Spontaneity, Entropy and Free Energy

Spontaneous Processes and Entropy

- **First Law**
  - "Energy can neither be created nor destroyed"
  - The energy of the universe is constant

Spontaneous Processes and Entropy

- **Spontaneous Processes**
  - Processes that occur without outside intervention
  - Spontaneous processes may be fast or slow
    - –Many forms of combustion are fast
    - –Conversion of diamond to graphite is slow

Thermodynamics and Spontaneity

- Thermodynamics predicts whether a process will occur under the given conditions.
  - –Processes that will occur are called **spontaneous**.

Thermodynamics and Spontaneity

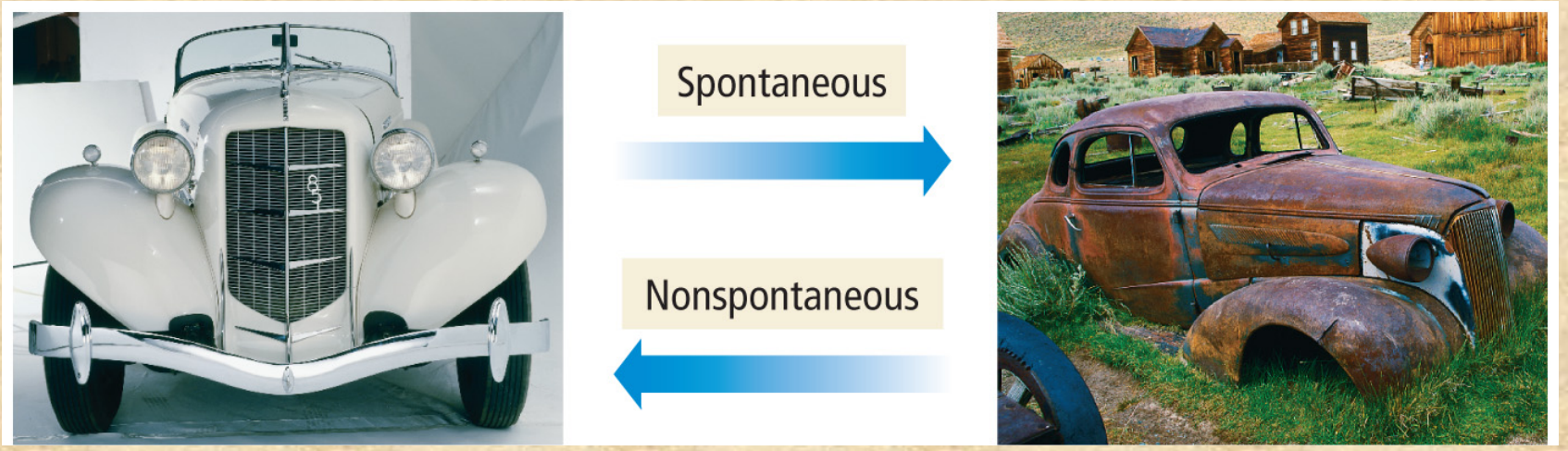
- Spontaneity is determined by comparing the **chemical potential energy** of the system before the reaction with the free energy of the system after the reaction.
  - If the system after reaction has less potential energy than before the reaction, the reaction is thermodynamically favorable.

