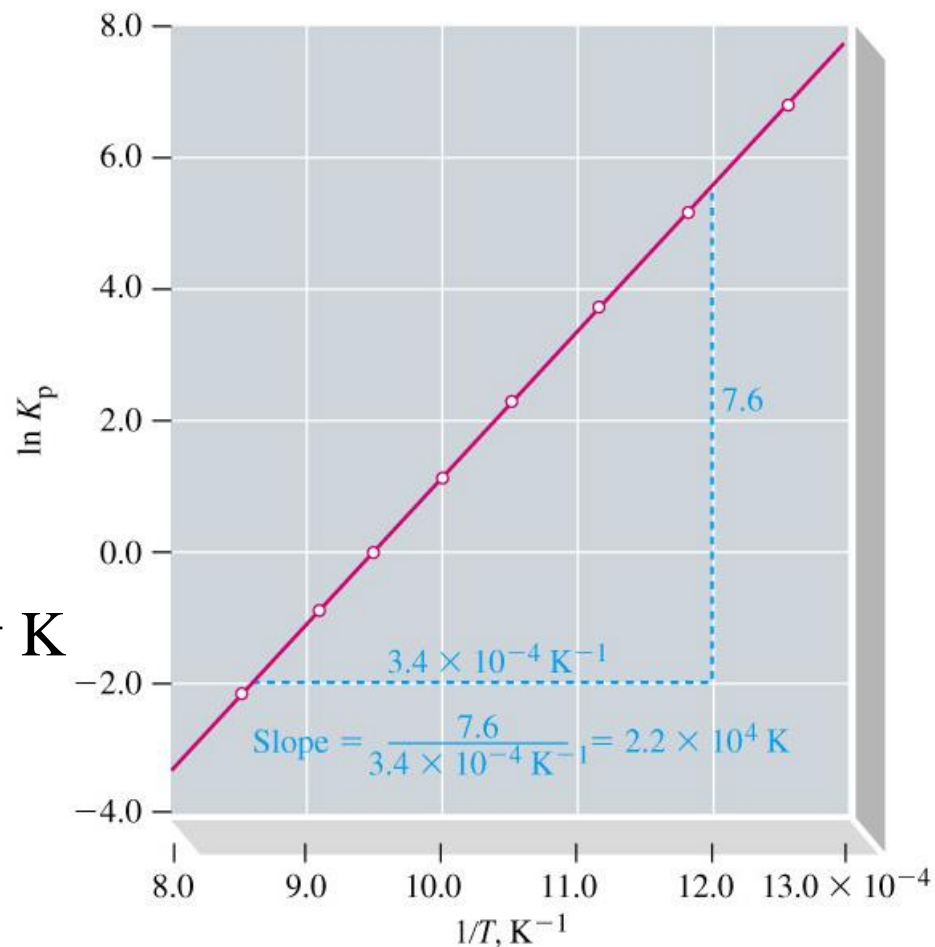
$$\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$slope = \frac{-\Delta H^\circ}{R}$$

$$-\Delta H^\circ = R \times slope$$

$$= -8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 2.2 \times 10^4 \text{ K}$$

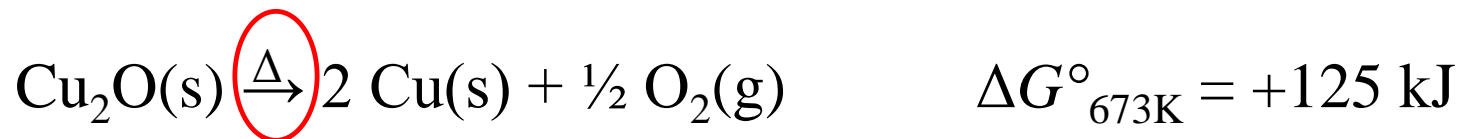
$$= -1.8 \times 10^2 \text{ kJ mol}^{-1}$$



## 19-8 Coupled Reactions

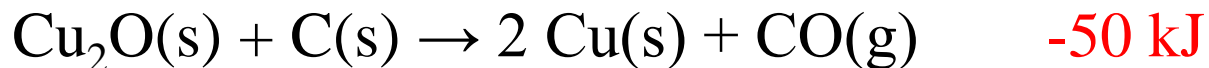
- ◆ In order to drive a non-spontaneous reactions we changed the conditions (i.e. temperature or electrolysis).
- ◆ Another method is to couple two reactions.
  - One with a positive  $\Delta G$  and one with a negative  $\Delta G$ .
  - Overall spontaneous process.

