**Topic 4J - Gibbs Free Energy**

# Free Energy

For any physical or chemical process, the overall change in entropy of the universe is the sum of the changes in the system and surroundings:

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

At constant pressure, the heat flow (q) = $\Delta H$. Thus, if only P-V work is done,

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

Hence (at constant temperature),

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

Multiplying through by T:

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

rearranging yields:

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

We now define a new state function, G, the Gibbs Energy, or "Free Energy," to be the R.H.S. of the above equation:

$$\boxed{\Delta G = \Delta H - T\Delta S} = -T\Delta S_{univ}$$

Hence, since processes occur spontaneously only when $\Delta S_{univ} > 0$, then $-\Delta G/T$ must be $> 0$, or $\Delta G$ must be $< 0$, for a spontaneous process.

Since

$$\Delta G = \Delta H - T\Delta S = \Delta U + P\Delta V - T\Delta S$$

          ↑   ↑   ↑

       Internal Expansion  Energy
       Energy  work done  used to
           by system increase $S_{univ}$

the "Free Energy" is essentially the net change in energy of a system after performing P-V work (if any) and increasing $\Delta S_{univ}$. $\Delta G$ thus represents the maximum non-expansion (*e.g.*, electrical, mechanical, etc.) work that is available from a physical or chemical process.

## Conditions for Process Spontaneity

| | |
|---|---|
| $\Delta S_{univ} > 0$ | Spontaneous |
| $\Delta S_{univ} = 0$ | Reversible (equilibrium) |
| $\Delta S_{univ} < 0$ | Not spontaneous |
| | |
| $\Delta G_{sys} < 0$ | Spontaneous |
| $\Delta G_{sys} = 0$ | Reversible (equilibrium) |
| $\Delta G_{sys} > 0$ | Not spontaneous |

**Table 16.5**

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

| Various Possible Combinations of $\Delta H$ and $\Delta S$ for a Process and the Resulting Dependence of Spontaneity on Temperature | |
|---|---|
| Case | Result |
| $\Delta S$ positive, $\Delta H$ negative | Spontaneous at all temperatures |
| $\Delta S$ positive, $\Delta H$ positive | Spontaneous at high temperatures (where exothermicity is relatively unimportant) |
| $\Delta S$ negative, $\Delta H$ negative | Spontaneous at low temperatures (where exothermicity is dominant) |
| $\Delta S$ negative, $\Delta H$ positive | Process not spontaneous at *any* temperature (reverse process is spontaneous at *all* temperatures) |

**Various possible combinations of $\Delta H$ and $\Delta S$ for a process and the resulting dependence of spontaneity on temperature**
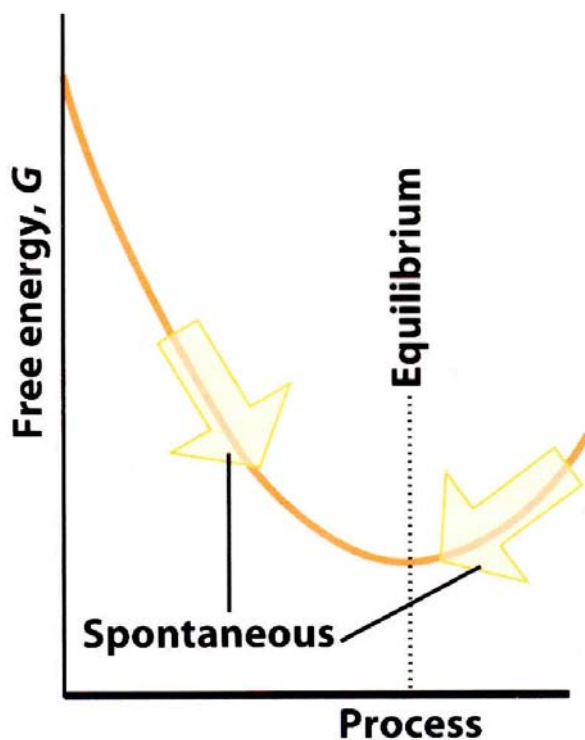
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**FIGURE 7.22** At constant temperature and pressure, the direction of spontaneous change is toward lower free energy. The equilibrium state of a system corresponds to the lowest point on the curve.

