

Spontaneity, Entropy, and Free Energy

Entropy

Spontaneity

Some processes occur spontaneously because the products are lower in energy than the reactants (exothermic processes). For example, the combustion of methane:



Some occur spontaneously even though the products are higher in energy than the reactants (endothermic processes). For example, the dissolving of ammonium chloride in water:

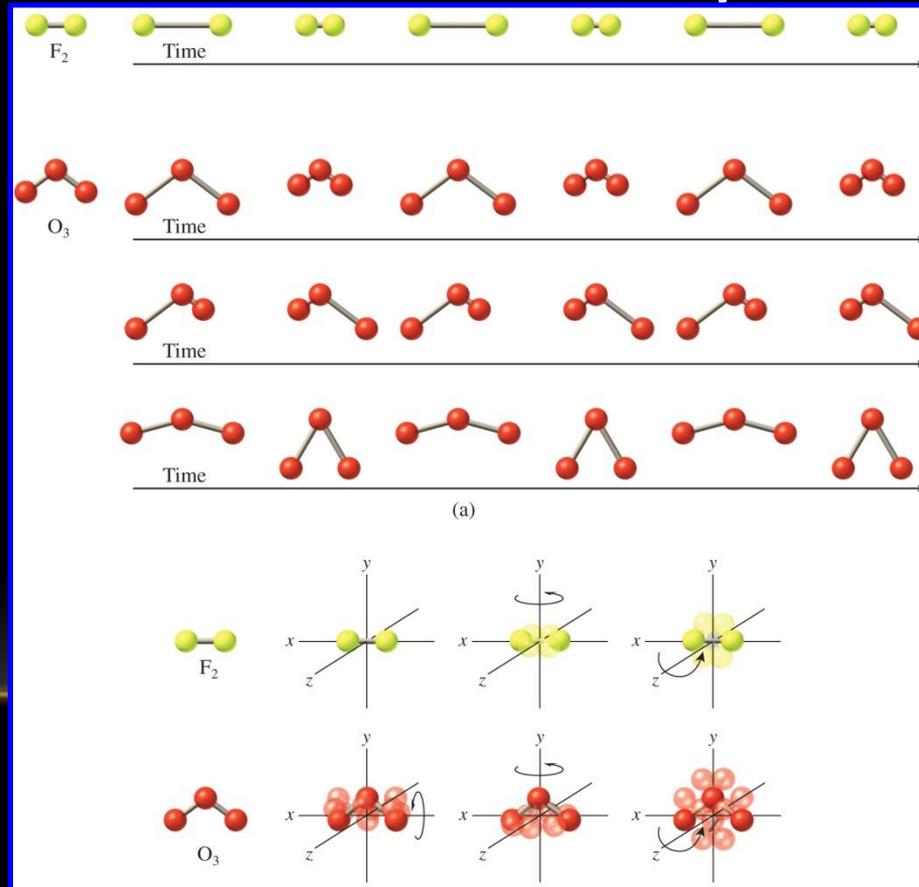


A negative ΔH is one driving force for spontaneity, but there must be something else too. That is entropy.

Entropy (S)

Entropy may be thought of as a measure of how dispersed the total energy of a system is.

The type of energy that is involved is kinetic energy. For molecules this can be due to translation (the whole molecule moves), rotation (the molecule spins), and vibration (the atoms within the molecule vibrate as if they're attached together with springs).



