18.7 Free Energy and the Spontaneity of Chemical Reactions

- An alternative approach involving a new thermodynamic property defined in terms of system properties, introduced by American mathematician Josiah Willard Gibbs.

- The **Gibbs free energy, G,** is the maximum amount of work energy that can be released to the surroundings by a system for a constant temperature and pressure system.

  - Gibbs free energy is often called the chemical potential because it is analogous to the storing of energy in a mechanical system.

The energy associated with a chemical reaction that can be used to do work. The free energy of a system is the sum of its enthalpy (H) plus the product of the temperature (Kelvin) and the entropy (S) of the system:

$$G = H - TS_{sys}$$

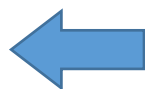$$\Delta G = \Delta H - T\Delta S_{svs}$$

Using:

$$\Delta S_{total} = \Delta S_{svs} + \Delta S_{surr}$$

$$\Delta S_{surr} = \frac{-\Delta H}{T}$$

$$\Delta G = -T\Delta S_{total}$$

$$\Delta S_{total} = \Delta S_{svs} - \frac{\Delta H}{T}$$

The free energy of reaction at standard state conditions:

$$\Delta G^{o}_{sys} = \Delta H^{o}_{sys} - T\Delta S^{o}_{sys}$$

- The **standard state** is the state of a material at a defined set of conditions.

- Gas = pure gas at exactly 1 atm pressure.

- Solid or Liquid = pure solid or liquid in its most stable form at exactly 1 atm pressure and temperature of interest.

  - Usually 25 °C

- Solution = substance in a solution with concentration 1 M.

The effect of H, S and T on Spontaneity

ΔH	ΔS	$\Delta G + \Delta H - T\Delta S$	Reaction Spontaneity	Example
−	+	−	Spontaneous at all temperatures	$2\,NO_2(g) \longrightarrow N_2(g) + 2\,O_2(g)$
+	−	+	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	− or +	Spontaneous at low temperatures where ΔH outweighs $T\Delta S$	$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$
			Nonspontaneous at high temperatures where $T\Delta S$ outweighs ΔH	
+	+	− or +	Spontaneous at high temperatures where $T\Delta S$ outweighs ΔH	$2\,HgO(s) \longrightarrow 2\,Hg(l) + O_2(g)$
			Nonspontaneous at low temperatures where ΔH outweighs $T\Delta S$	

Relation between Process Spontaneity and Signs of Thermodynamic Properties

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

CONCEPTUAL APPLY 18.10

What are the signs (+, -, or 0) of ΔH, ΔS and ΔG for the following spontaneous reaction of A atoms (red) and B atoms (blue)?
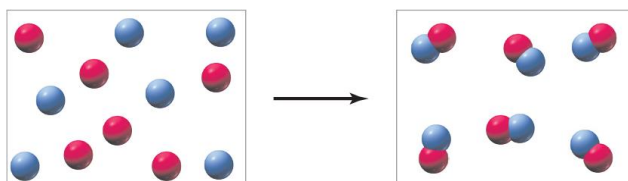
Example: Consider the reaction for the decomposition of carbon tetrachloride gas:

$CCl_{4(g)} \rightarrow C(s, graphite) + 2\ Cl_{2(g)}$ $\Delta H^{\circ} = +95.7$ kJ; $\Delta S^{\circ} = +142.2$ J/K

    a.   Calculate ΔG° at 25 °C and determine whether the reaction is spontaneous.

b.   If the reaction is not spontaneous at 25 °C, determine at what temperature (if any) the reaction becomes spontaneous.

18.8 – 18.9 Standard Free-Energy Changes for Reactions and Standard Free Energies of Formation

Gibbs free energy is also a state function. The free energy of a substance, like its enthalpy and entropy, depends on its temperature, pressure, physical state (solid, liquid, or gas), and concentration (in the case of solutions).

Standard-state conditions

- *Solids, liquids, and gases in pure form at 1 atm pressure*
- *Solutes at 1 M concentration*
- *A specified temperature, usually 25 °C*

For the Haber synthesis of $N_{2(g)}$ + 3 $H_{2(g)}$ $\rightleftharpoons$ $2NH_{3(g)}$, we can calculate $\Delta G°$ using $\Delta G°_{sys} = \Delta H°_{sys} - T\Delta S°_{sys}$

Where $\Delta H° = $ -92.2 kJ and $\Delta S° = $ -198.7 J/K then $\Delta G° = $ -33.0 kJ

Therefore, $\Delta G°_f$ for ammonia NH_3 is -33.0 kJ/2 mol, or -16.5 kJ/1 mol .

