Chemistry, The Central Science, 10th edition
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Chapter 19

Chemical Thermodynamics

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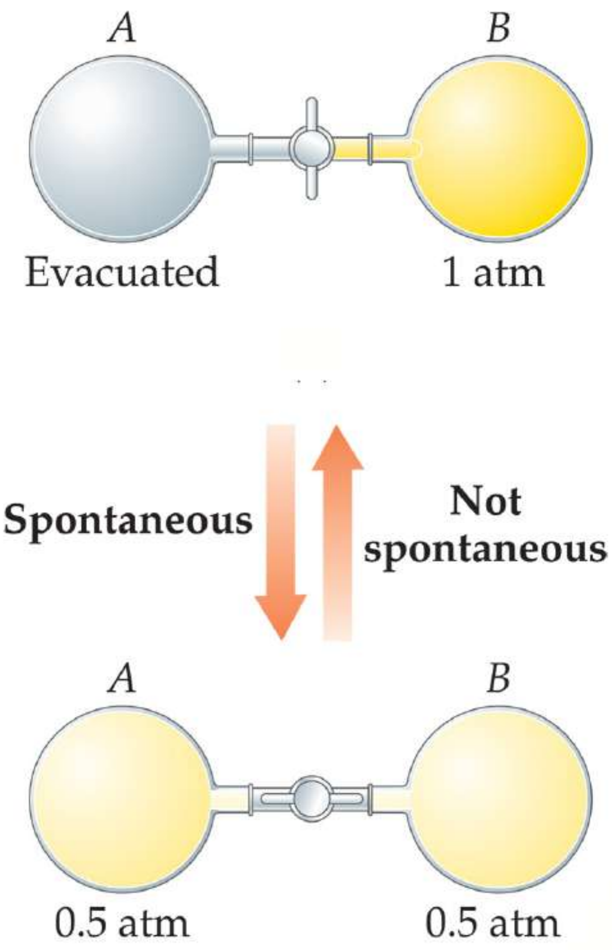
First Law of Thermodynamics

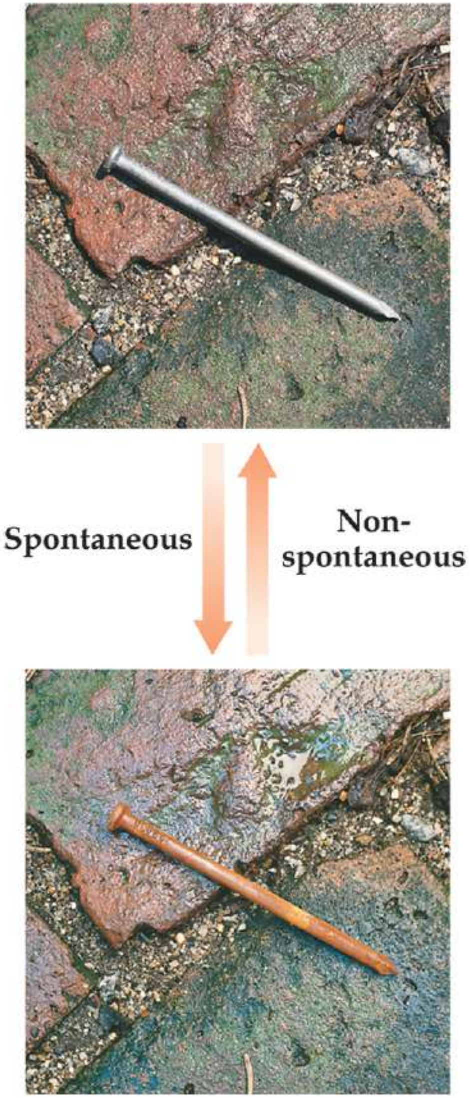
- You will recall from Chapter 5 that energy cannot be created nor destroyed.
- Therefore, the total energy of the universe is a constant.
- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.

Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously



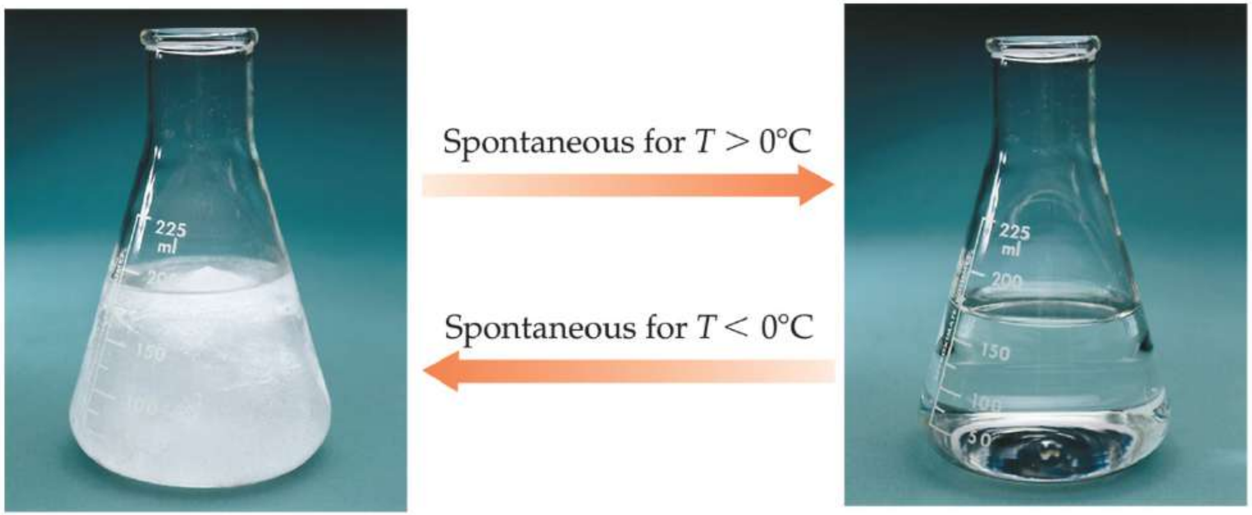
Spontaneous Processes



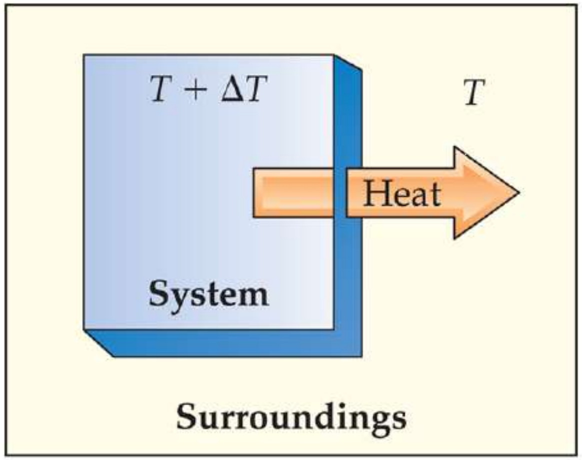
Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

Spontaneous Processes

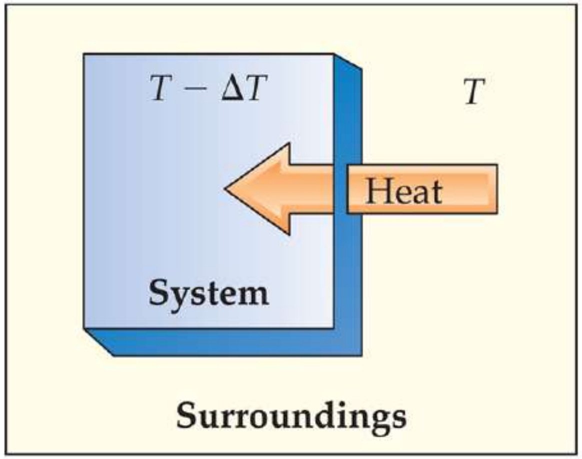
- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.



Reversible Processes

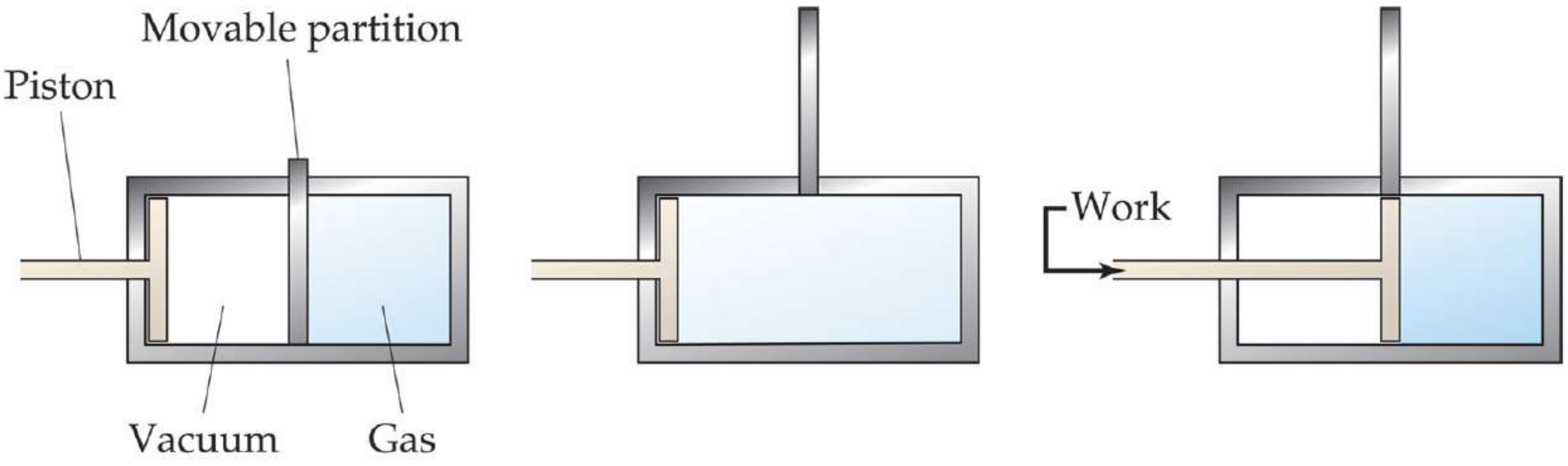


In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.



Changes are infinitesimally **small** in a reversible process.

Irreversible Processes



- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.

Entropy

- *Entropy* (*S*) is a term coined by Rudolph Clausius in the 19th century.
- Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered, $\frac{q}{T}$

Entropy

- Entropy can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.

Entropy

- Like total energy, *E*, and enthalpy, *H*, entropy is a state function.
- Therefore,

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

Entropy

- For a process occurring at constant temperature (an isothermal process):

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

q_{rev} = the heat that is transferred when the process is carried out **reversibly** at a constant temperature.
T = temperature in Kelvin.

Second Law of Thermodynamics

The second law of thermodynamics: The entropy of the universe does not change for reversible processes

and

increases for spontaneous processes.

Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Second Law of Thermodynamics

“You can’t break even”

Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Second Law of Thermodynamics

The entropy of the universe increases (real, spontaneous processes).

But, entropy can decrease for individual systems.

