# The first law:  transformation of energy into heat and work

Chemical reactions can be used to provide heat and for doing work.

Compare fuel value of different compounds.

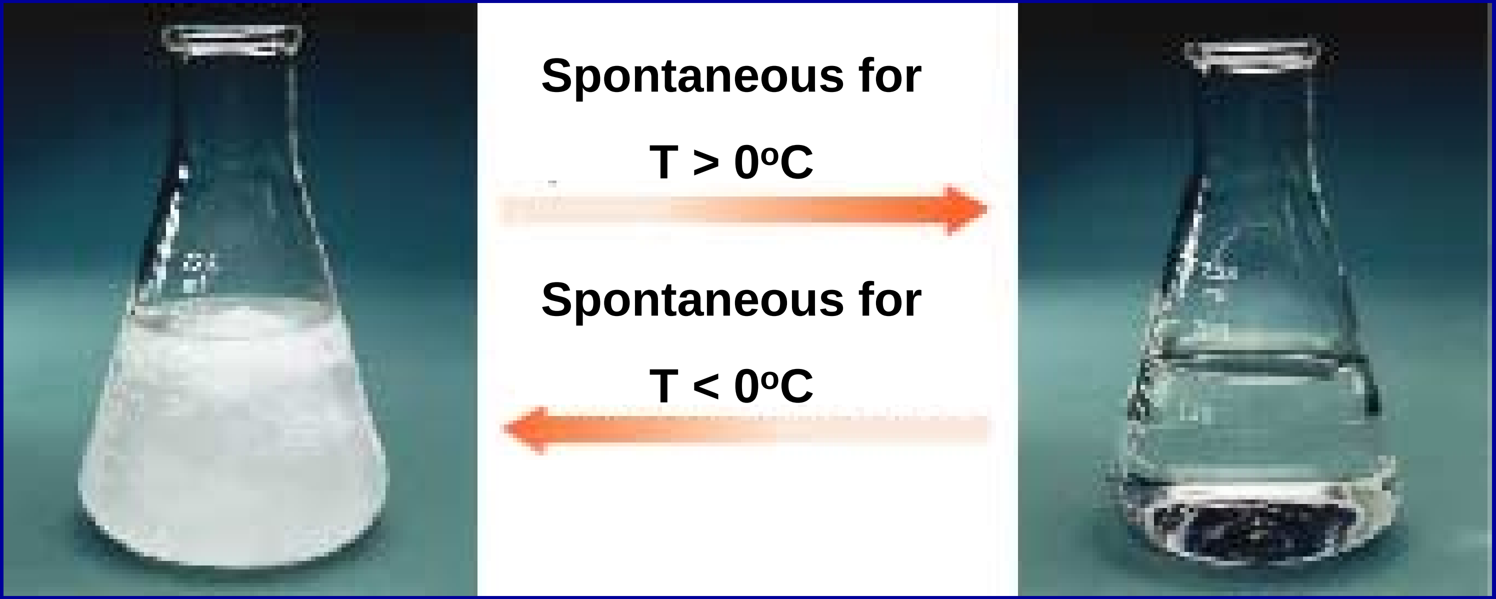
**What drives these reactions to proceed in the direction they do?**

**Why does combustion proceed spontaneously?**

**Why does NaCl dissolve spontaneously in water?**

# Spontaneous Processes

A spontaneous process is one that occurs by itself, given enough time, without external intervention



# Reversible vs Irreversible Processes

## Reversible processes

Are at equilibrium

Driving force is only infinitesimally greater than the opposing force

Process occurs in a series of infinitesimal steps, and at each step the system in at equilibrium with the surroundings

Would take an infinite amount of time to carry out

## Irreversible Process

Not at equilibrium; a spontaneous process

Reversal cannot be achieved by changing some variable by an infinitesimal amount

**Which direction will an irreversible process proceed to establish equilibrium?**

**What thermodynamic properties determine the direction of spontaneity?**

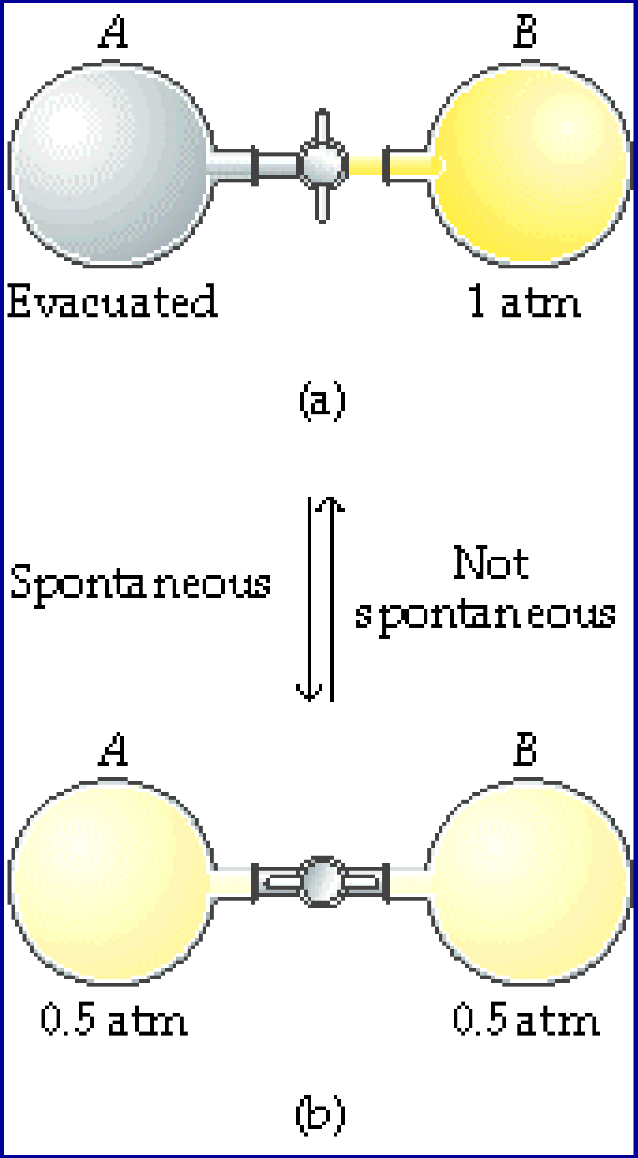
**The change in enthalpy during a reaction is an important factor in determining whether a reaction is favored in the forward or reverse direction.**

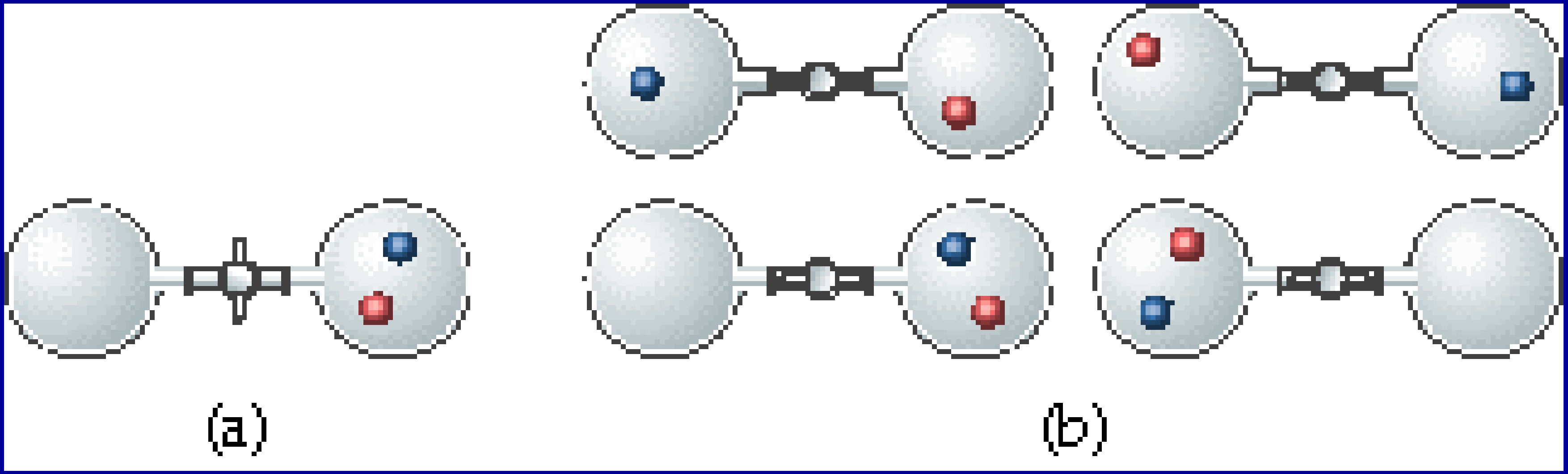
**Are exothermic reactions more likely to be spontaneous than endothermic?**

**Not necessarily - for example, melting of ice is spontaneous above $0^{o}$C and is endothermic.**

# Entropy

Consider the following expansion of a gas into a vacuum.