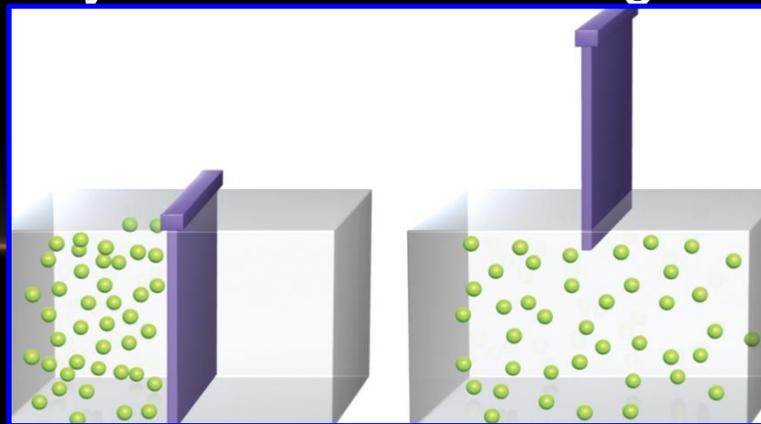
$$S = k \ln W$$

Here k is Boltzmann's constant:

$$k = \frac{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}}{6.022 \times 10^{23} \text{ mol}} = 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

W = number of available states.

That is, the number of equivalent ways the energy of the system can be arranged.