Reversible (ideal):

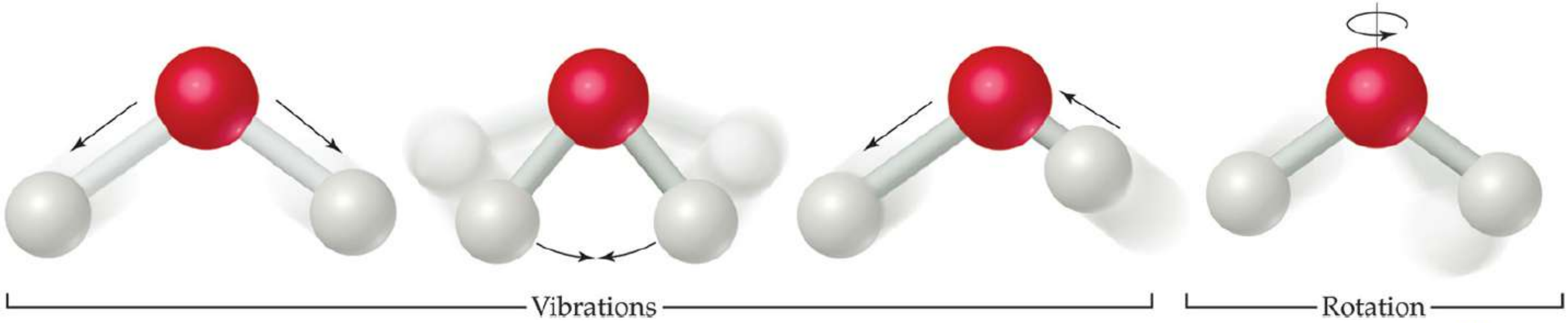
$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

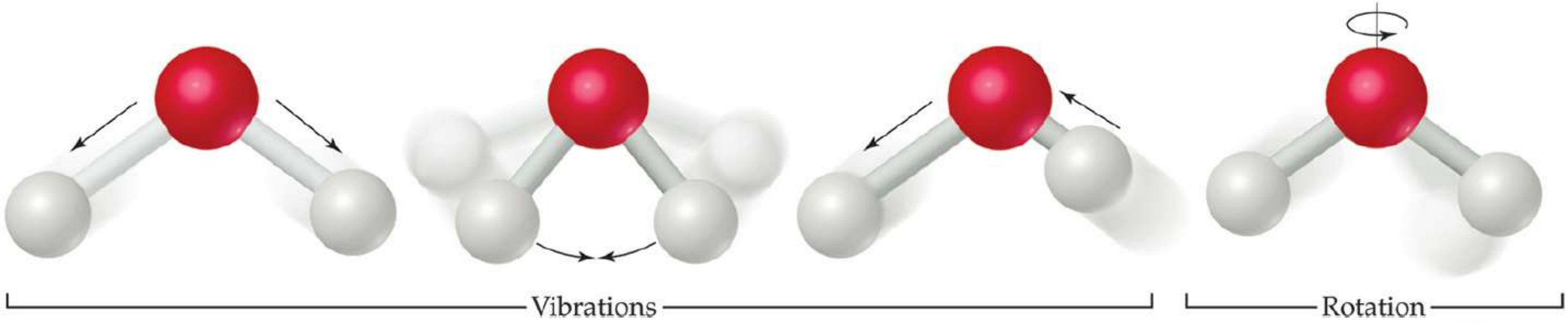
Entropy on the Molecular Scale

- Ludwig Boltzmann described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.



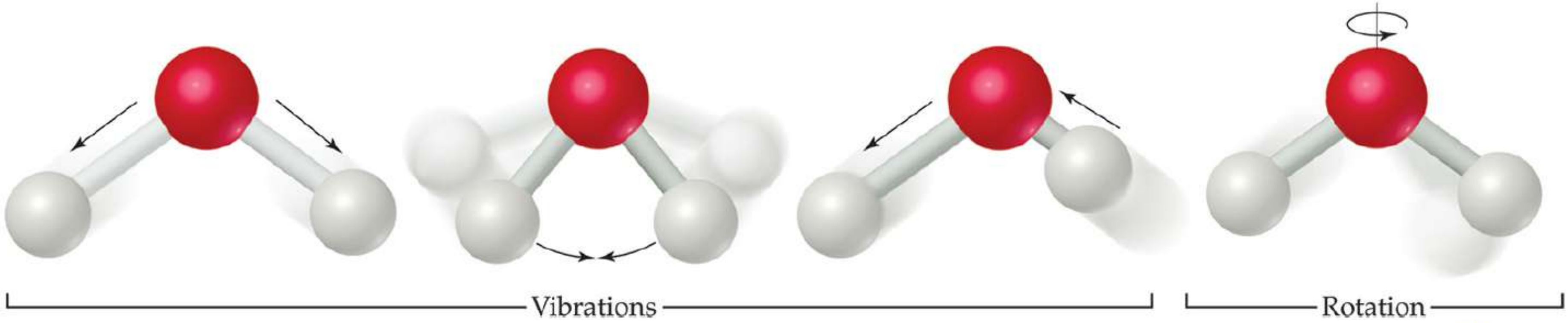
Entropy on the Molecular Scale

- Molecules exhibit several types of motion:
  - Translational: Movement of the entire molecule from one place to another.
  - Vibrational: Periodic motion of atoms within a molecule.
  - Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.



Entropy on the Molecular Scale

- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
  - ➢ This would be akin to taking a snapshot of all the molecules.
- He referred to this sampling as a **microstate** of the thermodynamic system.