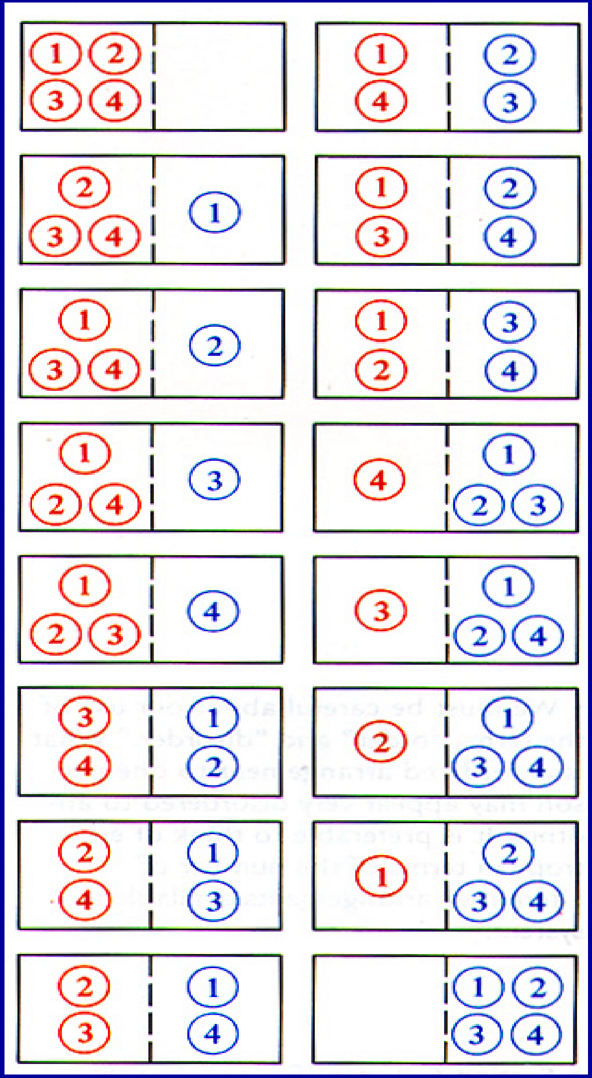




**When the valve is open, there are four possible arrangements or STATES; all states are equal in energy**

**Opening the valve allows this system of two particles, more arrangements; higher degree of DISORDER.**

**As the number of particles increases in the system, the number of possible arrangements that the system can be in increases**



**Processes in which the disorder of the system increases tend to occur spontaneously.**

Ice melts spontaneously at $T > 0^{o}C$ even though it is an endothermic process.

The molecules of water that make up the ice crystal lattice are held rigidly in place.

When the ice melts the water molecules are free to move around, and hence more disordered than in the solid lattice.

Melting increases the disorder of the system.

A similar situation arises in the dissolution of solid NaCl in water.

**The entropy, S, of a system quantifies the degree of disorder or randomness in the system; larger the number of arrangements available to the system, larger is the entropy of the system.**

**If the system is more disordered, entropy is larger**

**Like enthalpy, entropy is a state function; $\Delta S$ depends on the initial and final entropies of the system**

$$\Delta S = S_{final} - S_{initial}$$

If $\Delta S > 0 \Rightarrow S_{final} > S_{initial}$

If $\Delta S < 0 \Rightarrow S_{final} < S_{initial}$

So melting or vaporization increases entropy; freezing or condensation decrease entropy.

Likewise, expansion of a gas increases entropy, compression of a gas decreases entropy.

For a molecule: $S_{gas} > S_{liquid} > S_{solid}$

Comparing molecules, larger molecules tend to have higher entropy than smaller.

Example: entropy of $H_2(g)$ < entropy of $CCl_4(g)$

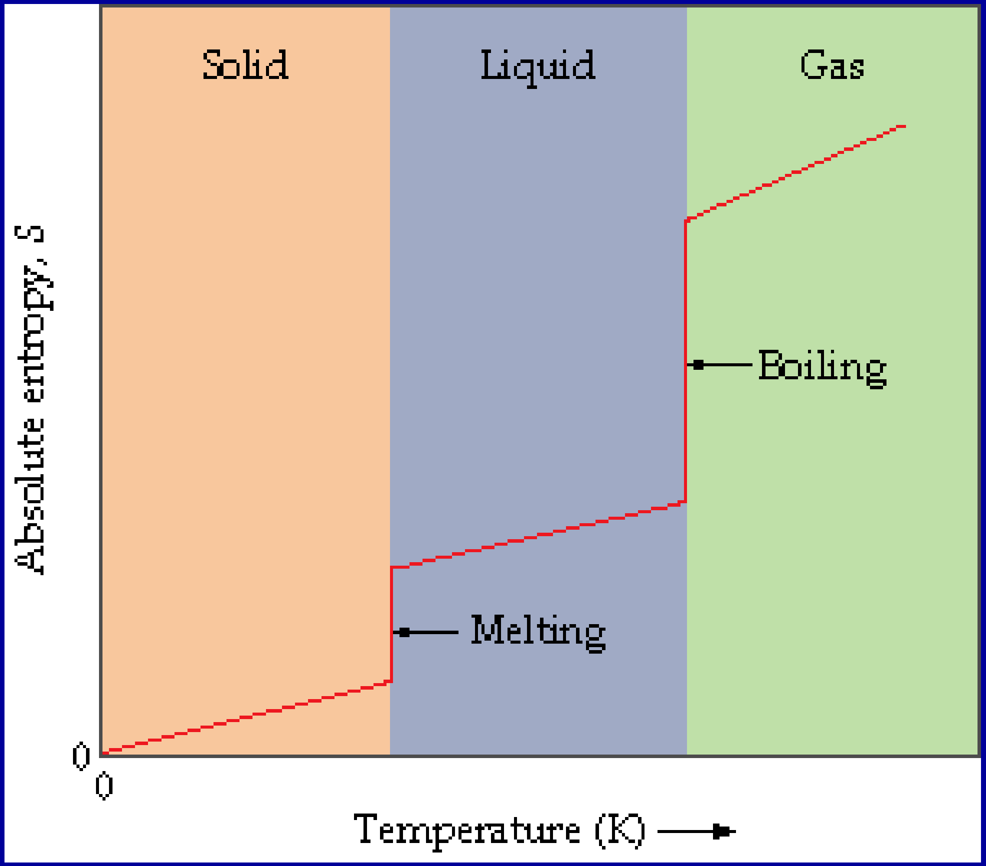
# Entropy and Temperature

**Third law of thermodynamics :**

**The entropy of a perfect crystalline substance at equilibrium approaches zero as the temperature approaches absolute zero.**

**For an isothermal process (constant temperature), change in entropy is defined as:**

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


Solid
Liquid
Gas
Boiling
Melting
Absolute entropy, S
0
0
Temperature (K)

The change in entropy, $\Delta S$, accompanying a phase transition, at constant pressure, can be expressed as:

$$\Delta S = \frac{\Delta H}{T}$$

For example, the $\Delta S$ accompanying vaporization at the normal boiling point of the liquid ($T_b$):

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

# Entropies of Reactions

Consider the following gas phase reaction:

$$2NO(g) + O_2\ (g) \text{ --> } 2NO_2(g)$$

Any reaction which results in a decrease in the number of gas phase molecules is accompanied by a decrease in entropy.