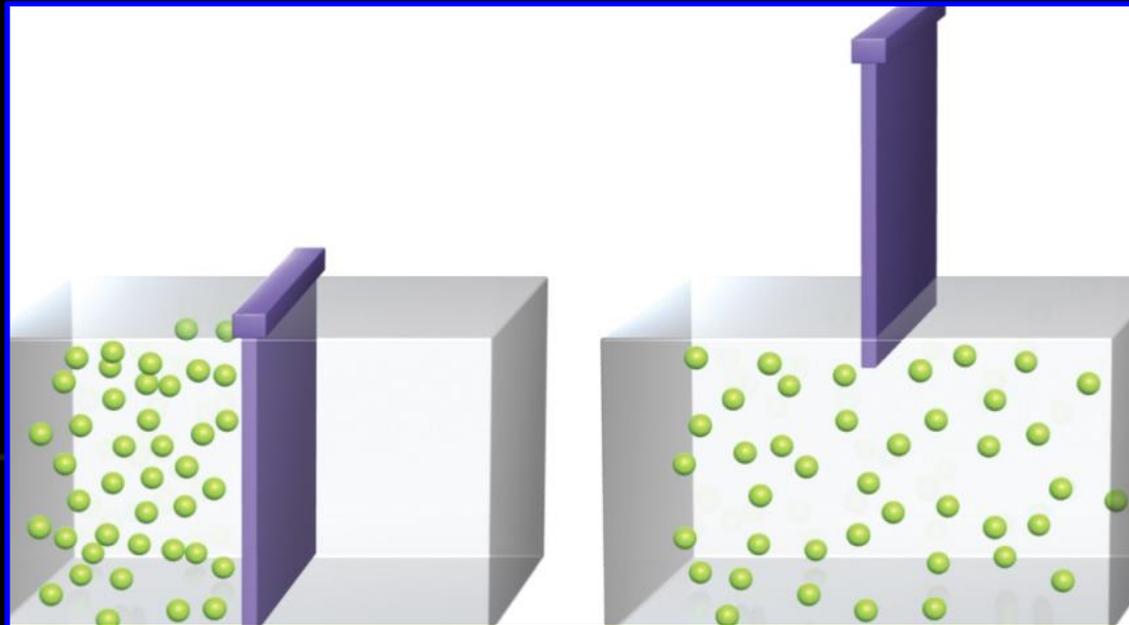


$$W = X^N$$

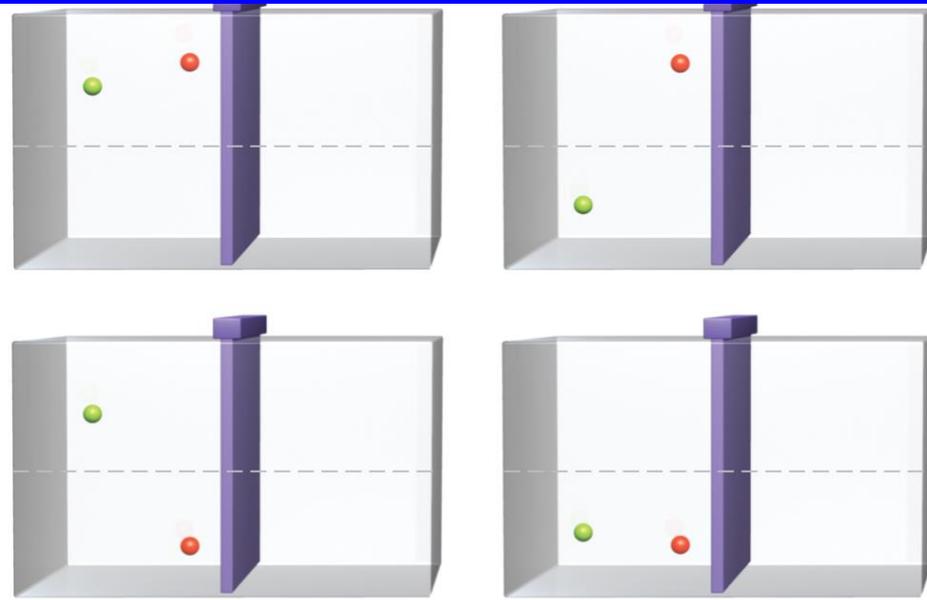
X = the number of different places a molecule can be.

(We can imagine dividing each side of the chamber below into smaller identical cells. X is the number of cells.)

N = the number of molecules.

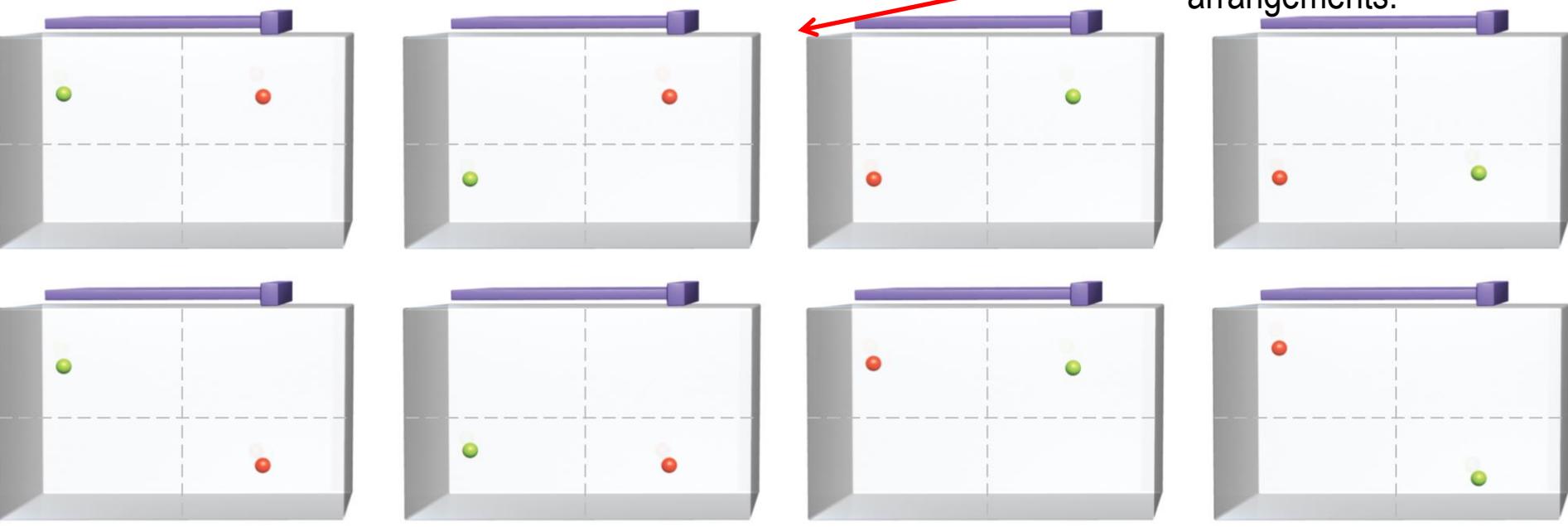


2 molecules, 2 cells
 on one side of the barrier
 = 4 possible states.
 $X^N = 2^2$.