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

**TABLE 7.5** Factors That Favor Spontaneity

| Enthalpy change | Entropy change | Spontaneous? |
|---|---|---|
| exothermic ($\Delta H < 0$) | increase ($\Delta S > 0$) | yes, $\Delta G < 0$ |
| exothermic ($\Delta H < 0$) | decrease ($\Delta S < 0$) | yes, if $|T\Delta S| < |\Delta H|$, $\Delta G < 0$ |
| endothermic ($\Delta H > 0$) | increase ($\Delta S > 0$) | yes, if $T\Delta S > \Delta H$, $\Delta G < 0$ |
| endothermic ($\Delta H > 0$) | decrease ($\Delta S < 0$) | no, $\Delta G > 0$ |

**TABLE 10.5**    Results of the Calculation of $\Delta S_{univ}$ and $\Delta G°$ for the Process $\boxed{H_2O(s) \rightarrow H_2O(l)}$ at $-10°C$, $0°C$, and $10°C$*

| $T$ (°C) | $T$ (K) | $\Delta H°$ (J/mol) | $\Delta S°_{sys}$ * ($J\ K^{-1}\ mol^{-1}$) | $\Delta S_{surr} = -\dfrac{\Delta H°}{T}$ ($J\ K^{-1}\ mol^{-1}$) | $\Delta S_{univ} = \Delta S°_{sys} + \Delta S_{surr}$ ($J\ K^{-1}\ mol^{-1}$) | $T\Delta S°$ (J/mol) | $\Delta G° = \Delta H° - T\Delta S°$ (J/mol) |
|---|---|---|---|---|---|---|---|
| $-10$ | 263 | $6.03 \times 10^3$ | 22.1 | $-22.9$ | $-0.8$ | $5.81 \times 10^3$ | $+2.2 \times 10^2$ |
| 0 | 273 | $6.03 \times 10^3$ | 22.1 | $-22.1$ | 0 | $6.03 \times 10^3$ | 0 (EQUIL.) |
| 10 | 283 | $6.03 \times 10^3$ | 22.1 | $-21.3$ | $+0.8$ | $6.25 \times 10^3$ | $-2.2 \times 10^2$ |

* Note that at 10°C, $\Delta S°$ ($\Delta S_{sys}$) controls, and the process occurs even though it is endothermic. At $-10°C$ the magnitude of $\Delta S_{surr}$ is larger than that of $\Delta S°$, so the process is spontaneous in the opposite (exothermic) direction.