# Smelting Copper Ore



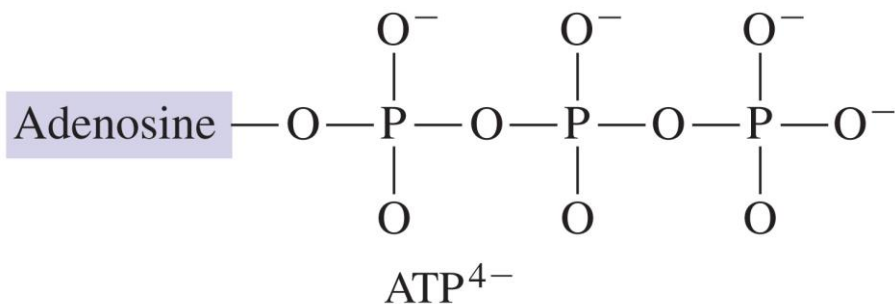
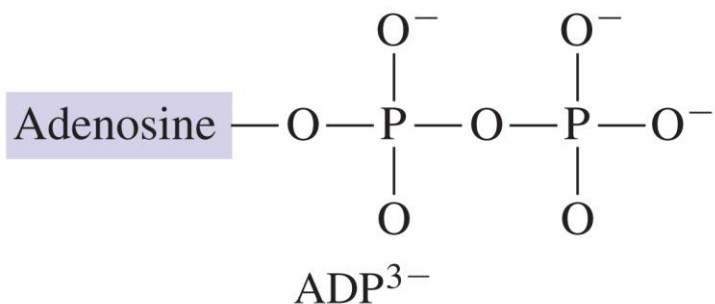
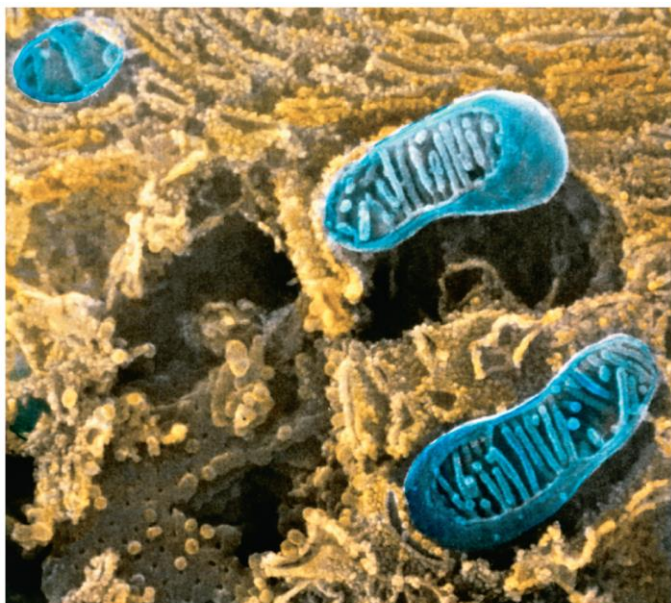
*Non-spontaneous reaction:*  $\text{Cu}_2\text{O(s)} \rightarrow 2 \text{Cu(s)} + \cancel{\frac{1}{2} \text{O}_2\text{(g)}} + 125 \text{ kJ}$

*Spontaneous reaction:*  $\text{C(s)} + \cancel{\frac{1}{2} \text{O}_2\text{(g)}} \rightarrow \text{CO(g)} \quad -175 \text{ kJ}$