Now open the barrier.
 There are 16 possible
 states, 4^2 . 8 of these
 states have one
 molecule on each side
 (shown). 4 have both
 molecules on the left and
 4 have both on the right.
 The most probable is the
 one with the largest
 number of possible
 arrangements.

(a)



(b)

Entropy Changes in a System

$$\begin{aligned}\Delta S_{\text{sys}} &= S_{\text{final}} - S_{\text{initial}} \\ &= k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}} \\ &= k \ln \frac{(X_{\text{final}})^N}{(X_{\text{initial}})^N} = k N \ln \left(\frac{X_{\text{final}}}{X_{\text{initial}}} \right)\end{aligned}$$

Since X is the number of cells, if the volume of one cell is v , the total volume, $V = Xv$, or

$$X = \frac{V}{v}$$

Entropy Changes in a System

this gives us:

$$\Delta S_{sys} = k N \ln \left(\frac{V_{final}}{V_{initial}} \right)$$

but $k = \frac{R}{N_A}$ and $N = n \times N_A$ so

$$\Delta S_{sys} = nR \ln \left(\frac{V_{final}}{V_{initial}} \right)$$

(ONLY FOR THE ISOTHERMAL EXPANSION OF AN IDEAL GAS)

Entropy Changes in a System

Calculate the change in entropy when 0.2345 moles of an ideal undergoes an isothermal expansion from 5.712 L to 6.988 L.

0.3921 J/K

Standard Entropy S°

The standard entropy of a substance is the entropy of that substance at 1 atm pressure. The temperature is not part of the definition and must be specified.

Here are some standard entropies at 25°C.

Substance	S° (J/K · mol)	Substance	S° (J/K · mol)
H ₂ O(<i>l</i>)	69.9	C(diamond)	2.4
H ₂ O(<i>g</i>)	188.7	C(graphite)	5.69
Na(<i>s</i>)	51.05	O ₂ (<i>g</i>)	205.0
Na(<i>l</i>)	57.56	O ₃ (<i>g</i>)	237.6
Na(<i>g</i>)	153.7	F ₂ (<i>g</i>)	203.34
He(<i>g</i>)	126.1	Au(<i>s</i>)	47.7
Ne(<i>g</i>)	146.2	Hg(<i>l</i>)	77.4

Explain relative S° 's for adjacent species in this table.

Change in Entropy for a Reaction - ΔS_{rxn}

For the generic reaction



$$\Delta S_{\text{rxn}}^{\circ} = [cS^{\circ}(\text{C}) + dS^{\circ}(\text{D})] - [aS^{\circ}(\text{A}) + bS^{\circ}(\text{B})]$$

or

$$\Delta S_{\text{rxn}}^{\circ} = \sum nS^{\circ}(\text{products}) - \sum mS^{\circ}(\text{reactants})$$

For the dissolution of ammonium chloride in water:



$$\Delta S_{\text{soln}}^{\circ} = (112.8 \text{ J/K}\cdot\text{mol} + 56.5 \text{ J/K}\cdot\text{mol}) - 94.56 \text{ J/K}\cdot\text{mol} = +74.7 \text{ J/K}\cdot\text{mol}$$

The Sign of ΔS_{sys}^o

Increased volume increases the number of energy states available to the system, and thus its entropy.

Increasing the temperature of a system increases the number of energy states available, and thus the entropy.

The more complex a molecule is, the more modes of vibration and rotation it has, and thus the more energy states available to it, increasing its entropy.

The greater the molar mass the more energy states available to a molecule, and thus the greater its entropy.

When a system goes from one phase to another, the phase with more possible arrangements has the greater entropy.