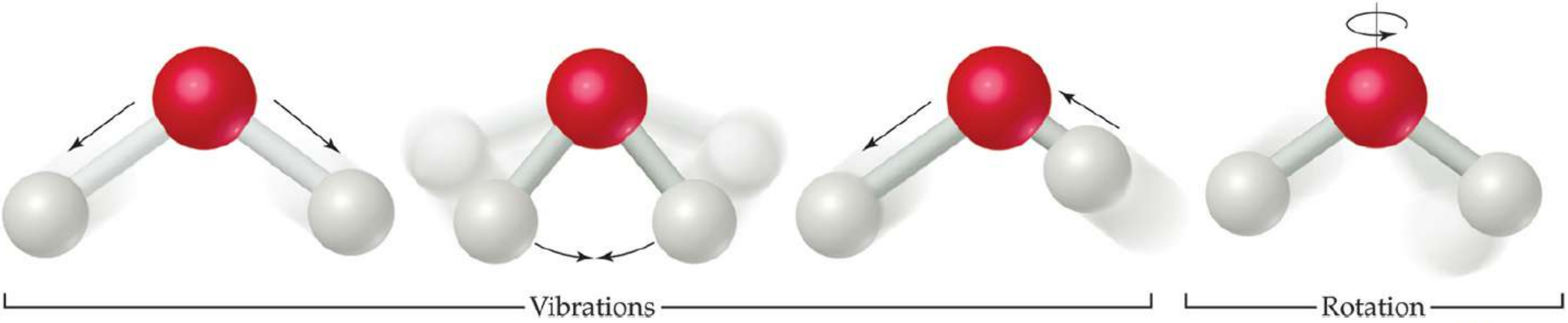


Entropy on the Molecular Scale

- Each thermodynamic state has a specific number of microstates, *W*, associated with it.
- Entropy is

$$S = k \ln W$$

where *k* is the Boltzmann constant, 1.38×10^{-23} J/K.



Entropy on the Molecular Scale

Implications:

- more particles

-> more states -> more entropy

- higher T

-> more energy states -> more entropy

- less structure (gas vs solid)

-> more states -> more entropy

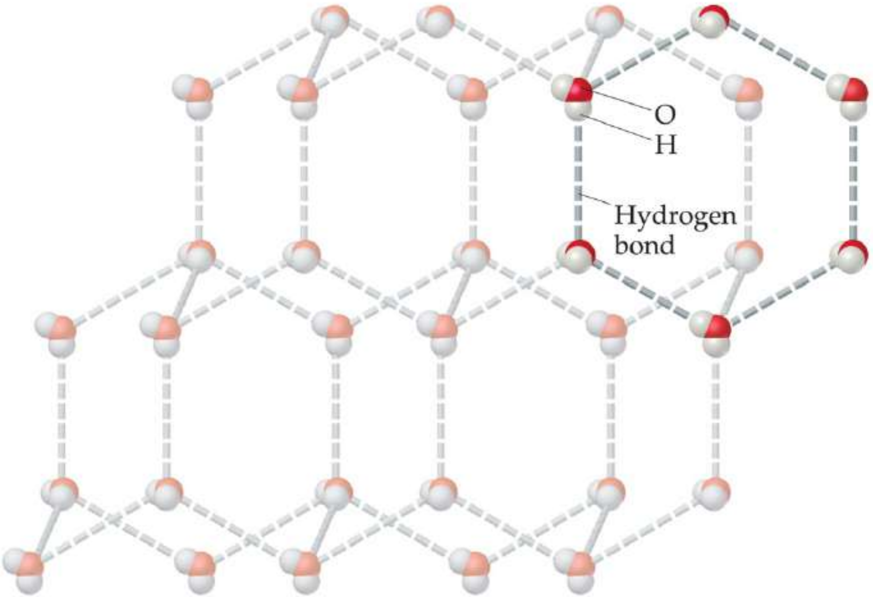
Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy tends to increase with increases in
  - Temperature.
  - Volume (gases).
  - The number of independently moving molecules.

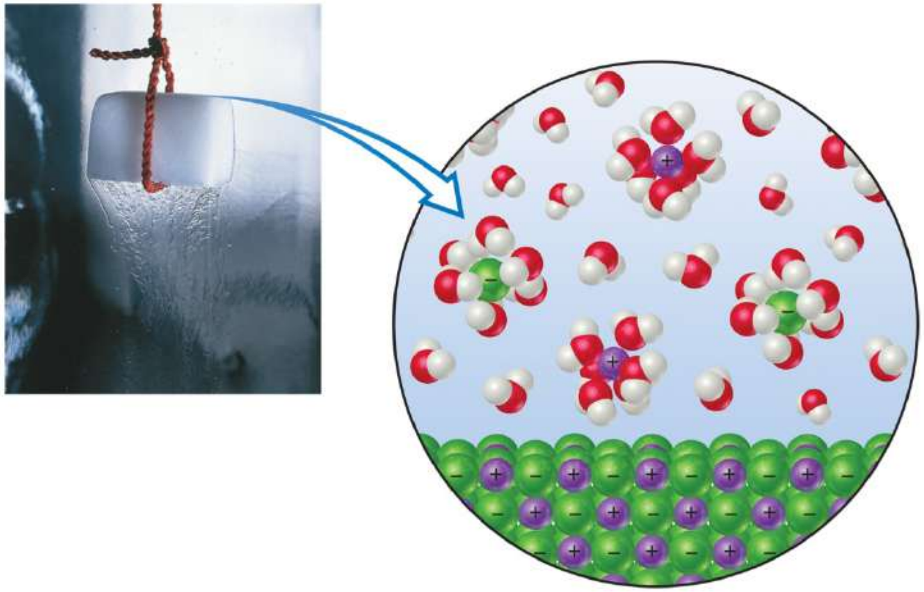
Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- Therefore,

S(*g*) > *S*(*l*) > *S*(*s*)



Solutions



Dissolution of a solid:

Ions have more entropy (more states)

