

Section 16.2

Entropy



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Learning Objectives



- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

Reversible Processes

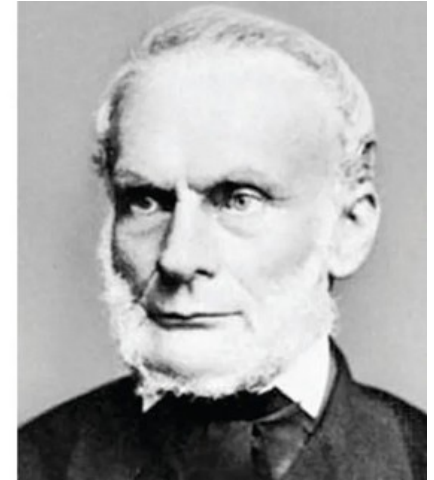


- A **reversible process** is one that takes place at such a slow rate that it is always at equilibrium
- Its direction can be changed (it can be “reversed”) by an infinitesimally small change in some condition.
- The idea of a reversible process is a formalism required to support the development of various thermodynamic concepts
 - No real processes are truly reversible
 - They are classified as irreversible

Hinting at Entropy



- In 1824, Nicolas Léonard Sadi Carnot published the results of an extensive study regarding the efficiency of steam heat engines.
- Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place.



Entropy



- In 1865, Clausius named this property **entropy** (S) and defined its change for any process as the following:

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

- Similar to other thermodynamic properties, this new quantity is a state function
 - Its change depends only upon the initial and final states of a system.

Entropy and Microstates



- Ludwig Boltzmann developed a statistical model that relates the entropy of a system to the **number of microstates** (W).
- A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system.
- The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

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

Entropy as a State Function



- The change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

- The change in entropy does not depend on the path only on the final and initial states.
- This is not just a property of entropy, all thermodynamic state functions operate this way.

Microstates



- An increase in the number of microstates, $W_f > W_i$, yields an increase in system entropy, $\Delta S > 0$.
- A reduction in the number of microstates, $W_f < W_i$, yields a decrease in system entropy, $\Delta S < 0$.
- Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called **distributions**.
- *The most probable distribution is the one of greatest entropy.*

Microstates and Probability



Scaling Microstates

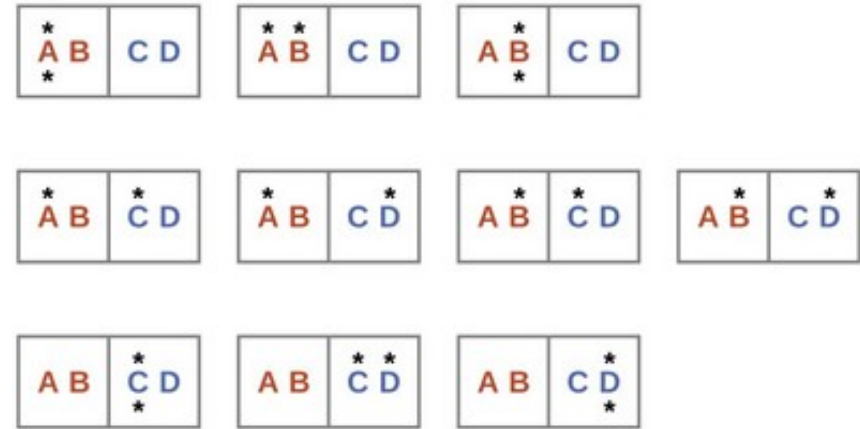


- Adding more particles to the previous system would result in an exponential increase in microstates (2^N).
- Having even one mole of particles would result in an extremely large number of microstates ($N \approx 10^{23}$).
- Regardless of the number of particles in the system the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

Heat as Microstates



- Consider a system consisting of two objects, each containing two particles and two units of thermal energy, “*”
- The hot object is comprised of particles **A** and **B** and initially contains both energy units.
- The most likely result is the flow of heat to yield the uniform dispersal of energy.