When a chemical reaction occurs, if more gas molecules are produced than consumed the overall entropy increases.

The System, the Surroundings, and the Universe

Universe = System + Surroundings

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

For a constant pressure process $\Delta H_p = q$

If a process is exothermic $q_{\text{system}} < 0$ and $q_{\text{surroundings}} > 0$

For an endothermic process $q_{\text{system}} > 0$ and $q_{\text{surroundings}} < 0$

If q increases, there are more energy states available, and thus the entropy increases.

The Second Law of Thermodynamics

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

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

The Second Law of Thermodynamics says that in order for a process to be spontaneous ΔS_{univ} must be > 0 .

When $\Delta S_{univ} = 0$, the system is at equilibrium.

Is the following reaction a spontaneous process, a nonspontaneous process, or at equilibrium?



$$\Delta S_{rxn}^{\circ} = \left[2 \left(213.6 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) + 3 \left(69.9 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \right] - \left[161.0 \frac{\text{J}}{\text{K} \cdot \text{mol}} + 3 \left(205.0 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \right] = -139.1 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$\Delta H_{rxn}^{\circ} = \left[2 \left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) + 3 \left(-285.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[-276.98 \frac{\text{kJ}}{\text{mol}} \right] = -1367.4 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{surr}^{\circ} = -\frac{\Delta H_{rxn}}{T} = -\frac{-1367.4 \frac{\text{kJ}}{\text{mol}}}{295 \text{ K}} = +4.63_5 \frac{\text{kJ}}{\text{K} \cdot \text{mol}} = +4.63_5 \times 10^3 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} = 4.63_5 \times 10^3 \frac{\text{J}}{\text{K} \cdot \text{mol}} - 139.1 \frac{\text{J}}{\text{K} \cdot \text{mol}} = 4.49_6 \times 10^3 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

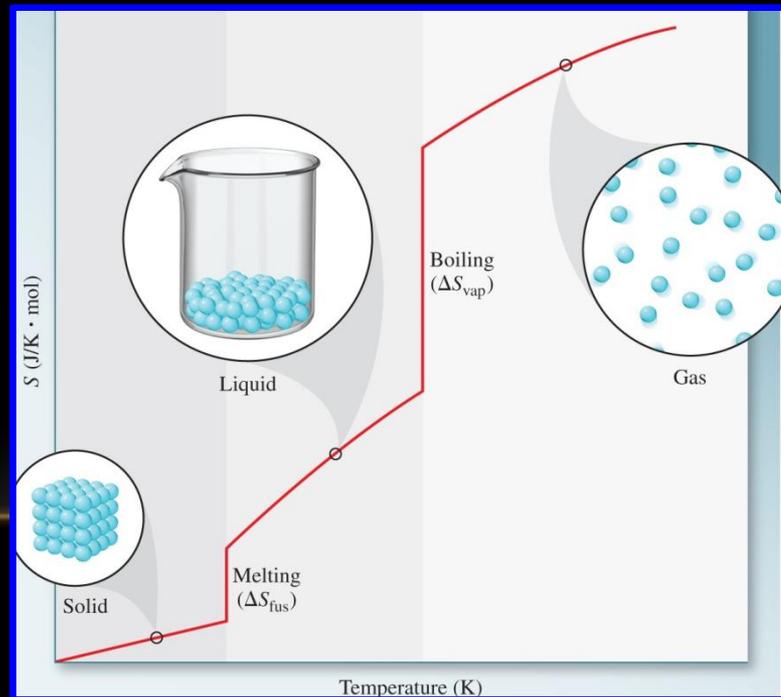
(SPONTANEOUS)

The Third Law of Thermodynamics:

The entropy of a perfect crystalline substance at 0 K (absolute zero) = 0 (exactly).

This allows us to measure the absolute entropy of a substance:

$\Delta S = S_{final} - S_{initial} = S_{final}$ (if we start with a perfect crystal at 0 K).