\* AT 273 K :    $S°(H_2O, l) = 63.2$ J/mol·K

$S°(H_2O, s) = 41.1$ J/mol·K

$\Delta S° = 22.1$ J/mol·K

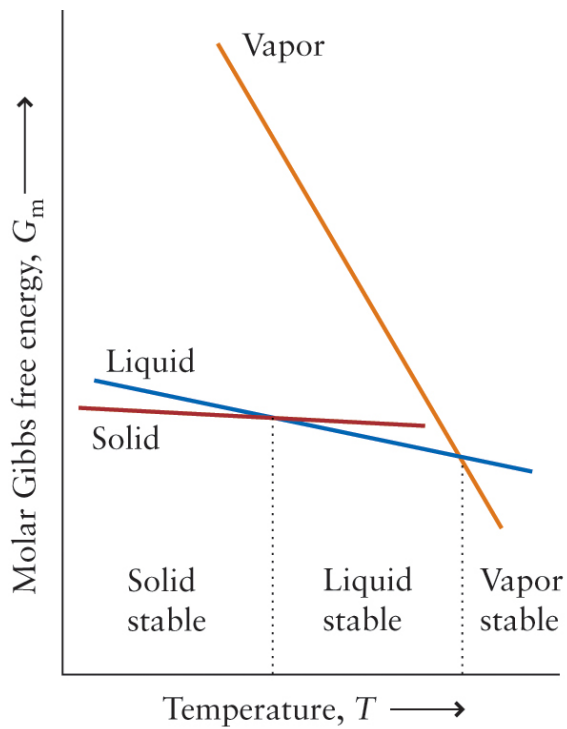$$H_2O\ (s) \rightleftarrows H_2O\ (l)$$
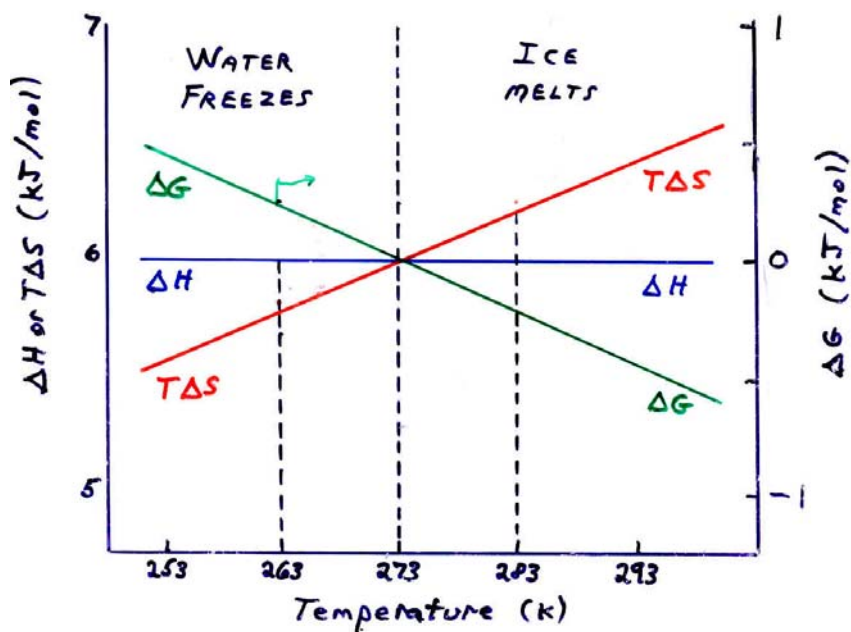
**FIGURE 9.25** The variation of the (molar) Gibbs free energy with temperature for three phases of a substance at a given pressure. The most stable phase is the phase with lowest molar Gibbs free energy. We see that, as the temperature is raised, the solid, liquid, and vapor phases in succession become the most stable.
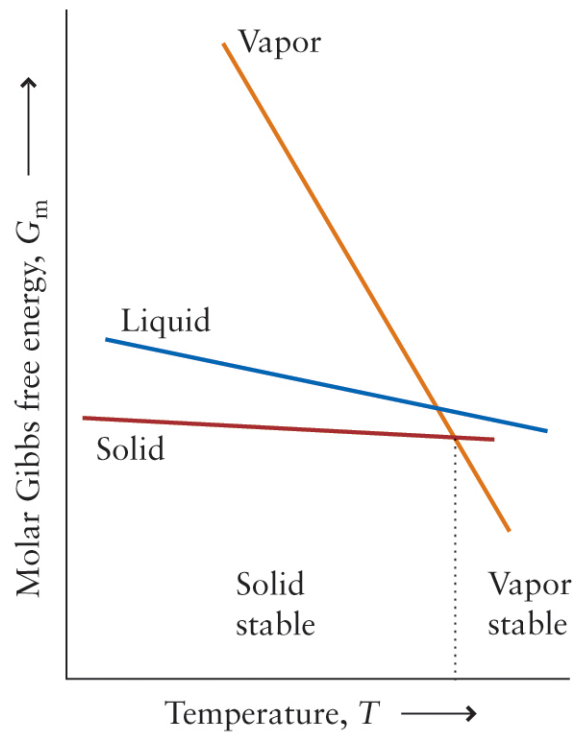


**FIGURE 9.26** For some substances and at certain pressures, the molar Gibbs free energy of the liquid phase might never lie lower than those of the other two phases. For such substances, the liquid is never the stable phase and, at constant pressure, the solid sublimes when the temperature is raised to the point of intersection of the solid and vapor lines.

Although only <u>changes</u> in most state functions, such as U, H, and G are important (or measurable), <u>absolute</u> entropies <u>are</u> significant because T = 0 (absolute zero) corresponds to a condition of perfect order (zero disorder) and, hence, zero entropy.  For perfect crystals of all substances, $S_{T=0} = 0$, which is a statement of the <u>Third Law</u> of Thermodynamics.

In general, the absolute entropy of a substance increases with increasing temperature and with increasing complexity of the molecule.

