Chapter 16 Part 1

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Spontaneity

- A spontaneous process is one that occurs naturally under certain conditions
  - Ex. Iron rusts into iron oxide when exposed to Earth's environment
- A nonspontaneous process requires a continual input of energy from an external source in order to occur
  - Ex. At room temperature heat must be applied to vaporize water into steam

Spontaneity and Speed

- The spontaneity of a process is not correlated to the speed of the process
- Spontaneous processes can rapidly or so slowly that they cannot be observed over a reasonable period of time

Dispersal of Matter and Energy

- Spontaneous processes lead to a greater dispersal of matter and energy
- Dispersal of matter
  - Gas particles will spontaneously diffuse throughout a room without the application of any external energy
- Dispersal of energy
  - Hot objects will spontaneously transfer thermal energy to cooler objects without the application of any external energy

Dispersal of Matter

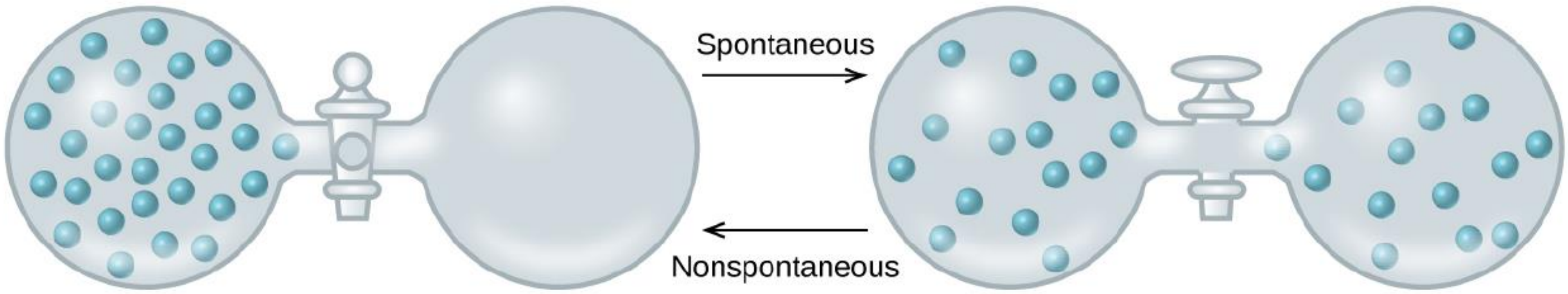


Figure 16.4 An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Entropy (S)

- Entropy can generally be defined as the disorder in a system

Entropy

Identify the incorrect description of entropy.

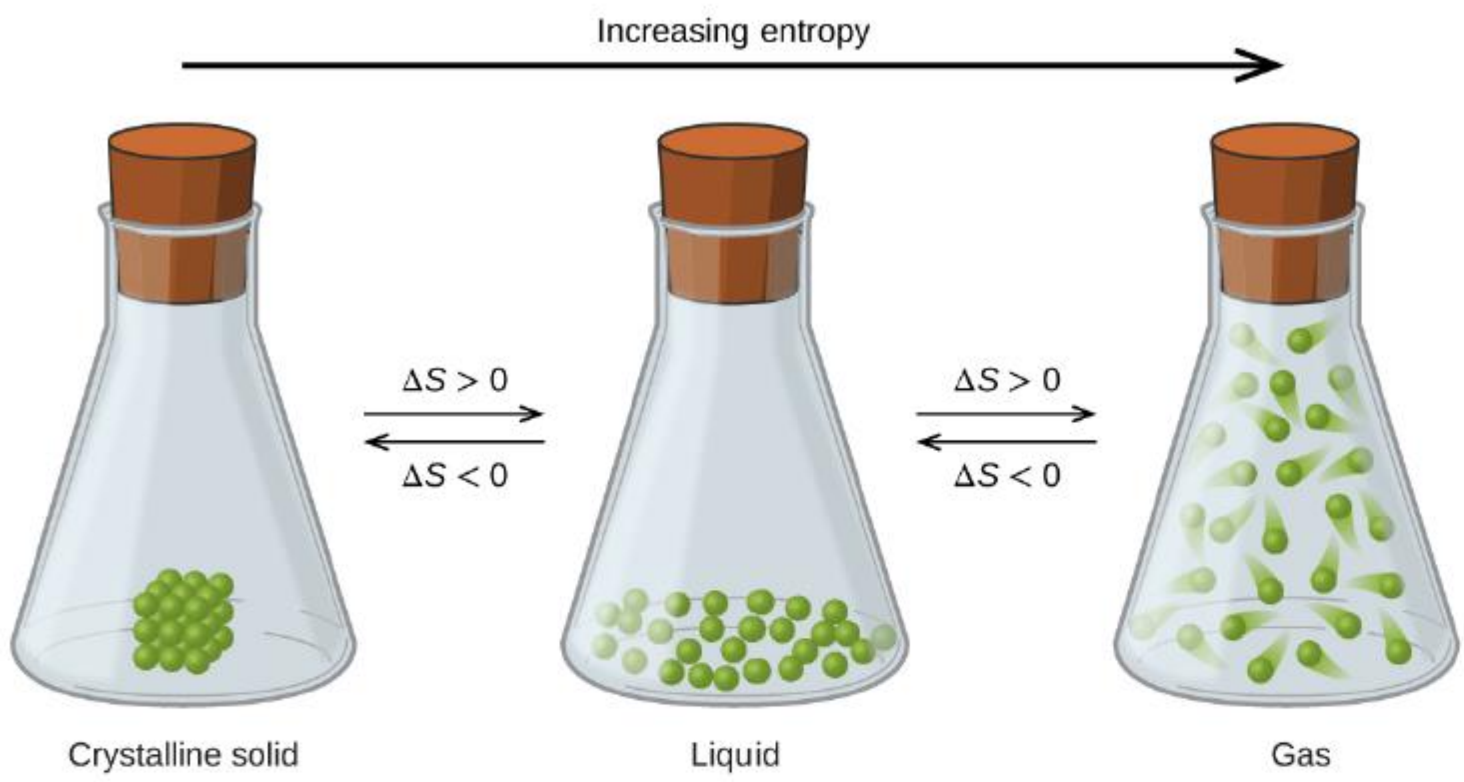
A. degree of disorder in a system
B. degree of randomness in a system
C. internal energy of a system
D. how spread out the energy of a system is