Reactions that increase the number of gas phase molecules tend to be accompanied by positive changes in entropy.

Dissolution reactions are typically accompanied by an increase in entropy since the solvated ions are more disordered than the ions in the crystal lattice.

However, there are examples where the opposite is true:

$$MgCl_2(s) \dashrightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$$

Is accompanied by a negative change in entropy.

The **standard molar entropy, $S^o$**, is the **absolute** entropy of one mole of substance at 298.15K.

Units of molar entropy - J $K^{-1}$mol$^{-1}$

For the general reaction

$$aA + bB \dashrightarrow cC + dD$$

the standard entropy change is

$$\Delta S^o = cS^o\,(C) + dS^o\,(D) - aS^o\,(A) - bS^o\,(B)$$

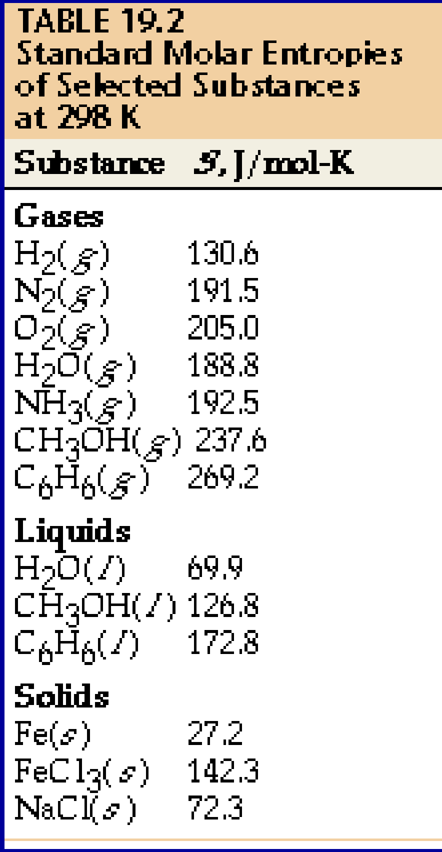


TABLE 19.2
Standard Molar Entropies of Selected Substances at 298 K

| Substance | $S^o$, J/mol-K |
|---|---|
| **Gases** | |
| $H_2(g)$ | 130.6 |
| $N_2(g)$ | 191.5 |
| $O_2(g)$ | 205.0 |
| $H_2O(g)$ | 188.8 |
| $NH_3(g)$ | 192.5 |
| $CH_3OH(g)$ | 237.6 |
| $C_6H_6(g)$ | 269.2 |
| **Liquids** | |
| $H_2O(l)$ | 69.9 |
| $CH_3OH(l)$ | 126.8 |
| $C_6H_6(l)$ | 172.8 |
| **Solids** | |
| $Fe(s)$ | 27.2 |
| $FeCl_3(s)$ | 142.3 |
| $NaCl(s)$ | 72.3 |

**The tabulated standard molar entropies of compounds can be used to calculate the standard entropy change accompanying a reaction.**

**Note: the standard molar entropies of the most stable forms of elements are not zero at 298.15 K.**

**As dictated by the 3rd law, entropy of a compound is zero at absolute zero (0K)**

Calculate the $\Delta S^o$ for the reaction:

$$N_2(g) + 3H_2\,(g) \dashrightarrow 2NH_3(g)$$

$$\Delta S^o = 2S^o\,(NH_3(g)) - S^o\,(N_2(g)) - 3S^o\,(H_2(g))$$

Using the tabulated values

$$\Delta S^o = -198.3\ J/K$$

Reaction is accompanied by a decrease in entropy - why?

# Conditions for spontaneous processes

The change in enthalpy does not necessarily determine whether a process will be spontaneous or not.

How about change in entropy?

While many spontaneous processes occur with an increase in entropy, there are examples of spontaneous processes that occur with the system's entropy decreasing.

For example, below 0°C, water spontaneously freezes even though the process is accompanied by a decrease in entropy.

**What happens to the entropy of the surroundings when the entropy of the system changes?**

**For example, when water freezes, the heat liberated is taken up by the surroundings, whose entropy increases.**

**Define the change in entropy of the universe, $\Delta S_{universe}$:**

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$$

**The second law of thermodynamics states:**

**For a process to be spontaneous, the entropy of the universe must increase.**

**$\Delta S_{universe} = \Delta S_{system} + \Delta s_{surrounding} > 0$ for a spontaneous process**

If $\Delta S_{universe} < 0$ => non-spontaneous process

If $\Delta S_{universe} > 0$ => spontaneous process

If $\Delta S_{universe} = 0$ => the process is at equilibrium

Need to know $\Delta S_{universe}$ to determine if the process will proceed spontaneously.

# The Gibbs Free Energy Function

The **Gibbs free energy function, G**, allows us to focus on the the thermodynamic properties of the system.

At constant pressure and temperature:

$$G = H - T S$$

Units of G - J

G is a state function, like H and S

The change in the free energy function of the system accompanying a process at constant P and T is

$$\Delta G_{syst} = \Delta H_{syst} - T\Delta S_{syst}$$

What is the sign of $\Delta G$ for a spontaneous reaction?

At constant T

$$\Delta S_{surr} = \frac{q_{surr}}{T}$$

The change in heat of the system during a process, is equal in magnitude but opposite in sign to the heat change of the surroundings.

$$q_{surr} = -q_{syst}$$

Hence,

$$\Delta S_{surr} = \frac{q_{surr}}{T} = -\frac{q_{syst}}{T}$$

# At constant pressure:

$$q_{syst} = q_p = \Delta H$$

$$\Delta S_{surr} = -\frac{\Delta H_{syst}}{T}$$

$\Delta S_{universe} = \Delta S_{syst} + \Delta S_{surrounding} > 0$ for a spontaneous process

$$\Delta S_{universe} = \Delta S_{syst} - \frac{\Delta H_{syst}}{T} > 0$$

$$\Delta S_{universe} = \Delta S_{syst} - \frac{\Delta H_{syst}}{T} > 0$$

Mutliplying by T

$T\ \Delta S_{syst} - \Delta H_{syst} > 0$ for a spontaneous reaction

$\Rightarrow \Delta H_{syst} - T\ \Delta S_{syst} < 0$ for a spontaneous reaction

$\Rightarrow \Delta G_{syst} < 0$ for a spontaneous reaction

For a process at constant P and T

$\Delta G_{syst} < 0$ => spontaneous

$\Delta G_{syst} > 0$ => non spontaneous

$\Delta G_{syst} = 0$ => equilibrium

The sign of $\Delta G$ is determined by the relative magnitudes of $\Delta H$ and $T\Delta S$ accompanying the process

$$\Delta G_{syst} = \Delta H_{syst} - T\Delta S_{syst}$$

Or simply: $\Delta G = \Delta H - T\Delta S$

# The Gibbs Free Energy Function and Phase Transitions

$H_2O(l) \dashrightarrow H_2O(s)$

Normal freezing point of $H_2O$ = 273.15K

The measured change in enthalpy is the enthalpy of fusion - enthalpy change associated when one mole of liquid water freezes at 1atm and 273.15K