Thermodynamics and Spontaneity

- Spontaneity ≠ fast or slow

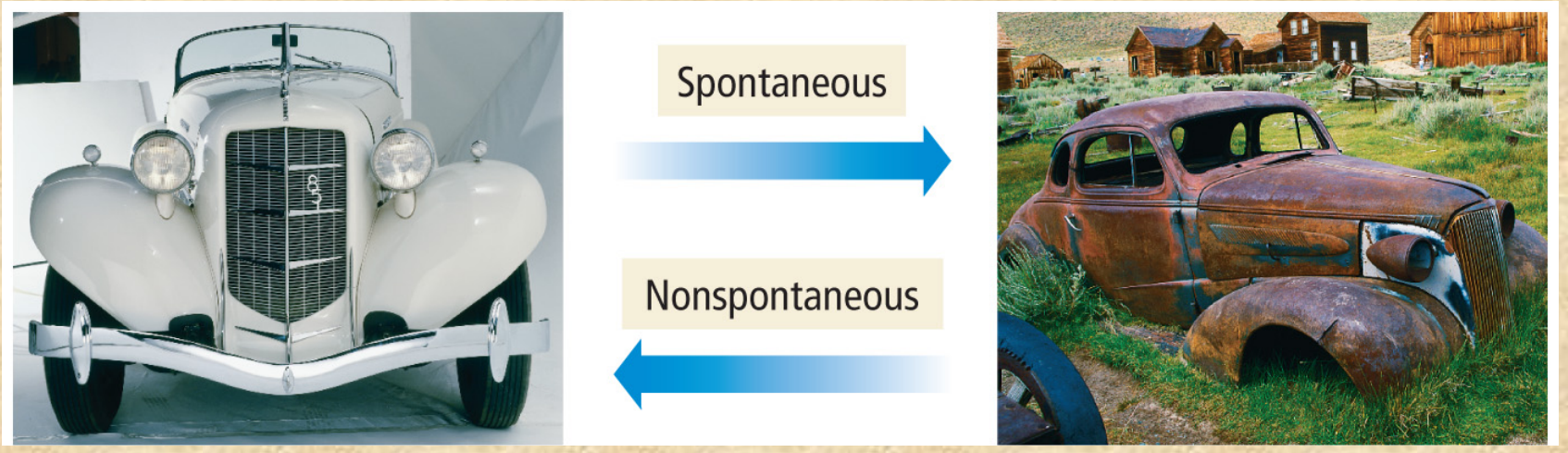
Reversibility of Process

- Any spontaneous process is irreversible because there is a net release of energy when it proceeds in that direction.
- A reversible process will proceed back and forth between the two end conditions.
  - Any reversible process is at equilibrium.
  - This results in no change in free energy.



Reversibility of Process

- If a process is spontaneous in one direction, it *must* be nonspontaneous in the opposite direction.



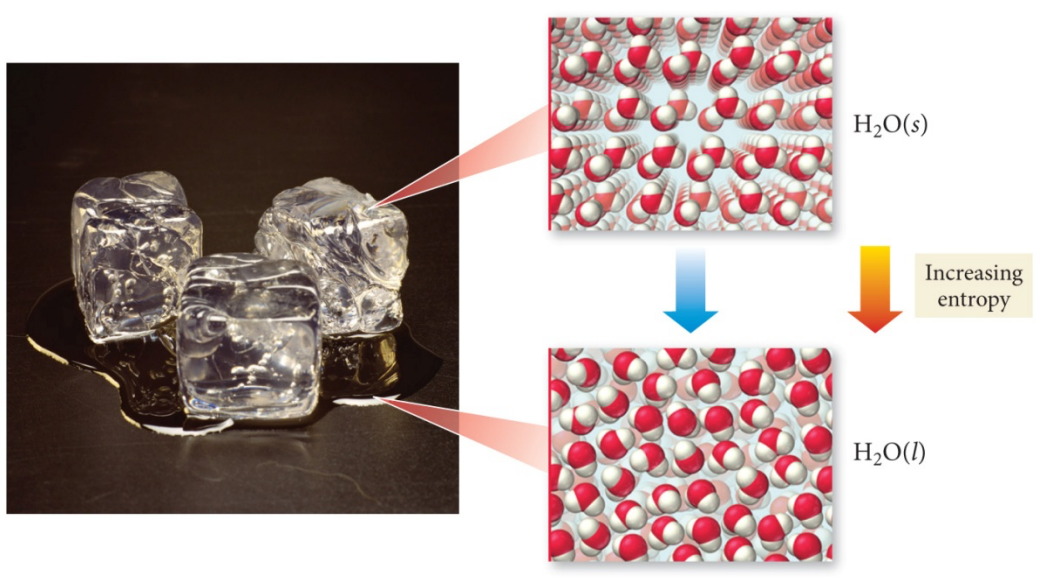
Spontaneous Processes

- Spontaneous processes occur because they release energy from the system.
- Most spontaneous processes are:
  - **Exothermic**
- But there are some spontaneous processes that are:
  - **Endothermic**
- [**THINKING**] How can something absorb potential energy, yet have a net release of energy?