Entropy change (ΔS)

Entropy generally increases in each of the following cases

- Pure liquids or liquid solutions are formed from solids
- Gases are formed from solids or liquids
- The number of molecules of gas increases as a result of a chemical reaction
- The temperature of a substance increases

Entropies of different states of matter



Qualitatively Predicting Entropy Changes

Predict whether each of the following processes involves an increase or decrease in entropy or whether the outcome is uncertain.

A. $2\ NH_4NO_3(s) \rightarrow 2\ N_2(g) + 4\ H_2O(g) + O_2(g)$
B. $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$
C. $C_{12}H_{22}O_{11}(aq) \rightarrow C_{12}H_{22}O_{11}(s)$
D. $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

Entropy Change

Identify the process with a negative value for ΔS.

A. dissolving salt in water
B. ice melting
C. particles getting confined to a single side of a container
D. heating a solid until it decomposes resulting both gaseous and solid products

Entropy

- Entropy is based on two measurable quantities: heat and temperature
- As the more energy (heat) is added to a system, the more disordered the system becomes

Entropy

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

- q is the heat of a process
- T is the temperature of the system in Kelvin

Another look at ΔS

$$\Delta S = \frac{\mathrm{q}}{\mathrm{T}}$$

In words means

$$\text{Increase in disorder} = \frac{\text{Thermal energy gained}}{\text{Average kinetic energy of particles}}$$

Determining ΔS for Phase Transitions

What is the standard entropy of vaporization in J mol^{-1} K^{-1} of water at 373 K, given that the standard molar enthalpy of vaporization is 40.7 kJ mol^{-1}?

Standard entropies of reaction

$$\Delta S^{\circ}_{\mathrm{rxn}} = \sum \Delta S^{\circ}_{\mathrm{f}}(\mathrm{products}) - \sum \Delta S^{\circ}_{\mathrm{f}}(\mathrm{reactants})$$

Calculating ΔS from Standard Molar Entropies

Calculate the standard molar entropy change for the conversion of nitrogen monoxide to nitrogen dioxide. The standard molar entropies of $NO(g)$, $O_2(g)$, and $NO_2(g)$ are $210.8\ J\ K^{-1}$, $205.1\ J\ K^{-1}$, and $240.0\ J\ K^{-1}$, respectively.

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g) \qquad \Delta S^\circ = ?$$

Standard Entropies

Determine the standard entropy change for this reaction. $3\ A_2(g) \rightarrow 2\ A_3(g)$

A. –100 J
B. –50 J
C. 50 J
D. 100 J
E. 150 J

Substance(state)	S° (J/mol · K)
A(g)	150
$A_2(g)$	200
$A_3(g)$	250

First Law of Thermodynamics

- Energy cannot be created or destroyed

Second Law of Thermodynamics

- All spontaneous processes cause an increase in the entropy of the universe

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The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	reversible (system is at equilibrium)

Third Law of Thermodynamics

- The entropy of a pure, perfect crystalline substance at 0 K is zero

Entropy of the Universe

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

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T_{surr}}$$

- ΔS_{univ} is the entropy of the universe
- ΔS_{sys} is the entropy of the system
- ΔS_{surr} is the entropy of the surroundings
- q_{surr} is the heat of the surroundings
- T_{surr} is the temperature of the surroundings

Spontaneity and ΔS_{univ}

The entropy change a process is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at $-10.00°C$? Is it spontaneous at $+10.00°C$?

Spontaneity and ΔS_{univ}

Consider the following reaction at 298.15 K.

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g)$$

A. Use the given standard entropy values to calculate ΔS_{sys} in $J\ mol^{-1}\ K^{-1}$.

Substance	ΔS° ($J\ mol^{-1}\ K^{-1}$)
$CO_2(g)$	213.7
$H_2O(g)$	188.8
$O_2(g)$	205.2
$C_3H_8(g)$	270.3

Spontaneity and ΔS_{univ}

Consider the following reaction at 298.15 K.

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$$

B. If the reaction above releases 2044 kJ mol^{-1} of heat, calculate ΔS_{surr} in J mol^{-1} K^{-1}.

Spontaneity and ΔS_{univ}

Consider the following reaction at 298.15 K.

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$$

C. Calculate ΔS_{univ} in $J\ mol^{-1}\ K^{-1}$.

D. Will the reaction be spontaneous?