Because S and G are state functions, at constant T and P:

$$\Delta S^\circ_{reaction} = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$

$$\Delta G^\circ_{reaction} = \sum \Delta G^\circ_{f,\,products} - \sum \Delta G^\circ_{f,\,reactants}$$

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

$$= \sum \Delta H^\circ_{f,\,products} - \sum \Delta H^\circ_{f,\,reactants}$$
$$- T\left\{ \sum S^\circ_{products} - \sum S^\circ_{reactants}\right\}$$

For the reaction:

$$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$$

at a constant pressure of 1 atm (from Appendix 2):

$$\Delta G^\circ_r = \Delta G^\circ_f(CO_2) + \Delta G^\circ_f(H_2) - \Delta G^\circ_f(CO) - \Delta G^\circ_f(H_2O)$$
$$= (-394.4) + (0.0) - (-137.2) - (-228.6)$$
$$= -28.6\ kJ$$

The free energy of reaction could also be calculated using values for enthalpies of formation and absolute entropies:

$$\Delta H^\circ_r = \Delta H^\circ_f(CO_2) + \Delta H^\circ_f(H_2) - \Delta H^\circ_f(CO) - \Delta H^\circ_f(H_2O)$$
$$= (-393.5) + (0.0) - (-110.5) - (-241.8)$$
$$= -41.2\ kJ$$

$$\Delta S^\circ_r = S^\circ(CO_2) + S^\circ(H_2) - S^\circ(CO) - S^\circ(H_2O)$$
$$= (213.7) + (130.7) - (197.7) - (188.8)$$
$$= -42.1\ J/K$$

Since the values of $S^\circ$ in Appendix 2 are for a temperature of 25°C (298.15K):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -41{,}200 - 298.15(-42.1)$$
$$= -28{,}600\ J$$
$$= -28.6\ kJ$$

which agrees with the value calculated above using free energies of formation.
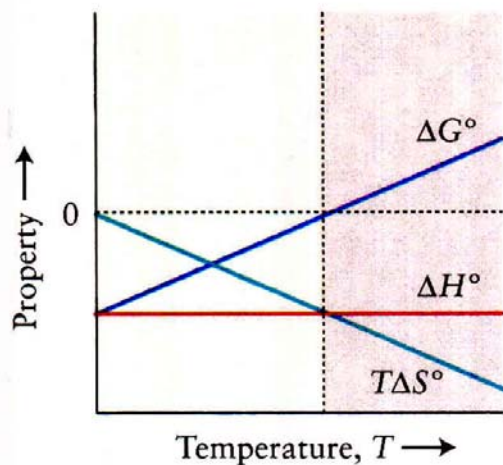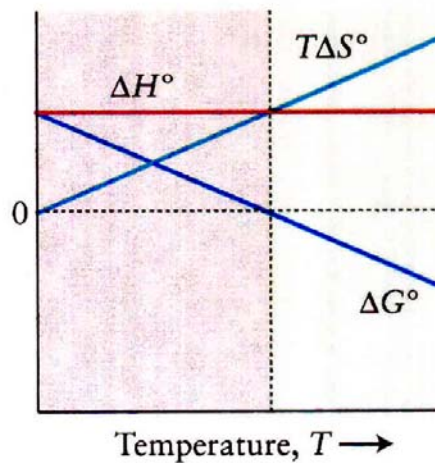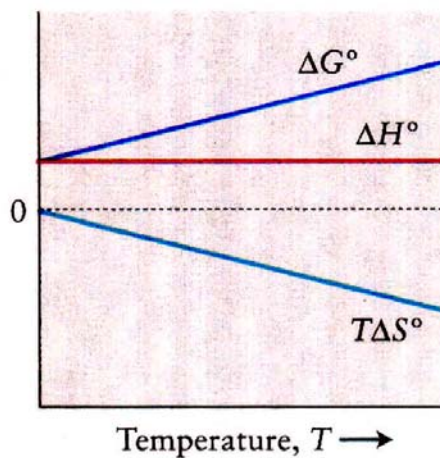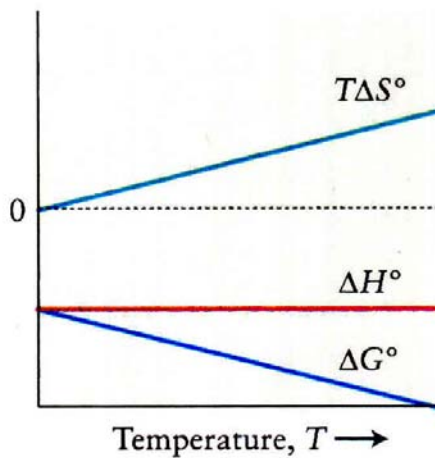
$$\Delta G° = \Delta H° - T\Delta S°$$