$\Delta H = -6007J$

Entropy change at 273.15K

$$\Delta S = \frac{\Delta H}{T} = \frac{-6007\ J}{273.15K} = -21.99\ J/K$$

$\Delta G = \Delta H - T\Delta S = -6007J - (273.15K)(-21.99J/K) = 0J$

Water and ice are at equilibrium at 273.15 K and 1atm

As water is cooled by 10K below 273.15K to 263.15K

In calculating $\Delta G$ at 263.15K assume that $\Delta H$ and $\Delta S$ do not change

$\Delta G = \Delta H - T\Delta S = -6007J - (263.15K)(-21.99J/K) = -220J$

Since $\Delta G < 0$ water spontaneously freezes

At 10K above the freezing point, 283.15K

$\Delta G = \Delta H - T\Delta S = -6007J - (283.15K)(-21.99J/K) = 219J$

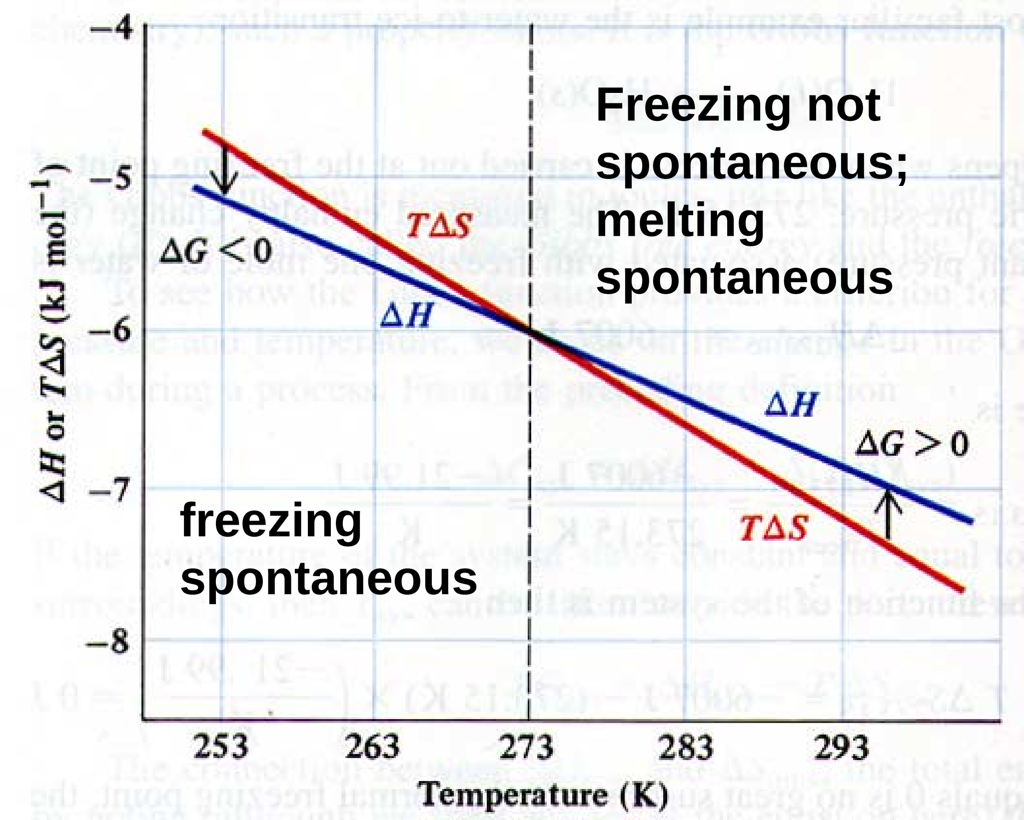
Since $\Delta G > 0$ water does not spontaneously freeze at 283.15K, 10K above the normal freezing point of water

Above 273.15K, the reverse process is spontaneous - ice melts to liquid water.

**For phase transitions, at the transition temperature, the system is at equilibrium between the two phases.**

**Above or below the transition temperature, the phase is determined by thermodynamics.**

**$\Delta$G is the driving force for a phase transition.**



**Plot of ΔH and TΔS vs T for the freezing of water. At 273.15 K the system is at equilibrium, ΔG = 0**

# Standard Free-Energy Changes

The standard molar free energy function of formation, $\Delta G_f^o$, is the change in the free energy for the reaction in which one mole of pure substance, in its standard state is formed from the most stable elements of its constituent elements, also in their standard state.

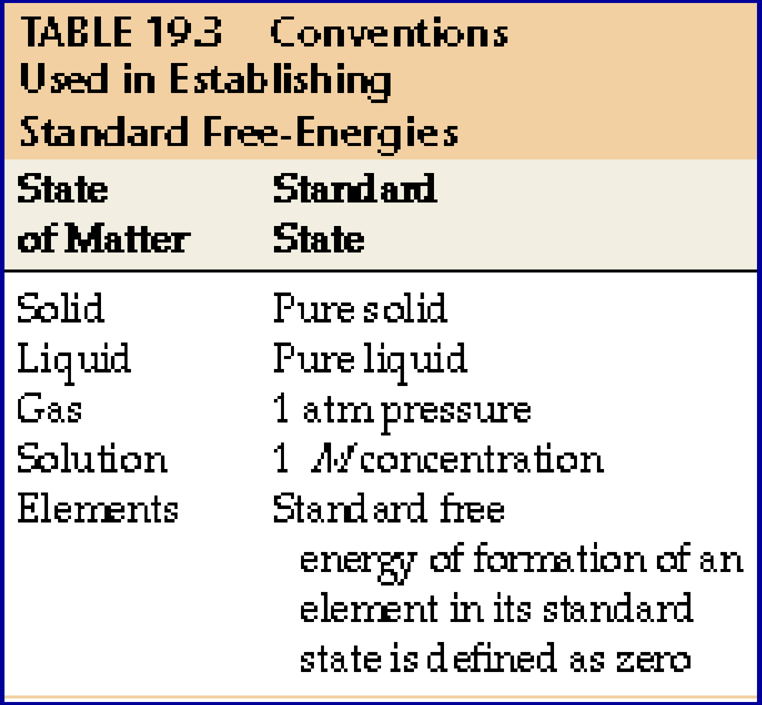


TABLE 19.3 Conventions Used in Establishing Standard Free-Energies

| State of Matter | Standard State |
|---|---|
| Solid | Pure solid |
| Liquid | Pure liquid |
| Gas | 1 atm pressure |
| Solution | 1 *M* concentration |
| Elements | Standard free energy of formation of an element in its standard state is defined as zero |

$C(s) + O_2(g) \text{ --> } CO_2(g)$

Calculate $\Delta G_f^o$, for this reaction.

$\Delta G_f^o = \Delta H_f^o - T\ \Delta S^o$

$\Delta H_f^o(CO_2(g)) = -393.51$ kJ

$\Delta S^o = S^o(CO_2(g)) - S^o(C(s)) - S^o(O_2(g)) = 2.86\ J\ K^{-1}$

$\Delta G_f^o = -394.36$ kJ at 298K

# Standard Free Energies of Reactions

For a reaction: aA + bB --> cC + dD

$$\Delta G^o = c\,\Delta G_f^o(C) + d\,\Delta G_f^o(D) - a\,\Delta G_f^o(A) - b\,\Delta G_f^o(B)$$

$$\Delta G^o = \Sigma\,\Delta G_f^o\,(\text{products}) - \Sigma\,\Delta G_f^o\,(\text{reactants})$$

The standard free energy of formation of elements in their most stable form at 298.15K has been set to zero.

$$\Delta G^o = \Delta H^o - T\,\Delta S^o$$

$$\Delta H^o = \Sigma\,\Delta H_f^o\,(\text{products}) - \Sigma\,\Delta H_f^o\,(\text{reactants})$$

$$\Delta S^o = \Sigma\,S^o\,(\text{products}) - \Sigma\,S^o\,(\text{reactants})$$

Problem: Calculate the standard free-energy change for the following reaction at 298K:

$$N_2(g) + 3H_2\ (g) \dashrightarrow 2NH_3(g)$$

Given that $\Delta G_f^o[NH_3(g)] = -16.66$ kJ/mol.