The standard free-energy change $\Delta G°$ (for a reaction is the change in free energy that occurs when reactants in their standard states are converted to products in their standard states. As with $\Delta H°$, the value of $\Delta G°$ is an extensive property, depending on sample size.

$$\triangle G^0 = \sum n \triangle G_f^0 \text{ (products)} - \sum n \triangle G_f^0 \text{ (reactants)}$$

Table 18.3 Standard Free Energies of Formation for Some Common Substances at 25 °Celsius

Substance	Formula	$\Delta G_f°$ [kJ/mol]	Substance	Formula	$\Delta G_f°$ [kJ/mol]
Gases			**Liquids**		
Acetylene	C_2H_2	209.9	Acetic acid	CH_3CO_2H	−390
Ammonia	NH_3	−16.5	Ethanol	CH_3CH_2OH	−174.9
Carbon dioxide	CO_2	−394.4	Methanol	CH_3OH	−166.6
Carbon monoxide	CO	−137.2	Water	H_2O	−237.2
Ethylene	C_2H_4	68.1	**Solids**		
Hydrogen	H_2	0	Calcium carbonate	$CaCO_3$	−1129.1
Methane	CH_4	−50.8	Calcium oxide	CaO	−603.3
Nitrogen	N_2	0	Diamond	C	2.9
Nitrogen dioxide	NO_2	51.3	Graphite	C	0
Dinitrogen tetroxide	N_2O_4	99.8	Iron(III) oxide	Fe_2O_3	−742.2

Example: Determine the $\Delta G°_{rxn}$ (in kJ/mol) for the following reaction:

2 $C_{(s)}$ + 2 $H_{2(g)}$ $\rightleftharpoons$ $C_2H_{4(g)}$
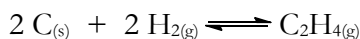
18.10 Free-Energy Changes for Reactions Under Nonstandard-State Conditions

The sign of the standard free-energy change ΔG° tells us the direction of spontaneous reaction when both reactants and products are present at standard-state conditions. then, how do we calculate the free-energy change, ΔG° for a reaction when the reactants and products are present at nonstandard-state pressures and concentrations?

The free energy change for a process may be viewed as a measure of its driving force. A negative value of ΔG represent a finite driving force the proves in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG = 0, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

The following equation relates the standard-state free energy of reaction with the free energy of reaction at any moment in time during a reaction (not necessarily at standard-state conditions):

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

ΔG = free energy at any moment

ΔG° = standard-state free energy

R = ideal gas constant = 8.314 J/mol-K

T = temperature (Kelvin)

lnQ = natural log of the **reaction quotient**

Reaction quotient (Q_c or Q_p) - The mathematical product of the concentrations (or partial pressures) of the products of a reaction divided by the mathematical product of the concentrations (or partial pressures) reactants of a reaction **AT ANY MOMENT IN TIME**.

ΔG = Free-energy change under nonstandard conditions

Example: For the Haber synthesis of ammonia:

$$N_{2(g)} + 3 H_{2(g)} \rightleftharpoons 2NH_{3(g)},$$
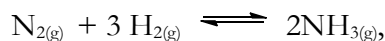
Calculate the free-energy change for ammonia synthesis at 25 °C (298 K) given the following sets of partial pressures:

1.0 atm N_2, 3.0 atm H_2 and 0.02 atm NH_3

18.11 Free Energy and Chemical Equilibrium

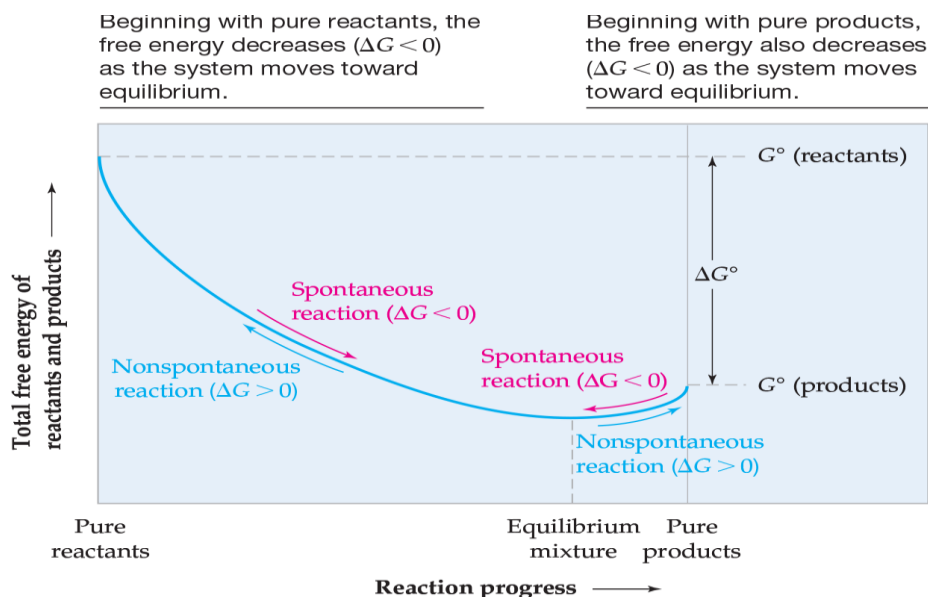When the reaction mixture is mostly reactants,

$$Q \ll 1 \quad RT \ln Q \ll 0 \quad \Delta G < 0$$

the total free energy decreases as the reaction proceeds spontaneously in the **forward** direction.

When the reaction mixture is mostly products,

$$Q \gg 1 \quad RT \ln Q \gg 0 \quad \Delta G > 0$$

The total free energy decreases as the reaction proceeds spontaneously in the **reverse** direction.

Beginning with pure reactants, the free energy decreases ($\Delta G < 0$) as the system moves toward equilibrium.

Beginning with pure products, the free energy also decreases ($\Delta G < 0$) as the system moves toward equilibrium.

Note: When $Q_c = K_c$ (or when $Q_p = K_p$), a reaction is at equilibrium.

It was stated earlier that when $\Delta G = 0$, a reaction is at equilibrium. Let's consider the above reaction at equilibrium:

$$\Delta G = \Delta G° + RT \ln Q$$
$$\text{At equilibrium,} \, \Delta G = \ 0 \text{ and } Q = K.$$
$$\Delta G° = -RT \ln K$$

If we move RTlnK to the opposite side by subtracting it from both sides, we get the following reaction which relates the free energy of a reaction to the equilibrium constant of a reaction:

Table 18.4: Relationship between the Standard Free-Energy Change and the Equilibrium Constant for a Reaction: $\Delta G° = -RT \ln K$

$\Delta G°$	$\ln K$	K	Comment
$\Delta G° < 0$	$\ln K > 0$	$K > 1$	The equilibrium mixture is mainly products.
$\Delta G° > 0$	$\ln K < 0$	$K < 1$	The equilibrium mixture is mainly reactants.
$\Delta G° = 0$	$\ln K = 0$	$K = 1$	The equilibrium mixture contains comparable amounts of reactants and products.

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As the magnitude of ΔG° changes, so does the equilibrium constant. K.

(c)
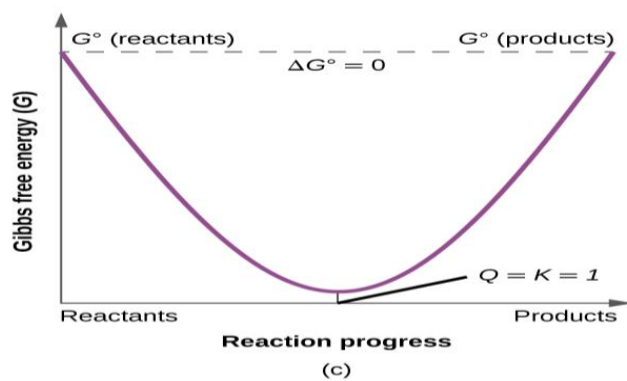
Use tabulated free energies of formation to calculate the equilibrium constant K_p for the reaction at 298 K:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO2(g)$