**FIGURE 9.28** The effect of an increase in temperature on the spontaneity of a reaction under standard conditions. In each case, "spontaneous" is taken to mean $\Delta G° < 0$ and "nonspontaneous" is taken to mean $\Delta G° > 0$. (a) An exothermic reaction with negative reaction entropy becomes spontaneous *below* the temperature marked by the vertical dotted line. (b) An endothermic reaction with a positive reaction entropy becomes spontaneous *above* the temperature marked by the vertical dotted line. (c) An endothermic reaction with negative reaction entropy is not spontaneous at any temperature. (d) An exothermic reaction with positive reaction entropy is spontaneous at all temperatures.
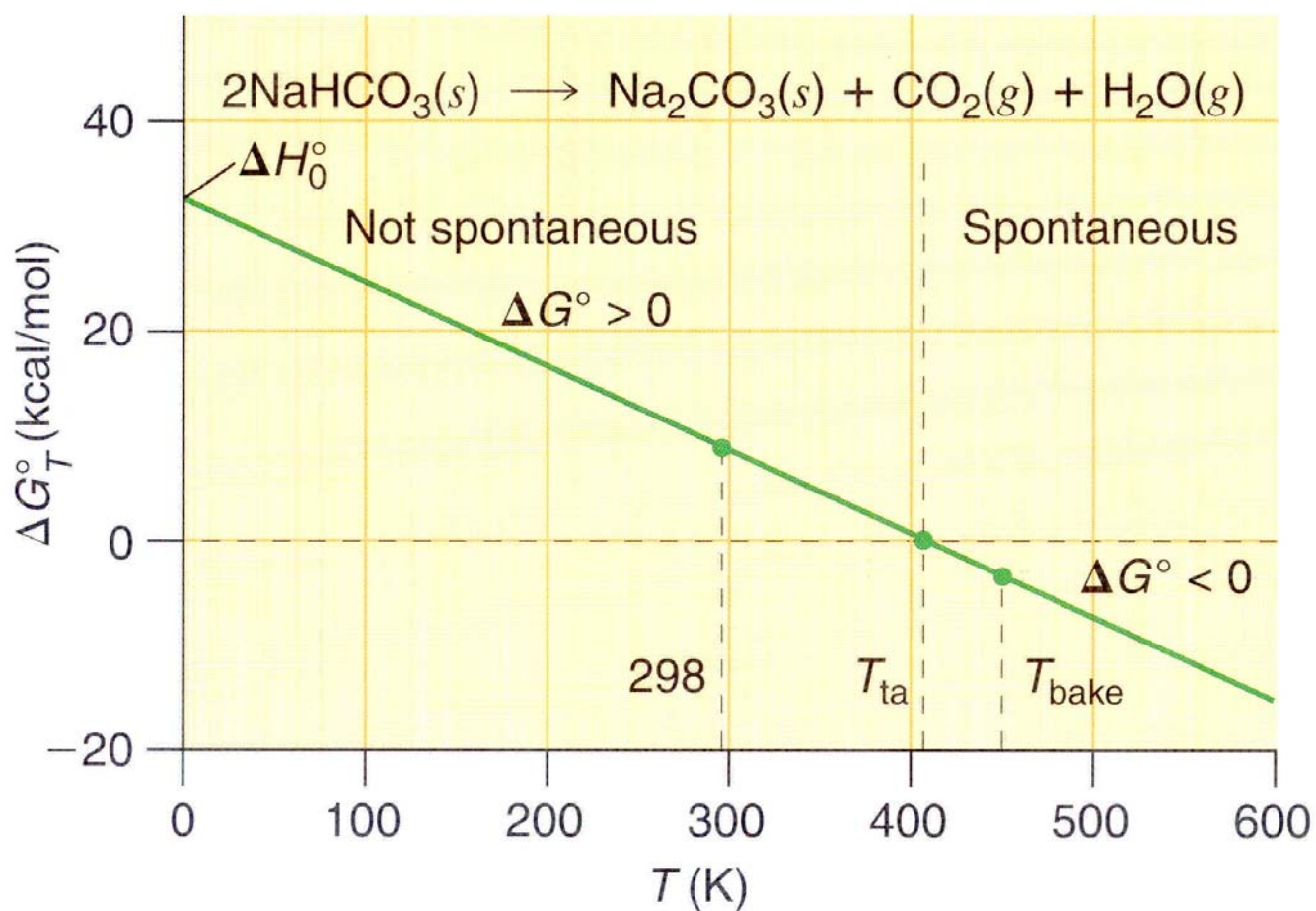
$\Delta S < 0$