What is the $\Delta G^o$ for the reverse reaction?

Since the reactants $N_2(g)$ and $H_2(g)$ are in their standard state at 298 K their standard free energies of formation are defined to be zero.

$$\Delta G^o = 2\,\Delta G_f^o[NH_3(g)] - \Delta G_f^o[N_2(g)] - 3\,\Delta G_f^o[H_2(g)]$$

$$= 2 \times -16.66 = -33.32 \text{ kJ/mol}$$

For the reverse reaction: $2NH_3(g) \dashrightarrow N_2(g) + 3H_2\ (g)$

$$\Delta G^o = +33.32 \text{ kJ/mol}$$

## Problem:

$$C_3H_8(g) + 5O_2(g) \dashrightarrow 3CO_2\,(g) + 4H_2O(l) \quad \Delta H^o = -\,2220\text{ kJ}$$

a) Without using information from tables of thermodynamic quantities predict whether $\Delta G^o$ for this reaction will be less negative or more negative than $\Delta H^o$.

b) Use thermodynamic data calculate $\Delta G^o$ for this reaction.

Whether $\Delta G^o$ is more negative or less negative than $\Delta H^o$ depends on the sign of $\Delta S^o$ since $\Delta G^o = \Delta H^o - T\,\Delta S^o$

The reaction involves 6 moles of gaseous reactants and produces 3 moles of gaseous product

=> $\Delta S^o < 0$ (since fewer moles of gaseous products than reactants)

Since $\Delta S^o < 0$ and $\Delta H^o < 0$ and $\Delta G^o = \Delta H^o - T\,\Delta S^o$

=> $\Delta G^o$ is less negative than $\Delta H^o$

b)

$\Delta G^o = 3\Delta G_f^o(CO_2\ (g))+4\Delta G_f^o(H_2O(l)-\Delta G_f^o(C_3H_8(g))-5\Delta G_f^o(O_2(g))$

$= 3(-394.4) + 4(-237.13) - (-23.47) - 5(0)$

$= -2108$ kJ

Note: $\Delta G^o$ is less negative than $\Delta H^o$

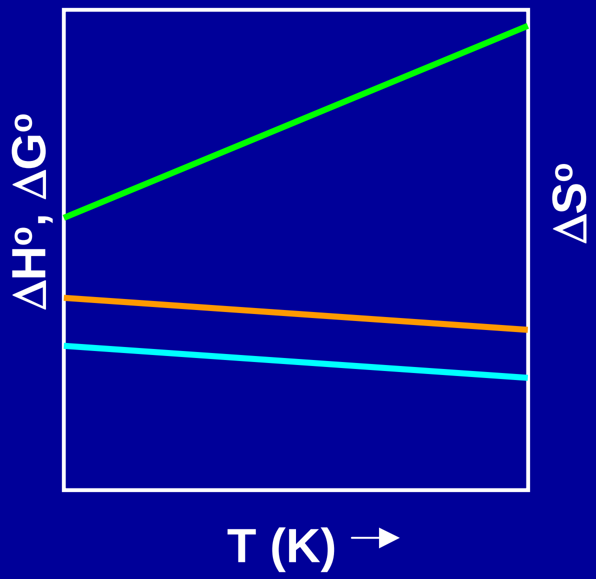
# Effect of temperature on $\Delta G^o$

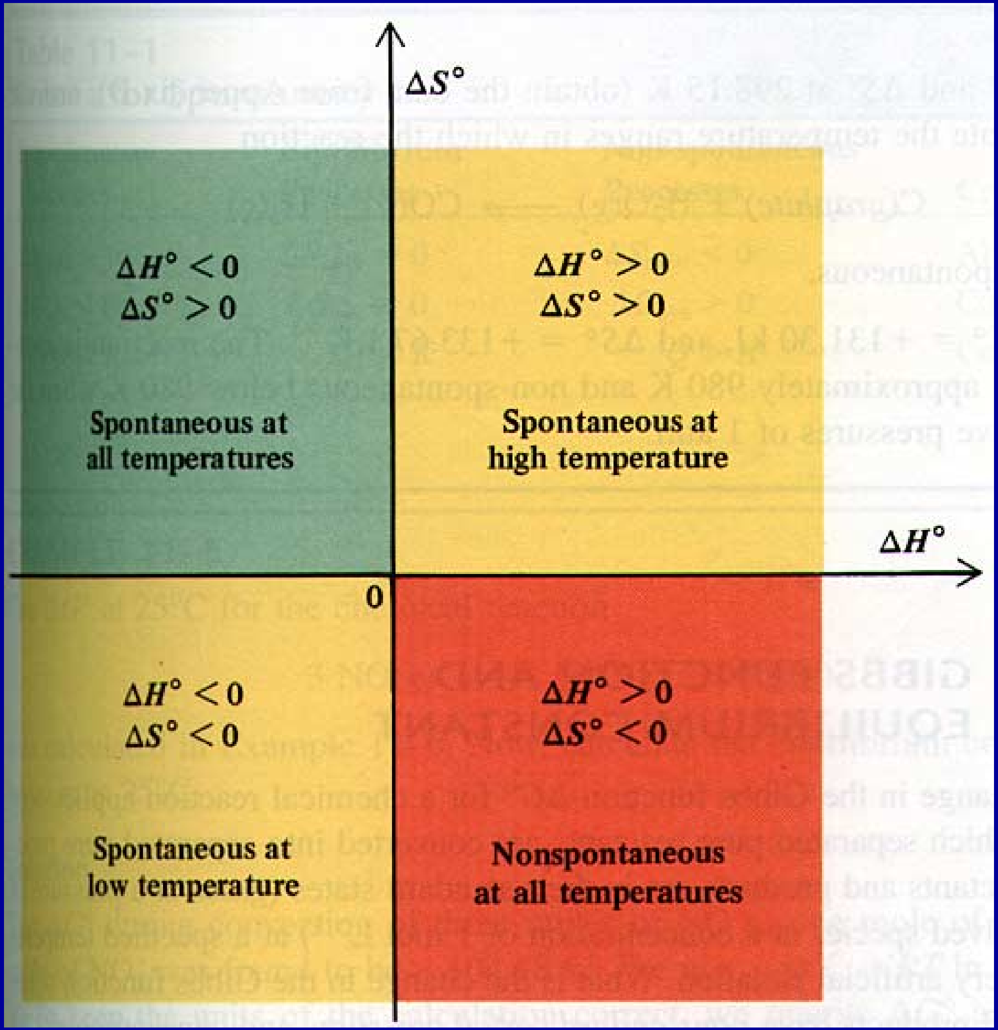
**Values of $\Delta G^o$ calculated using the tabulated values of $\Delta G_f^o$ apply only at 298.15K.**

**For other temperatures the relation:**

**$\Delta G = \Delta H^o - T\,\Delta S^o$**

**can be used, as long as $\Delta H^o$ and $\Delta S^o$ do not vary much with temperature**





$$\Delta G = \Delta H^o - T\,\Delta S^o$$

**At equilibrium $\Delta G^o = 0$** $\quad$ $$T_{eq} = \frac{\Delta H^o}{\Delta S^o}$$

**If both $\Delta H^o$ and $\Delta S^o$ are > 0, then temperatures above $T_{eq}$ the reaction is spontaneous, but below $T_{eq}$ reaction is non-spontaneous.**