Melting Ice (Think, don't write)

When a solid melts, the particles have more freedom of movement.

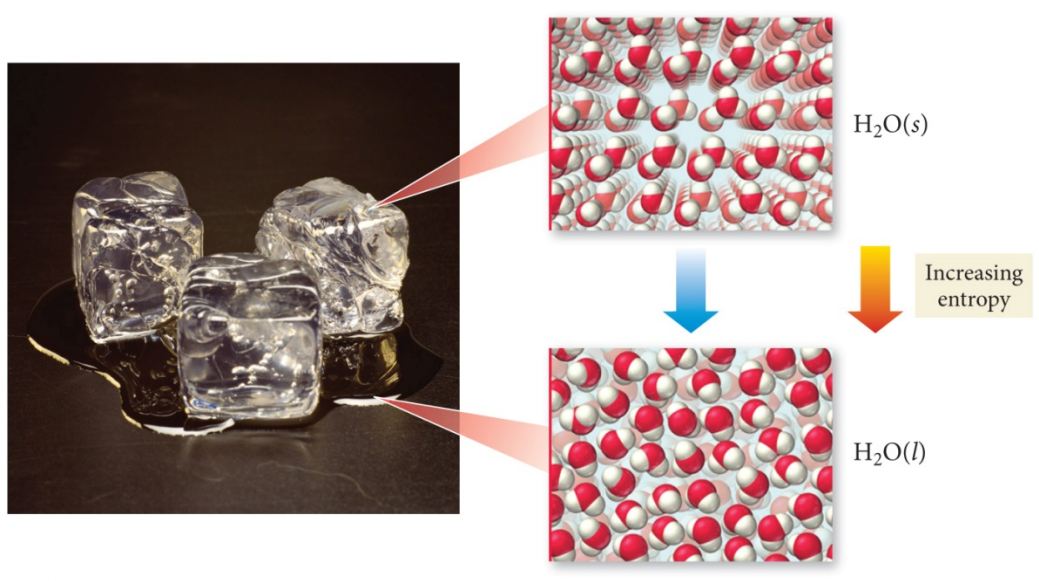
More freedom of motion increases the randomness of the system. When systems become more random, energy is released. We call this energy, entropy.



Melting Ice (Think, more…)

Melting is an endothermic process, yet ice will spontaneously melt above 0 ° C.

More freedom of motion increases the randomness of the system. When systems become more random, energy is released. We call this energy, entropy.



Factors Affecting Whether a Reaction Is Spontaneous

- There are two factors that determine whether a reaction is spontaneous. They are the **enthalpy change** and the **entropy change** of the system.

Factors Affecting Whether a Reaction Is Spontaneous

- The enthalpy change, ΔH, is the difference in the sum of the internal energy and PV work energy of the reactants to the products.

Factors Affecting Whether a Reaction Is Spontaneous

- The entropy change, ΔS, is the difference in randomness of the reactants compared to the products.

Enthalpy Change (review)

- ΔH generally measured in kJ/mol
- Stronger bonds = more stable molecules
- A Rxn is generally exothermic if the bonds in the products are stronger than the bonds in the reactants.
  - Exothermic = energy released; ΔH is negative.

Enthalpy Change (review)

- A Rxn is generally endothermic if the bonds in the products are weaker than the bonds in the reactants.
  - Endothermic = energy absorbed; ΔH is positive.
- The enthalpy change is favorable for exothermic reactions and unfavorable for endothermic reactions.