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

(a)
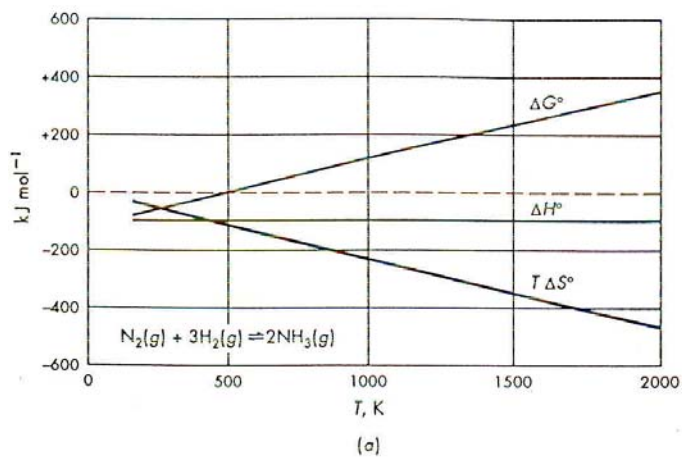
**FIGURE 5-8**

The temperature dependence of $\Delta G°$, $\Delta H°$, and $T\Delta S°$ over a large range of temperatures. In (a) $\Delta S°$ is negative. In (b) $\Delta S°$ is positive.

$\Delta S > 0$

$H_2O(g) + C(graphite) \rightleftharpoons CO(g) + H_2(g)$

(b)
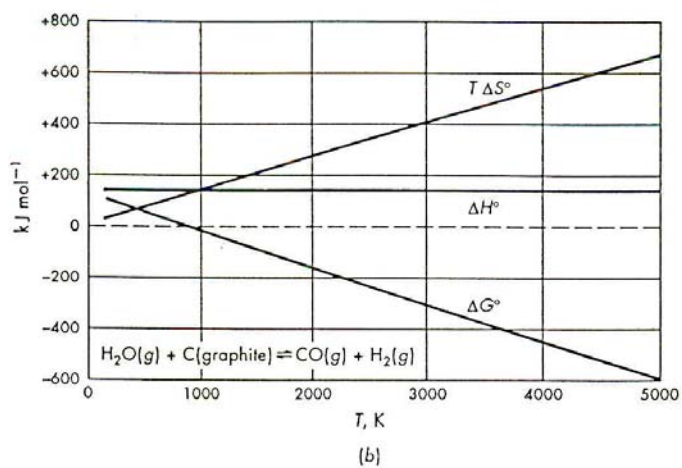
# Figure 11.8: Temperature Dependence of $\Delta G^\circ$

# Thermodynamics of Metabolism

Metabolism is the set of reactions that occurs in cells to sustain life. Groups of reactions that accomplish a particular need are called metabolic pathways. One of the most important of these is glycolysis, in which the combustion of glucose (a sugar) produces water and carbon dioxide:

$$C_6H_{12}O_6 \text{ (s)} + 6 \text{ } O_2 \text{ (g)} \rightarrow 6 \text{ } CO_2 \text{ (g)} + 6 \text{ } H_2O \text{ (}\ell\text{)}$$
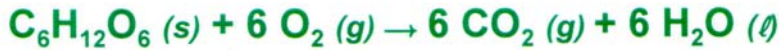
for which $\Delta H^\circ_r$ = - 2,808 kJ/mol, $\Delta S^\circ_r$ = +259 J/mol-K, and $\Delta G^\circ_r$ = - 2,872 kJ/mol