**If both $\Delta H^o$ and $\Delta S^o$ are negative, reaction is spontaneous below $T_{eq}$.**

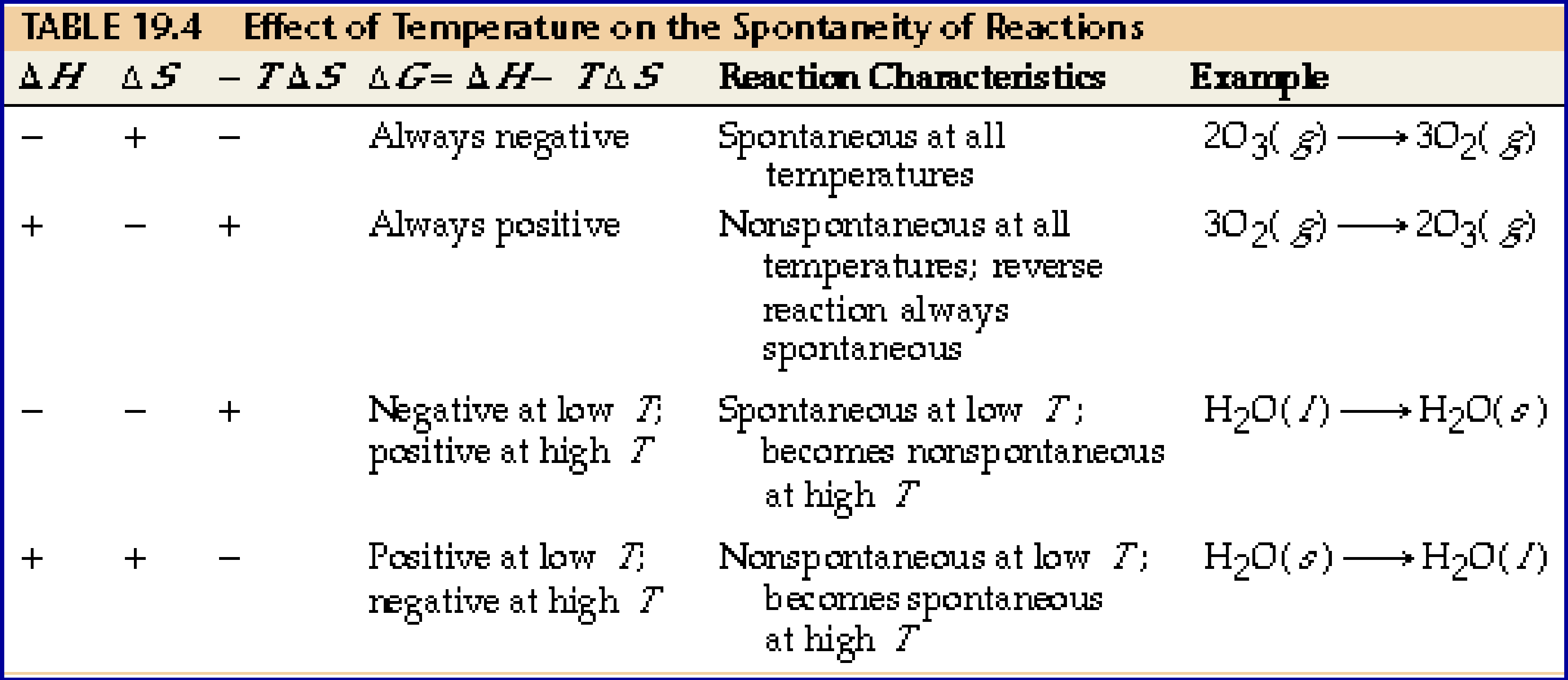


TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

| $\Delta H$ | $\Delta S$ | $-T\Delta S$ | $\Delta G = \Delta H - T\Delta S$ | Reaction Characteristics | Example |
|---|---|---|---|---|---|
| − | + | − | Always negative | Spontaneous at all temperatures | $2O_3(g) \longrightarrow 3O_2(g)$ |
| + | − | + | Always positive | Nonspontaneous at all temperatures; reverse reaction always spontaneous | $3O_2(g) \longrightarrow 2O_3(g)$ |
| − | − | + | Negative at low $T$; positive at high $T$ | Spontaneous at low $T$; becomes nonspontaneous at high $T$ | $H_2O(l) \longrightarrow H_2O(s)$ |
| + | + | − | Positive at low $T$; negative at high $T$ | Nonspontaneous at low $T$; becomes spontaneous at high $T$ | $H_2O(s) \longrightarrow H_2O(l)$ |

Problem: The normal boiling point is the temperature at which a pure liquid is in equilibrium with its vapor at 1atm.

a) write the chemical equation that defines the normal boiling point of liquid $CCl_4$

b) what is the value of $\Delta G^o$ at equilibrium?

c) Use thermodynamic data to estimate the boiling point of $CCl_4$.

a) $CCl_4(l) \rightleftharpoons CCl_4(g)$

b) At equilibrium $\Delta G = 0$. In any equilibrium for a normal boiling point, both the liquid and gas are in their standard states

Hence, $\Delta G^o = 0$.

c) $\Delta G^o = \Delta H^o - T\,\Delta S^o$ and since for the system is at equilibrium, $\Delta G^o = 0$

$$\Delta H^o - T\,\Delta S^o = 0$$

$$T = \frac{\Delta H^o}{\Delta S^o}$$

where for this system T is the boiling point

To determine the boiling point accurately we need the values of $\Delta H^o$ and $\Delta S^o$ for the vaporization process at the boiling point of $CCl_4$

However, if we assume that these values do not change significantly with temperature we can use the values of $\Delta H^o$ and $\Delta S^o$ at 298K from thermodynamic tables.

$\Delta H^{o}$ = (1mol)(-106.7 kJ/mol) - (1mol)(-139.3kJ/mol) = 32.6 kJ

$\Delta S^{o}$ = (1mol)(309.4 J/mol-K) -(1mol)(214.4 J/mol-K) = 95.0 J/K

$$T_b \sim \frac{\Delta H^{o}}{\Delta S^{o}} = \frac{32.6\ \text{kJ}}{0.095\ \text{kJ/K}} = 343\ \text{K}$$

(normal boiling point of $CCl_4$ is 338 K)

# The Gibbs Function and the Equilibrium Constant

For any chemical reaction, the free-energy change under non standard conditions, $\Delta G$, is

$$\Delta G = \Delta G^{o} + R\,T \ln Q$$

Q - reaction quotient

aA + bB -> cC + dD

$$Q = \frac{p_C^{c}\,p_D^{d}}{p_A^{A}\,p_B^{b}}$$

$$Q = \frac{[C]^{c}\,[D]^{d}}{[A]^{a}\,[B]^{b}}$$

Under standard conditions, reactants and products are in their standard states => $Q = 1$; hence $\ln Q = 0$ and $\Delta G = \Delta G^{o}$