Predicting the Sign of ΔS



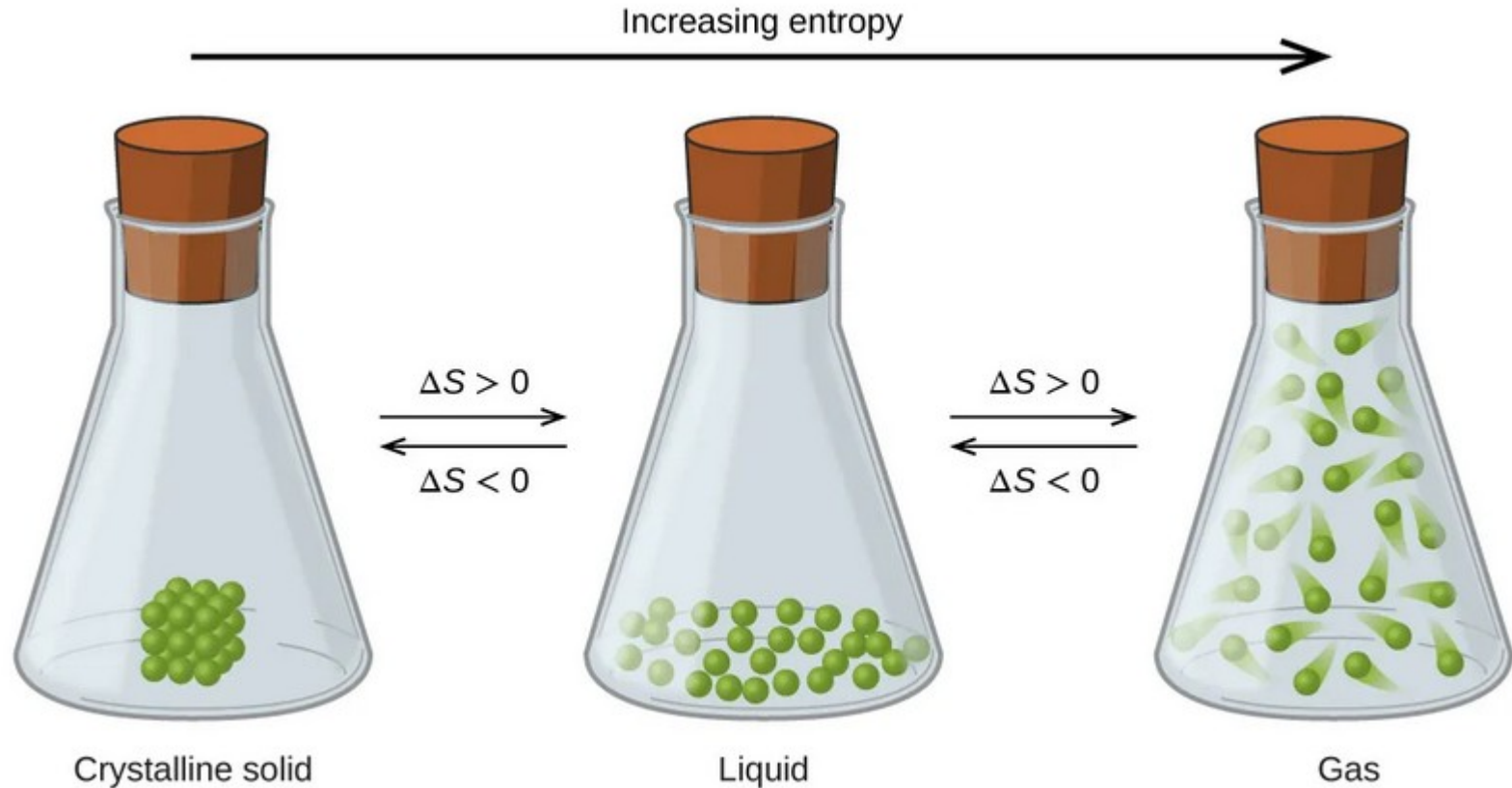
- In the solid phase, the atoms or molecules are restricted to nearly fixed positions, oscillating around these positions.
 - The number of microstates is relatively small.
- In the liquid phase, the atoms or molecules are free to move, though they remain in relatively close proximity to one another.
 - The number of microstates is greater than for solids, $S_{\text{liquid}} > S_{\text{solid}}$.
 - Melting results in an increase in entropy, $\Delta S > 0$.
 - Freezing results in a decrease in entropy, $\Delta S < 0$.

Entropy of Gases



- Atoms or molecules in the gas phase occupy a much greater volume than the liquid phase.
- Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates.
 - For any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$
 - Vaporization and sublimation result in an increase entropy, $\Delta S > 0$.
 - Condensation and deposition result in a decreases in entropy, $\Delta S < 0$.

Predicting the Sign of ΔS



Entropy of Temperature



- The temperature of a substance is proportional to the average kinetic energy of its particles.
 - Solids have more extensive vibrations.
 - Liquids and gases have more rapid translation of particles.
- At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader than at lower temperatures.
 - Kinetic energies are more dispersed.
- The entropy for any substance increases with temperature

Entropy of Temperature