But,

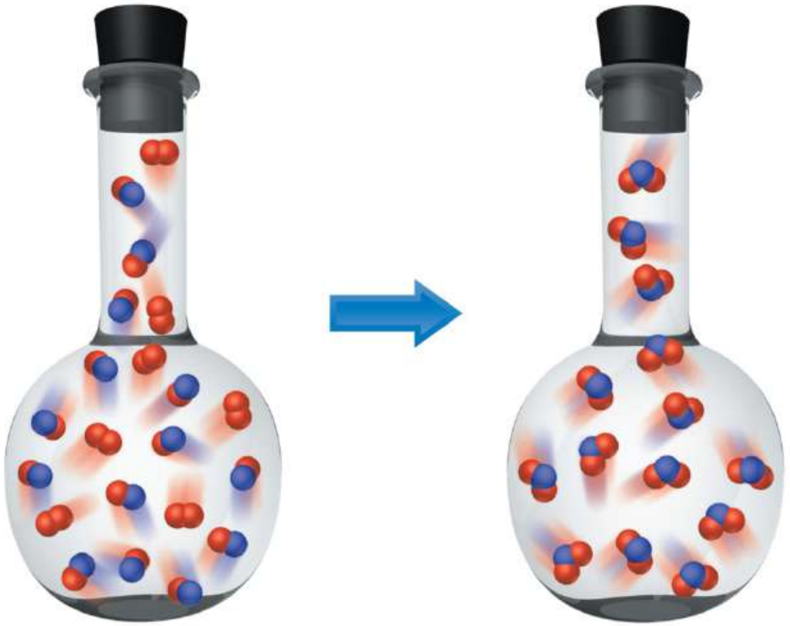
Some water molecules have less entropy (they are grouped around ions).

Usually, there is an overall increase in S.

(The exception is very highly charged ions that make a lot of water molecules align around them.)

Entropy Changes

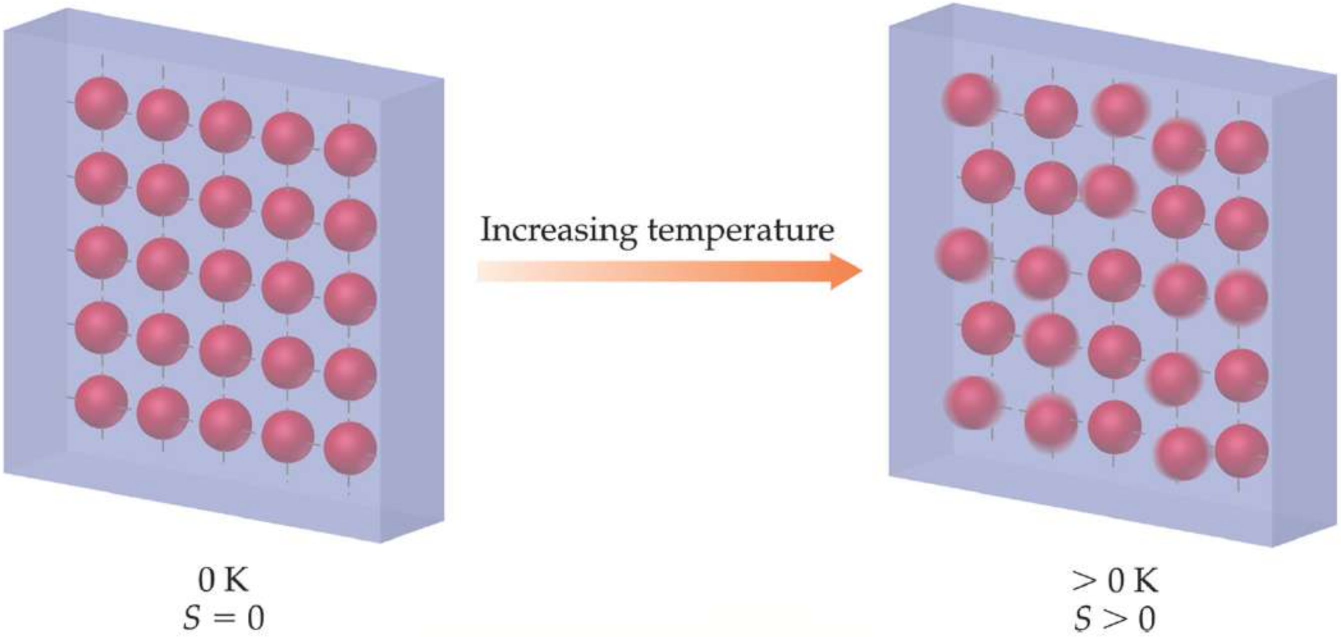
- In general, entropy *increases* when
  - Gases are formed from liquids and solids.
  - Liquids or solutions are formed from solids.
  - The number of gas molecules increases.
  - The number of moles increases.



Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero is 0.

$$S = k\ lnW = k\ ln1 = 0$$



Third Law of Thermodynamics

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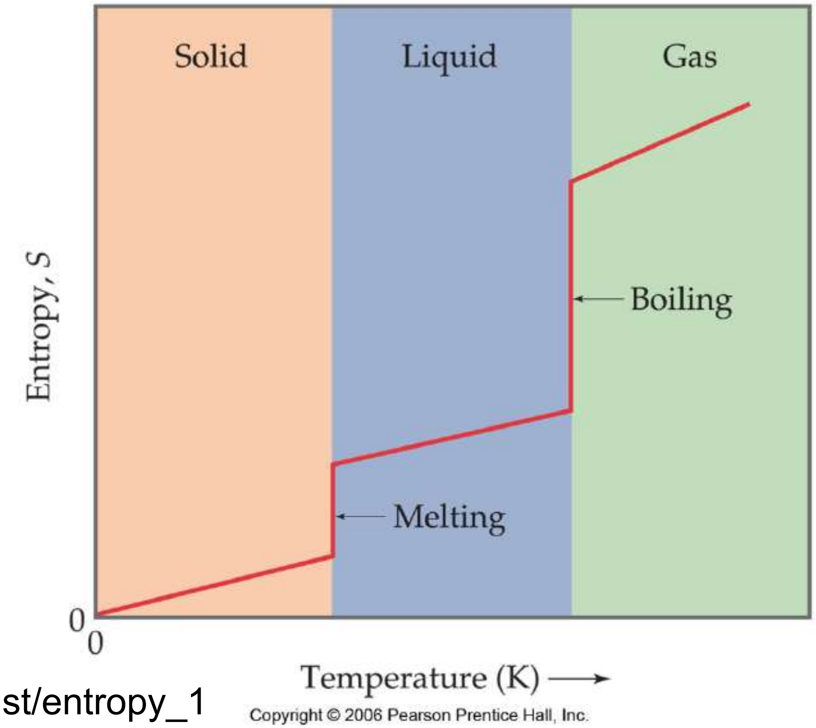
Entropy: Smiles for stab wounds 2004



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No stereotypes, labels, or genres can rationalize this. Fueled by the decay of the world, order and chaos unite, Entropy is born...