Gibb's Free Energy - G

Gibbs came up with a function that lets us predict spontaneity by only looking at the system (and not the surroundings).

For a process to be spontaneous $\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} > 0$.

Or, $\Delta S_{univ} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right) > 0$. Rearranging a little, we get $-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$

Gibbs defined G (called Gibb's free energy) as

$$G = H - TS$$

or

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

Gibbs's Free Energy - G

In the equation $\Delta G = \Delta H - T \Delta S$ everything pertains to the system. For an isothermal, isobaric process the condition for spontaneity is:

$$\Delta G < 0$$

For a system at equilibrium $\Delta G = 0$

If $\Delta G > 0$ the reverse process is spontaneous.

The Effect of Temperature on Spontaneity

T is the only variable we can adjust in the Gibb's equation.

When ΔH is	And ΔS is	ΔG will be	And the process is	Example
Negative	Positive	Negative	Always spontaneous	$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
Positive	Negative	Positive	Always nonspontaneous	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
Negative	Negative	Negative when $T\Delta S < \Delta H$ Positive when $T\Delta S > \Delta H$	Spontaneous at low T Nonspontaneous at high T	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$ (freezing of water)
Positive	Positive	Negative when $T\Delta S > \Delta H$ Positive when $T\Delta S < \Delta H$	Spontaneous at high T Nonspontaneous at low T	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$

We can affect spontaneity in the last two situations in this table. The temperature at which these processes switch from spontaneous to nonspontaneous is given by the equilibrium condition, $\Delta G = 0$. The temperature at which this occurs is given by:

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

The Effect of Temperature on Spontaneity

The following reaction is spontaneous below 1950 °C:



What is the standard entropy of $\text{Fe}(\text{OH})_3(s)$?

$$\Delta H_f^\circ(\text{Fe}(\text{OH})_3(s)) = -824.25 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}(l)) = -285.8 \text{ kJ/mol},$$

$$S^\circ(\text{Fe}(s)) = 27.2 \text{ J/K}\cdot\text{mol}$$

$$S^\circ(\text{O}_2(g)) = 205.0 \text{ J/K}\cdot\text{mol}$$

$$S^\circ(\text{H}_2\text{O}(l)) = 69.9 \text{ J/K}\cdot\text{mol}$$

$$463.7 \text{ J/K}\cdot\text{mol}$$

ΔG°

$\Delta G^\circ_{\text{rxn}}$ is the change in Gibb's free energy for a reaction when it occurs under standard state conditions. These are:

Gases: 1 atm

Liquids: Pure liquid

Solids: Pure solid

Elements: Most stable allotrope at 1 atm and 25 °C

Solutions: 1 M

ΔG°

For a chemical reaction under standard conditions:

$$\Delta G_{rxn}^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

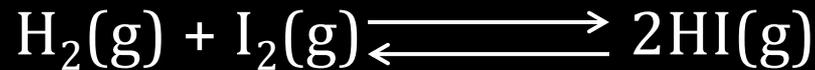
ΔG , not ΔG° determines whether a reaction is spontaneous or not under the conditions of the reaction.

ΔG° depends on temperature. A large, negative value of ΔG° tells us that the equilibrium favors the products. A large, positive value tells us the reactant are favored.

ΔG° and ΔG

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

$R = 8.314 \text{ J/K}\cdot\text{mol}$, T is the temperature in K, and Q is the reaction quotient. For example, for the reaction



$$\Delta G^\circ = 2.60 \text{ kJ/mol (Appendix 2)}$$

$$Q = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})}$$

The value (and sign) of ΔG depend on the pressures of the gases present.

ΔG° and ΔG

If the pressure of HI is 1.0 atm, H_2 and I_2 each 3.0 atm then $Q = 0.11$ and $\Delta G = -2.8$ kJ/mol and the process is spontaneous (at 25 °C).

