

Section 16.4

Free Energy



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Learning Objectives



- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

Gibbs Free Energy



- Determining Spontaneity with entropy alone can be difficult.
 - We need to measure the entropy change of both the system and the surroundings.
- Josiah Willard Gibbs proposed an alternative property capable of predicting spontaneity called **Gibbs Free Energy**.
- It is defined in terms of a *system's* enthalpy and entropy

$$G = H - TS$$

Free Energy Change



- Free energy is a state function
- At constant temperature and pressure, the **free energy change** (ΔG) may be expressed as:

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

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	at equilibrium

Deriving Gibbs Free Energy



- Beginning with the Second Law of Thermodynamics

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

- The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Deriving Gibbs Free Energy



- Multiplying both sides of this equation by $-T$, and rearranging yields the following:

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

- Comparing this equation to the previous one for free energy change shows the following relation:

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

What's “Free” about ΔG ?



- ΔG may be interpreted as representing the difference between the energy produced by the process, ΔH , and the energy lost to the surroundings, $T\Delta S$.

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

- This difference is the energy available (or “free”) to do useful work by the process.
 - If the process could somehow be made to take place reversibly.

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

- where w_{\max} refers to all types of work except expansion (pressure-volume) work.

Calculating Free Energy Change



- **Standard Gibb's Free Energy Change** (ΔG°) can be calculated from the standard enthalpy (ΔH°) and standard entropy (ΔS°).

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

Free Energy of Formation ΔG_f°



- The standard free energy change for a reaction may also be calculated from **standard free energy of formation** (ΔG_f°) values of the reactants and products involved in the reaction.
 - The free energy change that accompanies the formation of one mole of a substance from its elements in their standard states.
 - ΔG_f° is by definition zero for elemental substances in their standard states.



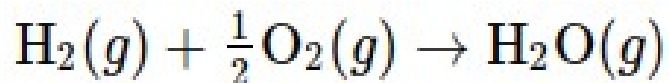
$$\Delta G^\circ = \sum \nu \Delta G^\circ (\text{products}) - \sum \nu \Delta G^\circ (\text{reactants})$$

$$= [x\Delta G_f^\circ (C) + y\Delta G_f^\circ (D)] - [m\Delta G_f^\circ (A) + n\Delta G_f^\circ (B)]$$

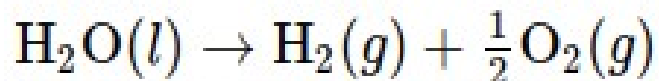
Free Energy Changes for Coupled Reactions



- Just like we used *Hess's Law* to calculate the enthalpy of a reaction, we can use the same technique to find the free energy change of a reaction.



$$\Delta G_f^\circ \text{ gas}$$



$$- \Delta G_f^\circ \text{ liquid}$$



$$\Delta G^\circ = \Delta G_f^\circ \text{ gas} - \Delta G_f^\circ \text{ liquid}$$

Temperature Dependence of Spontaneity



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

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Critical Temperature of Spontaneity

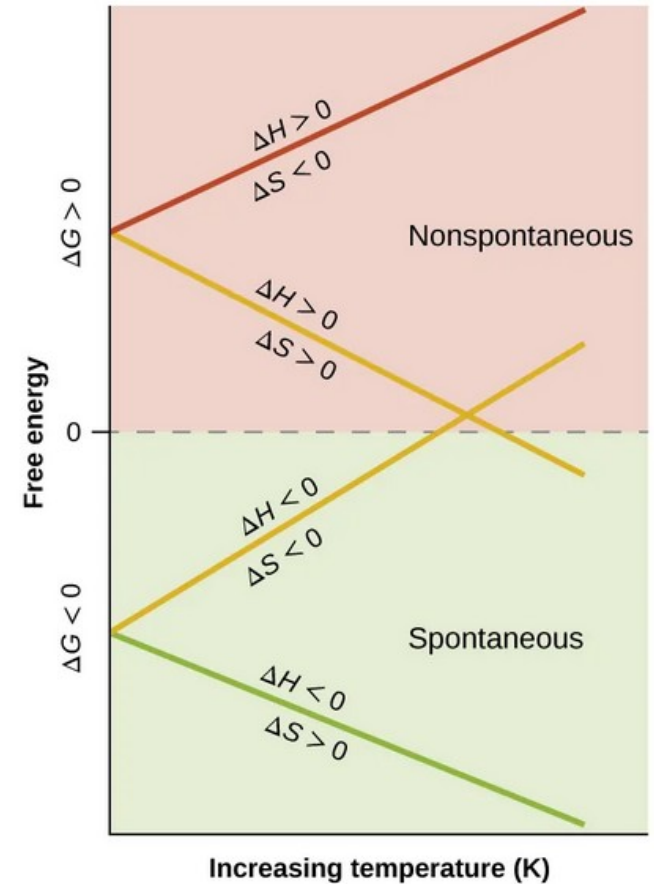


$$\Delta G = \Delta H - T\Delta S$$

$$y = b + mx$$

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

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



Free Energy and Nonstandard Conditions



- The free energy change for a process with reactants and products present under nonstandard conditions is:

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

- Pressures other than 1 bar; concentrations other than 1 M
- R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient.

Free Energy and Equilibrium



- When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate.
 - $Q = K$ and $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln K \quad (\text{at equilibrium})$$

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad K = e^{-\frac{\Delta G^\circ}{RT}}$$

- This form of the equation provides a useful link between these two essential thermodynamic properties,

Relations between ΔG° and K



K	ΔG°	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
$= 1$	$= 0$	Reactants and products are comparably abundant

Visualizing Reaction Progress