Music to make your head explode

http://www.garageband.com/artist/entropy_1

Standard Entropies

- These are molar entropy values of substances in their standard states.
- Standard entropies tend to increase with increasing molar mass.

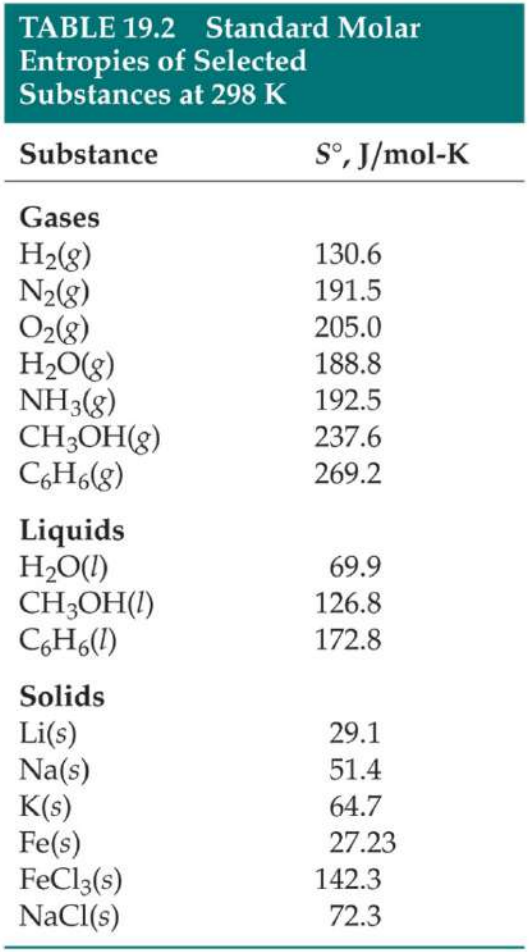
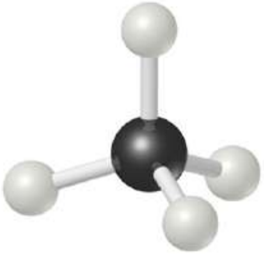


TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

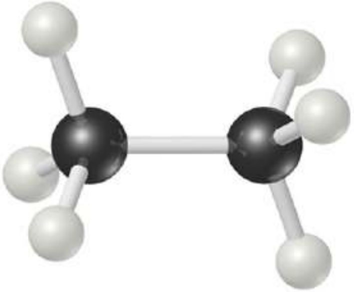
Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Standard Entropies

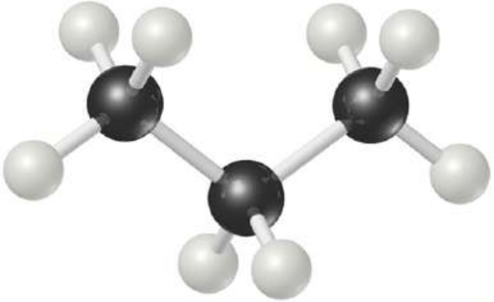
Larger and more complex molecules have greater entropies.



Methane, CH_4
$S° = 186.3\ J\ mol^{-1}\ K^{-1}$



Ethane, C_2H_6
$S° = 229.6\ J\ mol^{-1}\ K^{-1}$



Propane, C_3H_8
$S° = 270.3\ J\ mol^{-1}\ K^{-1}$

Entropy Changes

Entropy changes for a reaction can be calculated the same way we used for Δ*H:*

$$\Delta S_{rxn} = \Sigma S^{\circ}_{reactants} - \Sigma S^{\circ}_{products}$$

S° for each component is found in a table.

Note for pure elements:

$$S^{\circ} \neq 0$$

$$\Delta H^{\circ} = 0$$

Practical uses: surroundings & system

Entropy Changes in Surroundings

- Heat that flows into or out of the system also changes the entropy of the surroundings.
- For an isothermal process:

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

Practical uses: surroundings & system

Entropy Changes in Surroundings

- Heat that flows into or out of the system also changes the entropy of the surroundings.
- For an isothermal process:

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

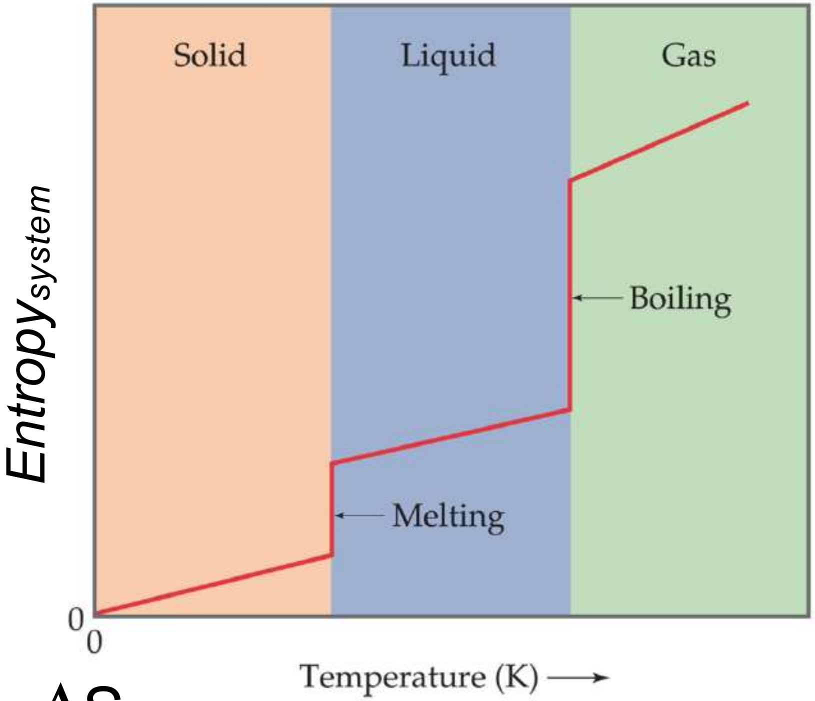
At constant pressure, q_{sys} is simply ΔH° for the system.