If we started with the pressure of HI at 3.0 atm, H_2 and I_2 each 1.0 atm then $Q = 9.0$ and $\Delta G = 8.0$ kJ/mol and the process is not spontaneous as written (it is in the reverse direction though).

ΔG° and K

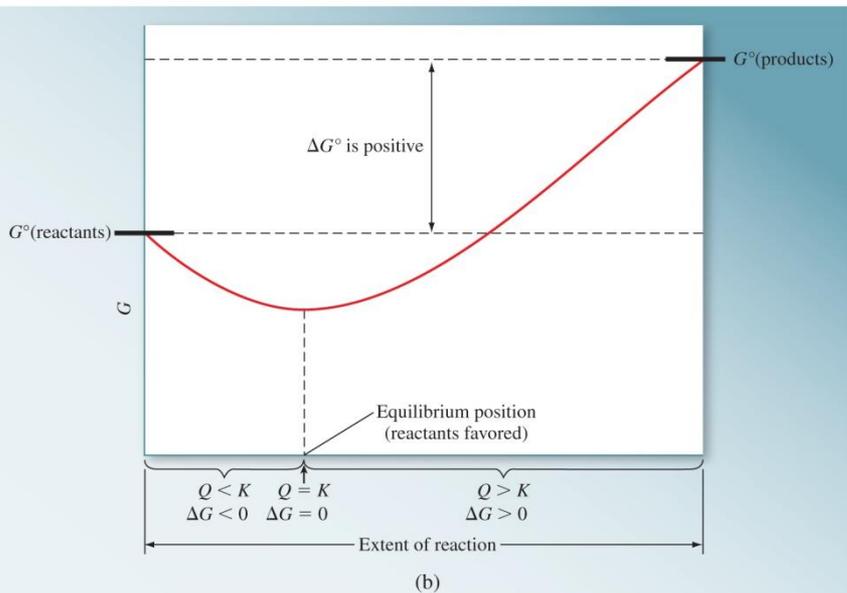
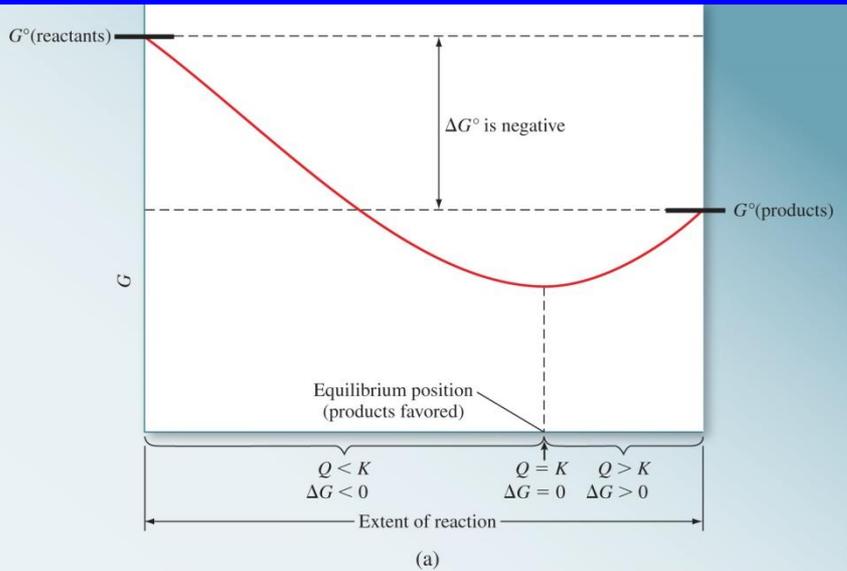
At equilibrium, $Q = K$ and $\Delta G = 0$:

$$0 = \Delta G^\circ + RT \ln K$$

or

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$



K	$\ln K$	ΔG°	Result at equilibrium
> 1	Positive	Negative	Products are favored.
$= 1$	0	0	Neither products nor reactants are favored
< 1	Negative	Positive	Reactants are favored.