Because the above reaction is exothermic, with a positive $\Delta S$, it is spontaneous at all temperatures. Some of the energy evolved during the reaction is dissipated as heat, but some is available to "drive" non-spontaneous reactions. One of the most important of these reactions is the conversion of adenosine diphosphate ($ADP^{3-}$) into adenosine triphosphate ($ATP^{4-}$):



Adenosine diphosphate (ADP)

Adenosine triphosphate (ATP)
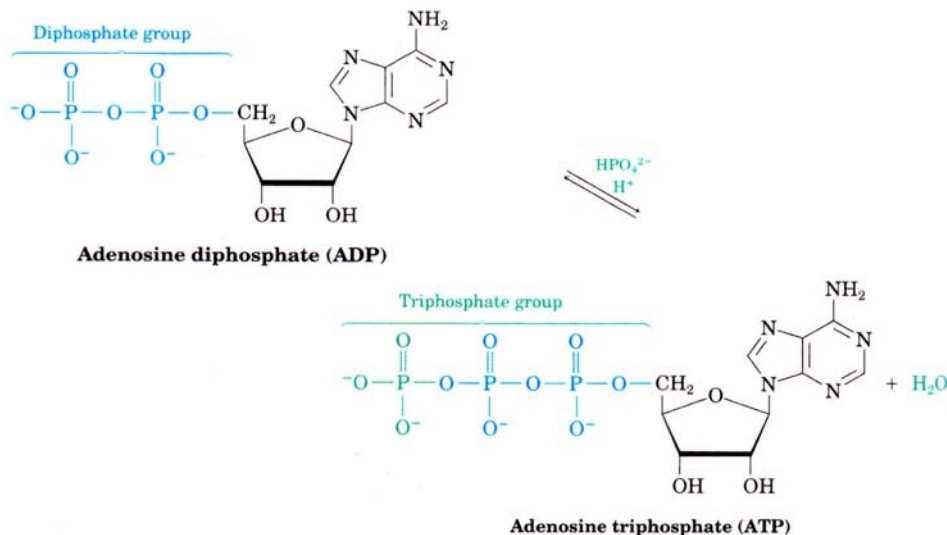
for which $\Delta H^{\circ}_r$ = +20.1 kJ/mol, $\Delta S^{\circ}_r$ = -35.2 J/mol-K, and $\Delta G^{\circ}_r$ = +34.5 kJ/mol.

      ATP is the primary medium for storage of free energy in living cells. It is composed of a linkage of D-Ribose (a sugar), adenine (a nucleobase), and three phosphate groups. Although its formation by the above reaction is non-spontaneous, it is "driven" by coupling it with the combustion of glucose. The coupling of these two reactions (liquid water is a product of both reactions) enables the overall process of ATP production to be spontaneous.

      If 100% of the energy released during glucose combustion were available, the reaction of one mole of glucose would enable the formation of approximately 83 moles of ATP (2,872/34.5). However, because more than half of the energy released by the combustion is dissipated as heat, the coupling produces only about 38 moles of ATP (46% efficient ).

      The first step in the glycolytic pathway is the transfer of one phosphate group from ATP to the No. 6 Carbon in glucose to produce glucose-6-phosphate (G6P):
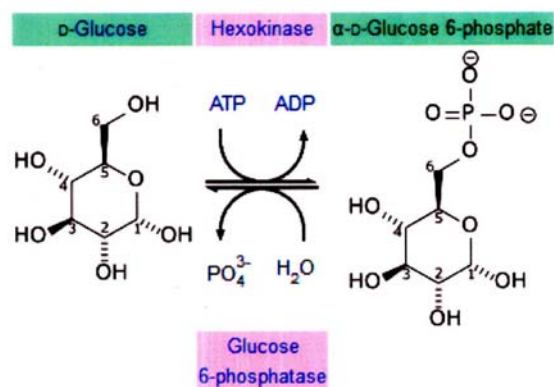
G6P then undergoes hydrolysis by water to re-generate a glucose molecule and release a phosphate ion:

$$G6P + H_2O \rightarrow glucose + phosphate$$

The net result of the above two reactions is:

$$ATP + H_2O \rightarrow ADP + phosphate$$

for which $\Delta G°_r$ = - 32.5 kJ/mol, thus making the overall process thermodynamically spontaneous.