*Spontaneous reaction!*

# Focus On Coupled Reactions in Biological Systems





# The Biological Standard State



$$\Delta G^\circ = -9.2 \text{ kJ mol}^{-1}$$

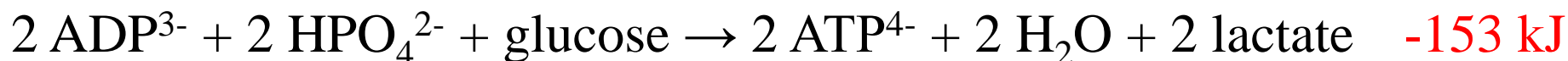
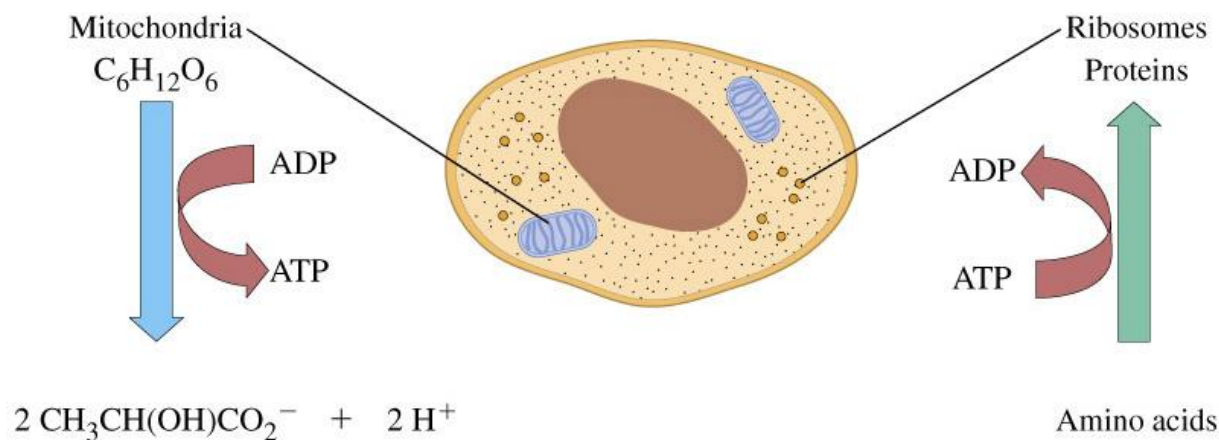
$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{ATP}} a_{\text{H}_2\text{O}}}{a_{\text{ADP}} a_{\text{P}_i} a_{\text{H}_3\text{O}^+}}$$

*But  $[\text{H}_3\text{O}^+] = 10^{-7} \text{ M}$  not  $1.0 \text{ M}$ .*

$$\begin{aligned}\Delta G &= -9.2 \text{ kJ mol}^{-1} + 41.6 \text{ kJ mol}^{-1} \\ &= +32.4 \text{ kJ mol}^{-1} = \Delta G^{\circ'}\end{aligned}$$

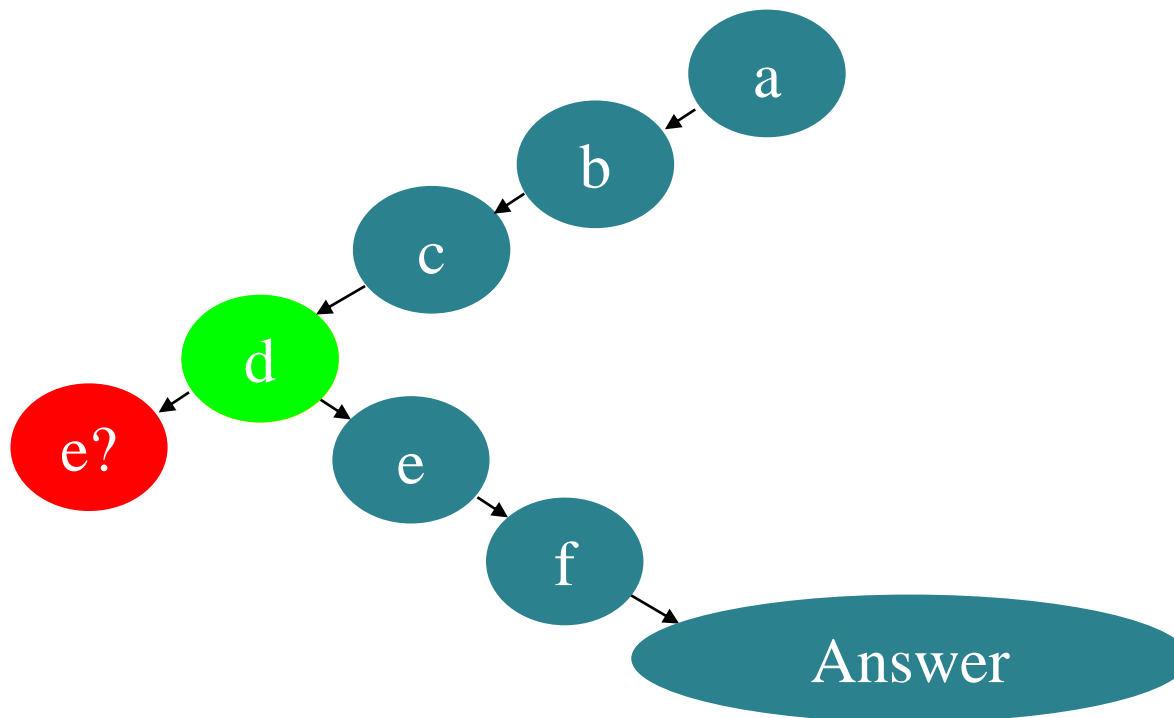
*ADP to ATP is not spontaneous and biological systems use glucose.*

# Focus On Coupled Reactions in Biological Systems



# End of Chapter Questions

- ◆ Work a problem from both ends to find the key log.



# End of Chapter Questions

- ◆ Work a problem from both ends to find the key log.