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^\circ}{T}$$

Link S and ΔH: Phase changes

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^{\circ}_{sys}}{T}$$

A phase change is isothermal (no change in T).



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For water:

ΔH_{fusion} = 6 kJ/mol

ΔH_{vap} = 41 kJ/mol

If we do this reversibly: $\Delta S_{surr} = -\Delta S_{sys}$

Practical uses: surroundings & system

Entropy Change in the Universe

- The universe is composed of the system and the surroundings.

Therefore,

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

- For spontaneous processes

$$\Delta S_{\text{universe}} > 0$$

Practical uses: surroundings & system

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

$$\Delta S_{surr} = \frac{-\Delta H^{\circ}_{sys}}{T}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H^{\circ}_{sys}}{T}$$

$$\underbrace{T\Delta S_{universe}} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

= – Gibbs Free Energy

Practical uses: surroundings & system

$$\underbrace{T\Delta S_{universe}} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

= – Gibbs Free Energy

Make this equation nicer:

$$-T\Delta S_{universe} = \Delta H^{\circ}_{sys} - T\Delta S_{system}$$

$$\boxed{\Delta G = \Delta H^{\circ}_{sys} - T\Delta S_{system}}$$

Practical uses: surroundings & system …Gibbs Free Energy

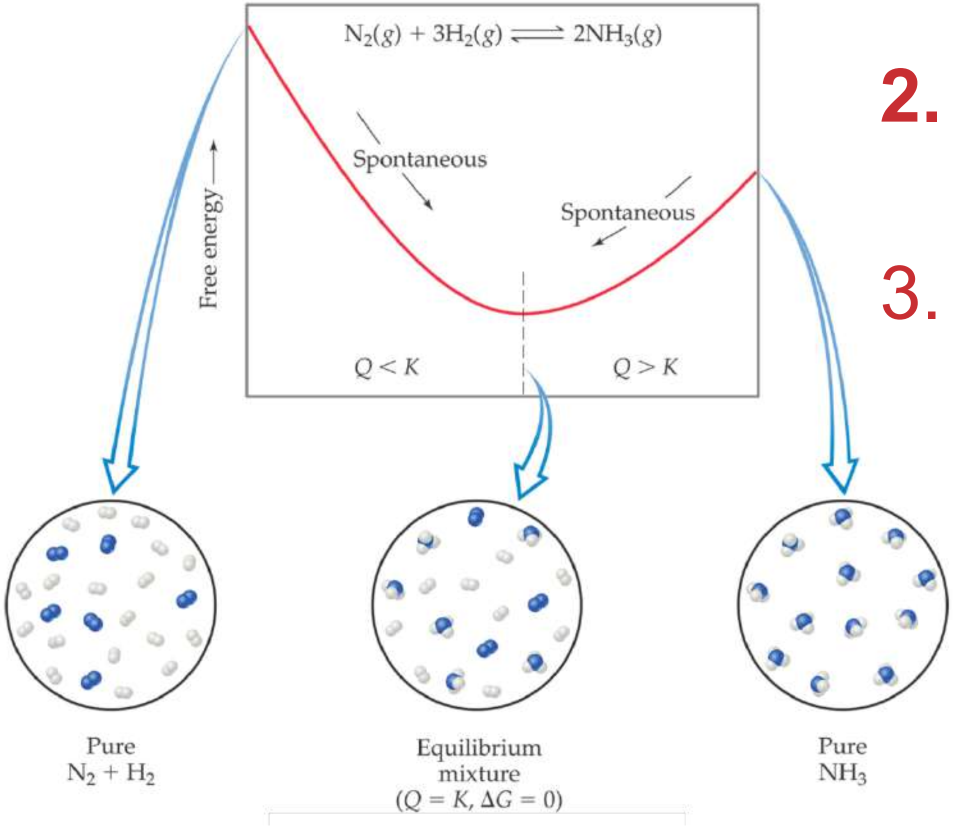
- $-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG.

For spontaneous processes: $\boldsymbol{\Delta S_{\text{universe}} > 0}$

And therefore: $\boldsymbol{\Delta G < 0}$

ΔG is easier to determine than $\Delta S_{\text{universe}}$.
So:
Use ΔG to decide if a process is spontaneous.

Gibbs Free Energy



1. If ΔG is negative, the forward reaction is spontaneous.
2. **If ΔG is 0, the system is at equilibrium.**
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

Standard Free Energy Changes

Standard free energies of formation, $\Delta G_f°$ are analogous to standard enthalpies of formation, $\Delta H_f°$.

$$\Delta G_f^\circ = \Sigma\Delta G^\circ_{reactants} - \Sigma\Delta G^\circ_{products}$$

$\Delta G°$ can be looked up in tables,

or

calculated from $S°$ and $\Delta H°$.

Free Energy Changes

Very key equation:

$$\Delta G = \Delta H^\circ_{sys} - T\Delta S_{system}$$

This equation shows how ΔG° changes with temperature.

(We assume S° & ΔH° are independent of T.)