At equilibrium $Q = K \Rightarrow \Delta G = 0$

$\Delta G^o = - R\,T \ln K$ or $K = e^{-\Delta G^o/RT}$

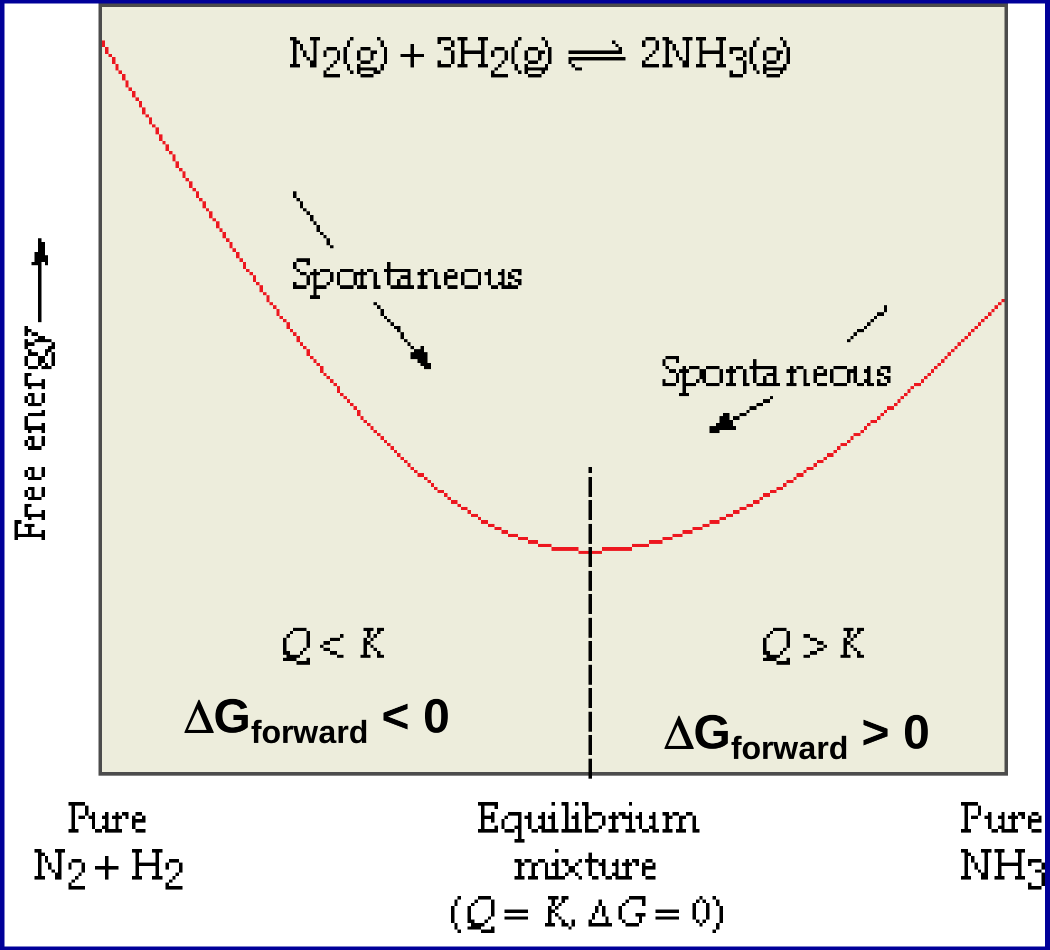
$$\Delta G = \Delta G^o + R\,T \ln Q = - RT \ln K + RT \ln Q$$

$$\Delta G = R\,T \ln \frac{Q}{K}$$

If $Q < K \Rightarrow \Delta G < 0$

If $Q > K \Rightarrow \Delta G > 0$

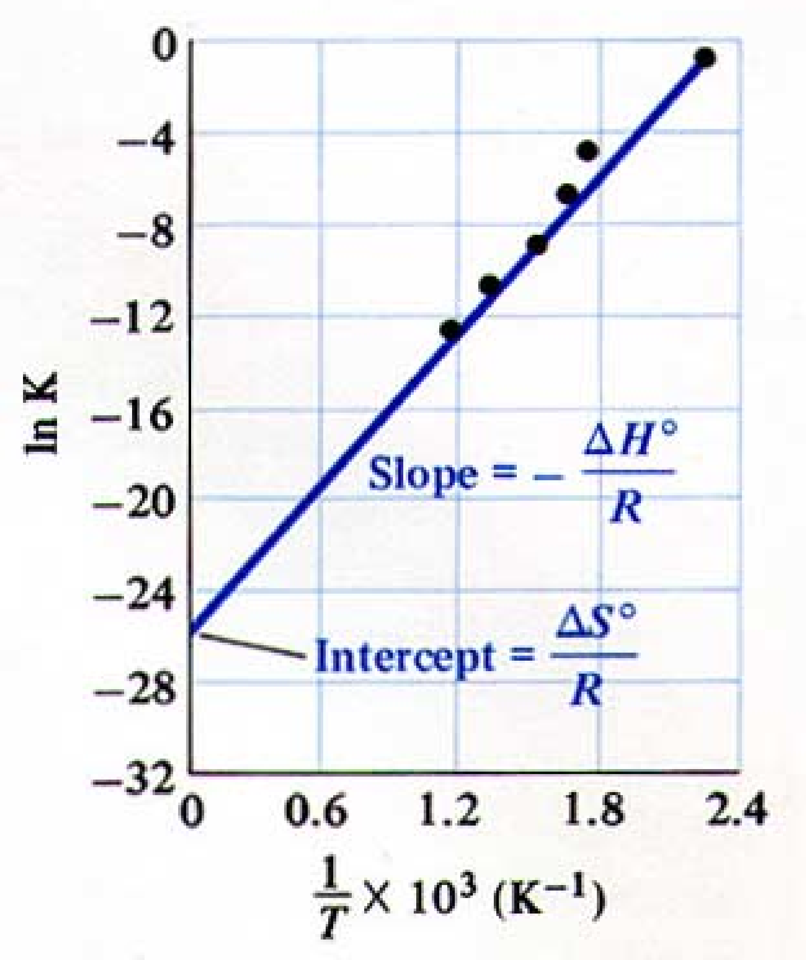
If $Q = K \Rightarrow \Delta G = 0$



**ΔG can be considered to be the slope of the line at any point along the curve. At equilibrium when Q=K, the slope = 0 and hence ΔG = 0**

# Temperature Dependence of K

$$\ln K = \frac{-\Delta G}{R\,T} = \frac{-\Delta H^o}{R\,T} + \frac{\Delta S^o}{R}$$



If the equilibrium constant of a reaction is known at one temperature and the value of ΔHº is known, then the equilibrium constant at another temperature can be calculated

$$\ln K_1 = \frac{-\Delta H^o}{R\,T_1} + \frac{\Delta S^o}{R}$$

$$\ln K_2 = \frac{-\Delta H^o}{R\,T_2} + \frac{\Delta S^o}{R}$$

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

For the equilibrium between a pure liquid and its vapor, the equilibrium constant is the equilibrium vapor pressure

$$\text{Liquid} \rightleftharpoons \text{Gas} \qquad K = P_{gas}$$

Hence

$$\ln \frac{p_1}{p_2} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Clausius-Clapeyron equation

The Clausius-Clapeyron equation indicates the variation of vapor pressure of a liquid with temperature

# Driving Non-spontaneous Reactions

**Because so many chemical and biological reactions are carried out under conditions of constant pressure and temperature, the magnitude of $\Delta G$ is a useful tool for evaluating reactions.**

**A reaction for which $\Delta G$ is large and negative (like the combustion of gasoline), is much more capable of doing work on the surroundings than a reaction for which $\Delta G$ is small and negative (like the melting of ice).**

The change in free energy for a process equals the maximum amount of work that can be done by the system on its surroundings in a spontaneous process at constant pressure and temperature

$$w_{max} = \Delta G$$

For non-spontaneous reactions ($\Delta G > 0$), the magnitude of $\Delta G$ is a measure of the minimum amount of work that must be done on the system to cause the process to occur.

Many chemical reactions are non-spontaneous.

For example: Cu can be extracted from the mineral chalcolite which contains $Cu_2S$.

The decomposition of $Cu_2S$ is non-spontaneous

$$Cu_2S \text{ --> } 2Cu(s) + S(s) \qquad \Delta G^o = +86.2 \text{ kJ}$$

Work needs to be done on this reaction, and this is done by coupling this non-spontaneous reaction with a spontaneous reaction so that the overall reaction is spontaneous.