Free Energy and Temperature

- There are two parts to the free energy equation:
    - ΔH°— the enthalpy term
    - $T\Delta S^\circ$ — the entropy term
- The temperature dependence of free energy comes from the entropy term.

Free Energy and Temperature

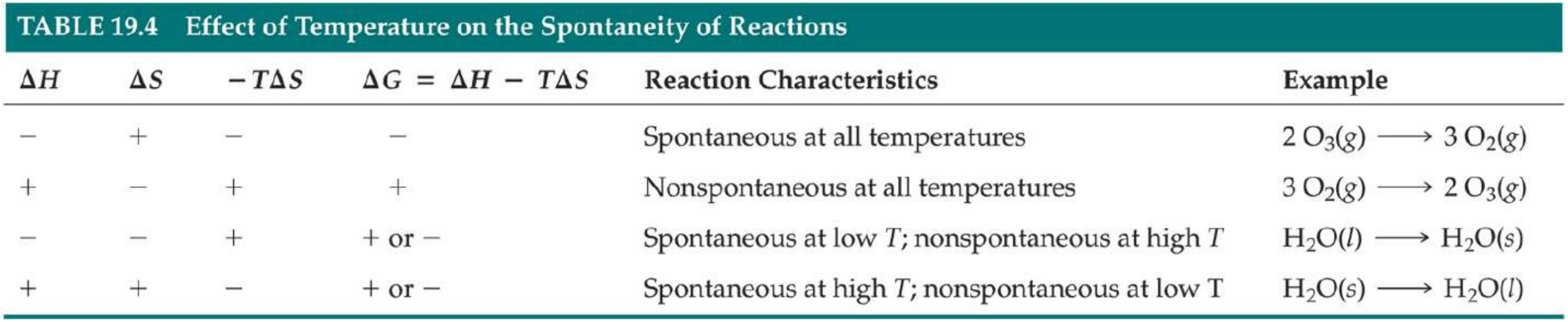


TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
$-$	$+$	$-$	$-$	Spontaneous at all temperatures	$2\,O_3(g) \longrightarrow 3\,O_2(g)$
$+$	$-$	$+$	$+$	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
$-$	$-$	$+$	$+$ or $-$	Spontaneous at low *T*; nonspontaneous at high *T*	$H_2O(l) \longrightarrow H_2O(s)$
$+$	$+$	$-$	$+$ or $-$	Spontaneous at high *T*; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

By knowing the sign (+ or -) of ΔS and ΔH, we can get the sign of ΔG and determine if a reaction is spontaneous.

Free Energy and Equilibrium

Remember from above:

If Δ*G* is 0, the system is at equilibrium.

So Δ***G*** must be related to the equilibrium constant, K (chapter 15). The ***standard*** free energy, Δ***G*°**, is directly linked to K_{eq} by:

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

Free Energy and Equilibrium

Under non-standard conditions, we need to use **ΔG** instead of **$\Delta G°$.**

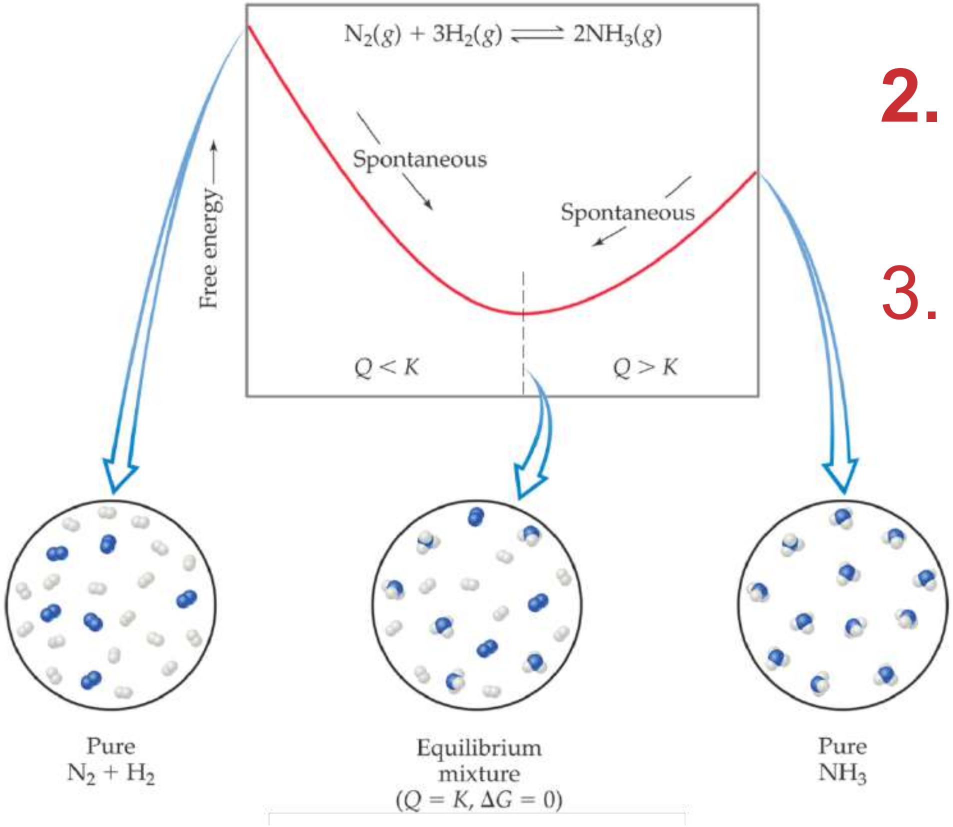
$$\Delta G^\circ = -RT \ln K$$

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

Q is the reaction quotiant from chapter 15.

Note: at equilibrium: **$\Delta G = 0$.**
away from equil, sign of **ΔG** tells which way rxn goes spontaneously.

Gibbs Free Energy



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