Consider the following reaction:

$S(s) + O_2(g) \text{-->} SO_2\ (g)$     $\Delta G^o = -300.4kJ$

Coupling this reaction with the extraction of Cu from $Cu_2S$

$Cu_2S \text{-->} 2Cu(s) + S(s)$     $\Delta G^o = +86.2\ kJ$

$S(s) + O_2(g) \text{-->} SO_2\ (g)$     $\Delta G^o = -300.4kJ$

Net:     $Cu_2S(s) + O_2\ (g) \text{-->} 2Cu(s) + SO_2(g)$     $\Delta G^o = -214.2kJ$

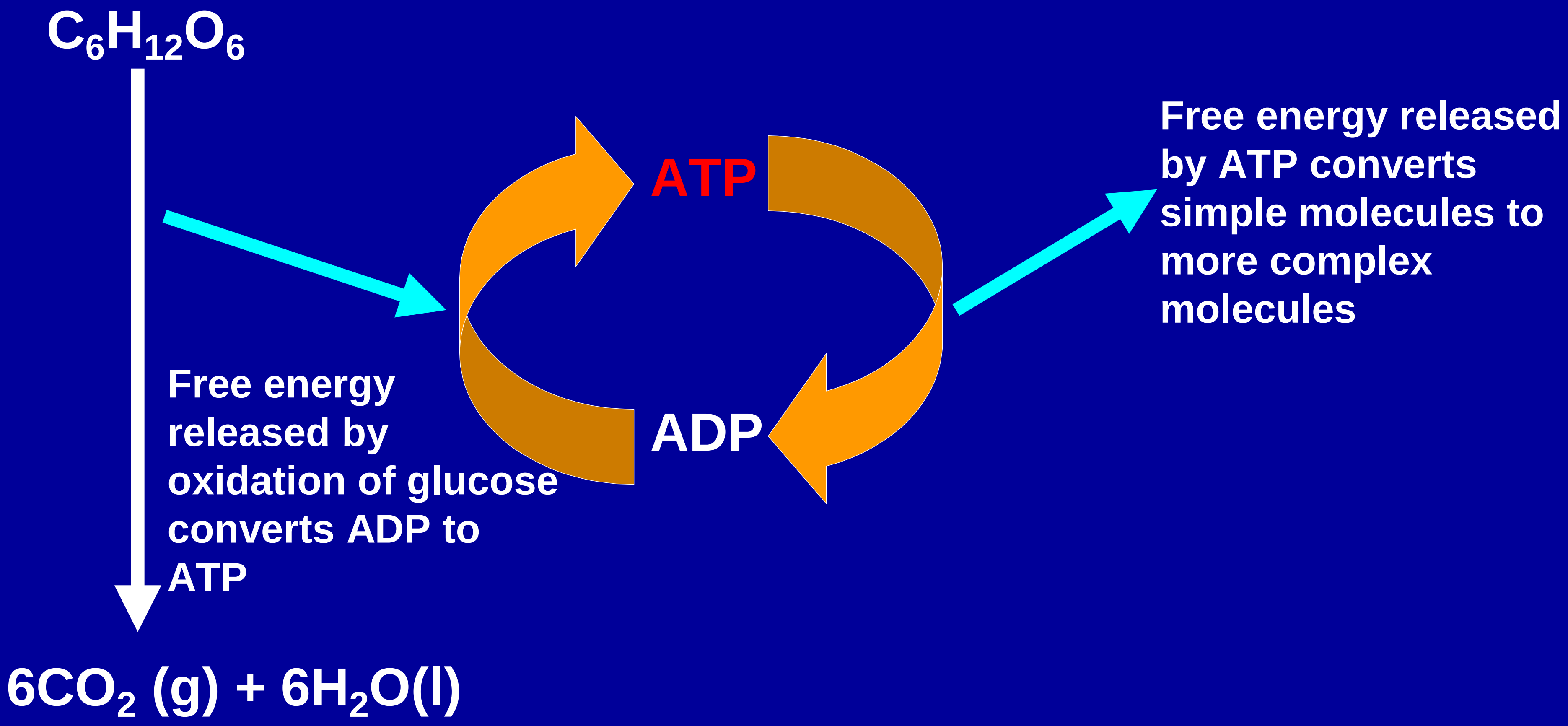
**Biological systems employ the same principle by using spontaneous reactions to drive non-spontaneous reactions.**

**The metabolism of food is the usual source of free energy needed to do the work to maintain biological systems.**

$C_6H_{12}O_6(s) + 6O_2\ (g) \dashrightarrow 6CO_2\ (g) + 6H_2O(l)$

$\Delta H^o = -2803\ kJ$

**The free energy released by the metabolism of glucose is used to convert lower-energy ADP (adenine diphosphate) to higher energy ATP (adenine triphosphate).**



$C_6H_{12}O_6$

ATP

ADP

Free energy released by oxidation of glucose converts ADP to ATP

Free energy released by ATP converts simple molecules to more complex molecules

$6CO_2\,(g) + 6H_2O(l)$

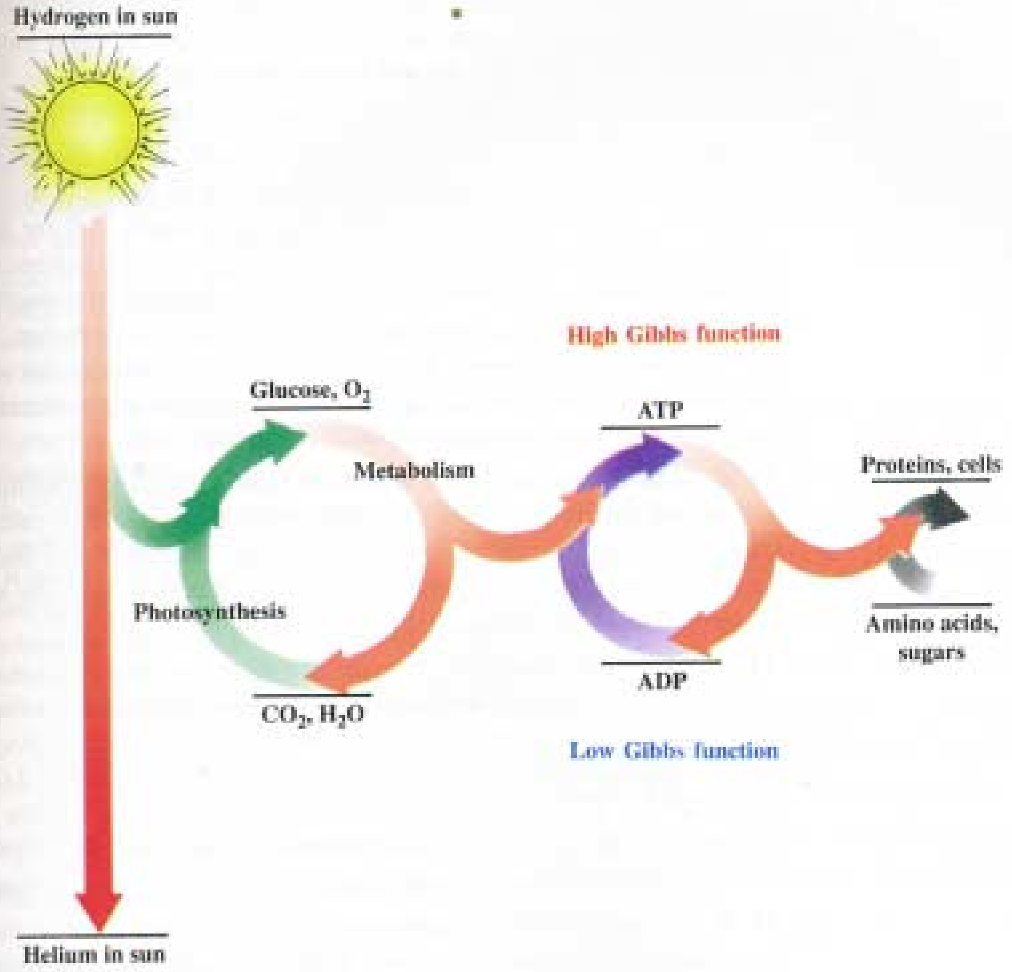


**Figure 11–A** The synthesis of glucose and other sugars in plants, the production of ATP from ADP, and the elaboration of proteins and other biological molecules are all processes in which the Gibbs function of the system must increase. They occur only through coupling to other processes in which the Gibbs function decreases by an even larger amount.